# 3D PRINTING – PRESENT AND FUTURE – A CHEMICAL ENGINEERING PERSPECTIVE

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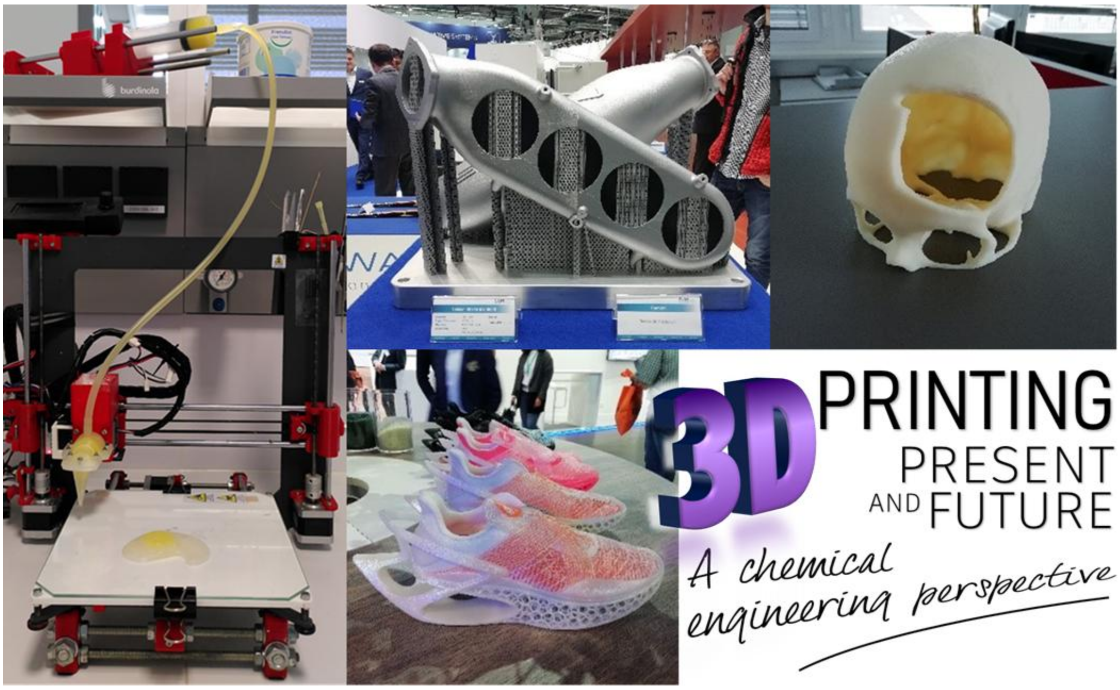
## GRAPHICAL ABSTRACT



## HIGHLIGHTS

- 3DP processes can benefit from knowledge available in many Chemical Engineering topic areas
- The creation of unique and/or complex-shaped objects by 3DP can be of great interest to Chemical Engineering
- The relationship between Chemical Engineering and 3DP is not evident to many chemical engineers
- Including 3D printing in the curriculum can enhance students’ learning motivation towards different engineering subjects

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## ABSTRACT

3D printing (3DP) has emerged in recent years as a form of processing with many exciting aspects. Today, it finds use in the industrial sector as well as among private individuals and small manufacturers, bringing manufacturing closer to end users and helping to bring a multitude of ideas and innovations to life. In this scenario, Chemical Engineering could play an essential role in 3DP, while it can also receive and benefit from many of the characteristics of this technology. This paper aims to highlight those that we consider the most productive meeting points between Chemical Engineering and 3DP, as well as the new techniques and applications that could benefit from this tandem in the future.

**Keywords:** 3D/4D printing, printable materials, alternative manufacturing technologies, innovation in Chemical Engineering

## 1. Introduction

Most of the traditional disciplines that are part of chemical engineering education, as well as some other complementary subjects, such as thermodynamics, fluid mechanics, reaction engineering, chemical product engineering, technical drawing and design, materials science, mixing operations, electricity and electronics, computational modelling, and simulation are involved in 3D printing (3DP) operations. Therefore, a chemical engineer dealing with 3DP would have left virtually nothing of that learned behind. On the other hand, 3DP is increasingly being used as a processing tool in research projects in the field of Chemical Engineering, and as such, it is essential to discuss the symbiotic relationship between Chemical Engineering and 3DP.

In this sense, Chemical Engineering has had and continues to have much to contribute to the evolution of 3DP. The development of new 3DP processes, techniques, and materials, as well as the optimisation of existing ones, need (or, at the very least, can benefit greatly) from the knowledge that Chemical Engineering comprises. But note that this benefit is, of course, not unidirectional but mutual.

3DP offers a multitude of exciting possibilities in many respects. However, in our opinion, its enormous potential can be summed up in two essential qualities: the ability to create complex shapes that are difficult (or prohibitively expensive) to achieve using other manufacturing techniques and the ability to do so on a small scale, as opposed to other methods that require the production of large quantities of the same products to be worthwhile.

In Chemical Engineering, obtaining complex or intricate shapes has one purpose that stands out above all others: increasing surface area. 3DP makes it possible to manufacture reactors, mixing devices, and packed columns with geometries that improve performance in continuous flow and batch processes [1–6]. Also, filters [7], adsorbent structures [8] and membranes [9,10] can be 3D printed, which can be very useful in environmental applications. And in this sense, there are also features of 3D printing that can help develop more sustainable chemical production systems. On the one hand, these technologies usually involve a reduced use of raw materials and easy reuse [11]. On the other hand, it is a way of bringing manufacturing closer to the place of sale or use, with the design being the only thing that travels, rather than the product and/or its components, thus reducing the environmental impact associated with transport.

At the laboratory scale or in relatively low-volume industries such as patient-specific pharmaceuticals, the equipment can be manufactured entirely by 3D printing [12]. In these cases, by choosing the proper technique and material, outstanding results can be obtained in less time, and at a lower cost, than conventional manufacturing techniques. While building large-scale equipment solely through 3D printing still has its hurdles, it can also help to manufacture some of its components; this is the case for structured catalysis [5,13,14] and. Thanks to 3DP, it is possible to manufacture catalysts with optimised geometries to maximise efficiency while minimising pressure drop [15].

A larger surface area is of interest not only to promote mass transfer. Heat transfer also benefits from such geometries. 3D printed heat exchangers, radiators, or diffusers can also improve efficiency compared to those manufactured using traditional techniques [5].

Creating unique objects is also of great interest to Chemical Engineering (and Science and Technology in general), especially during the research, development, and optimisation stages [16,17]. It is a natural vein in the field of product design. Autonomous fabrication by designers, nimbly bringing ideas into the real world, allows for a paradigm shift in the creative process. The continuous introduction of improvements or slight modifications can become quite difficult if it depends on third parties. In addition, the digital nature of this manufacturing technology makes it a good companion for computer simulation or modelling, such as computational fluid dynamics (CFD) [1,5,18–20]. In this sense, it presents itself as a powerful and versatile tool for experimental testing and evaluation of mathematical/theoretical analyses. It allows checking with a high degree of certainty whether the specifications will be met. And if not, it can be re-tested without 'wasting' time and money. Moreover, manufacturing by 3DP does not usually require overly expensive equipment or extensive user training to achieve very decent results (it would be for more complex cases). This characteristic makes 3DP an accessible technology to implement in any industry or laboratory, opening the doors of manufacturing to professionals with a wide range of skills (Figure 1).

Another great point is the possibility of creating prototypes or end products and the equipment itself. This capacity can be of enormous interest for process optimisation and even process scaling [21]. Although large-scale construction is still among the ‘must-haves’ of additive manufacturing, progress is also being made in this direction (such as 3D printing houses and small buildings). It may only be a matter of time before it becomes a competitive alternative in the ton’s territory. Indeed, manufacturing by 3D printing is considered the next manufacturing revolution [22,23]. However, most 3D printing processes have not yet reached their highest technology readiness level [24].

Malik et al. [25] have highlighted the technological revolution of 3D printing in Industry 4.0, which vastly changes the product manufacturing scenario. 3D printing is emerging as a sustainable technology and is playing a vital role as an essential pillar in implementing the concept of Industry 4.0. Thus, 3D printing, because of its technical benefits, offers advantages, particularly in weight savings, waste minimization and energy savings. However, it presents barriers and challenges associated with the implementation of these technologies at a mass scale, such as extending the range of printable materials, optimising the process to achieve higher production volumes, and improving the performance (accuracy, mechanical properties...) of the printed parts to be used as final product in a greater number of applications.

Moreover, the utilization and implementation of this technology will force the industry to shift towards an integrated modus operandi, where machinery (autonomous, interconnected, and intelligent), systems, and networks can exchange information and transfer the output to the systems of production management [26–28].

In any case, for those chemical engineers who strive to work with, manage, and understand new technologies, 3DP and other aspects of Industry 4.0 should represent an opportunity, a challenge, and not a threat.

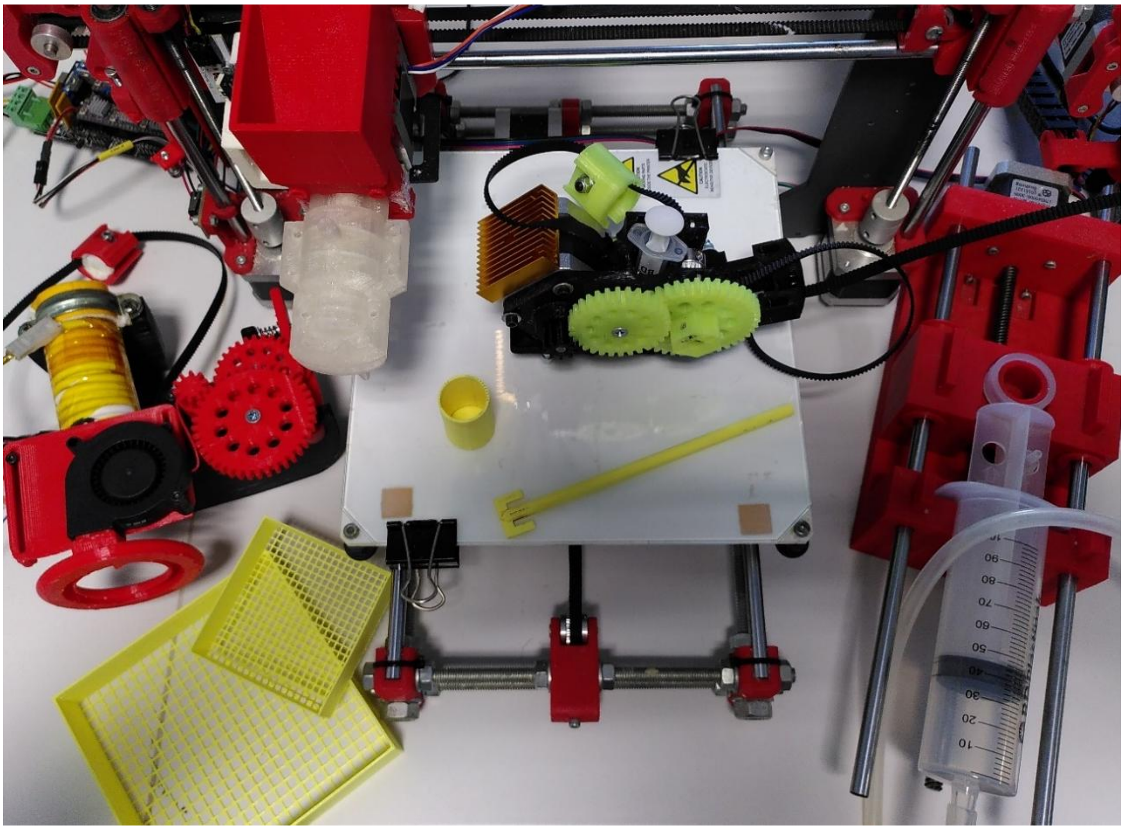

*Figure 1. 3D printed experimental extruders and labware*

## 2. From the outside... mostly

The most used materials in 3D printing are polymers since these materials, and 3D printers able to process them, are very affordable compared to the machines used to make metal and ceramic components. Affordable 3D printers have become a sought-after tool in workshops in many industrial settings to prepare spare parts, tools, and pieces of prototypes. 3D printed parts can be quickly fabricated and used to test practical solutions during the design of new products or solve production issues faced while manufacturing of new and existing products. Some companies have realised that 3DP can be used to produce custom-made designs, and there are already consumer and medical devices made by different 3DP polymer technologies in the market. Examples of 3D printed commercial products made from polymers include shoes [29], jewellery [30], frames for glasses [31], and orthodontic devices [32]. 3D printing with polymers is also being used directly at health care instructions (i.e., hospitals and clinics) primarily for presurgical planning; based on magnetic resonance imaging (MRI) and computed tomography (CT) data of patients, detailed 3D models of organs are fabricated, so that surgeons can easier visualize and safely practice the medical interventions [33]. Research has shown that 3D printed polymeric implants are viable alternatives to traditional metal implants even with human clinical trials [34], but their use can still be considered experimental medicine primarily due to regulatory issues. Moreover, a vital yet limiting aspect of the design and application of 3D printing is the selection of suitable materials to be used as biocompatible implantable "inks" [23,35–37]. Some examples of 3D printed products with polymeric materials are shown in Figure 22. Chemical Engineering is essential during the formulation of 3D printable polymers since different additives are needed, for example, to induce or inhibit polymerization, control the flow behaviour, and enhance the properties of the 3D printed parts.

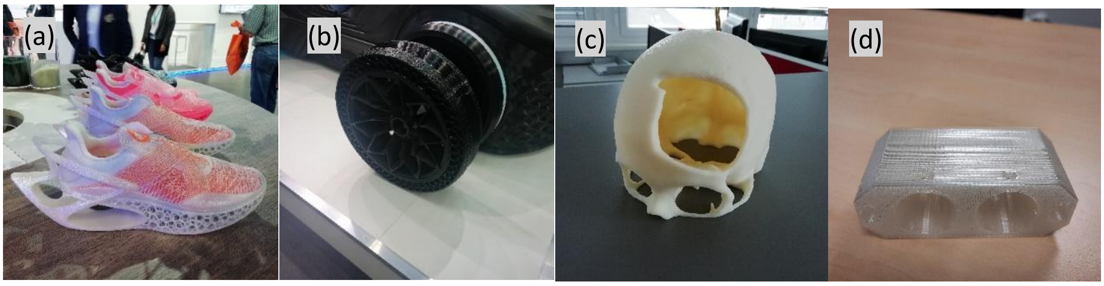

*Figure 2. Examples of 3D printed products made with polymers: (a) running shoes, (b) prototype non-pneumatic tire, (c) medical models for surgical planning, and (d) spare parts for laboratory equipment*

Polymers can be mixed with other materials to make composites that bring new functionality to the polymer and can still be processed by 3D printers that are suitable for polymers. Composite preparation requires knowledge in Chemical Engineering since the matrix and the fillers should be compatibilized and properly dispersed to obtain the best possible results. The additional materials can be continuous fibres [38] or particulates of organic [39] and inorganic materials [40] of many different shapes and sizes. The functionality of the fillers is related to mechanical reinforcement [41], enhancement of the thermal [42] and electrical conductivities [43], and making the polymer matrix magnetic [44] and photo responsive [45]. Combining these functional materials with 3D printing can produce more efficient devices and structures that can be fabricated to fit the required function, reducing the number of assembling steps [46]. Special types of composites are highly filled polymers that have a polymeric matrix and filler particles with more than 20 vol%. When the filler particles are sinterable materials, such as metal or ceramic powders, these highly filled polymers can be shaped by different 3D printed methods to obtain metal and ceramic specimens with complex geometries [47]. This type of indirect additive manufacturing is well suited for materials that are hard to process by direct 3D printing, such as ceramics [48], cermets and hard metals [49].

The development and implementation of ceramic 3D printing have been slower to a certain extent than that of polymers and metals. However, there is great interest in combining the properties of ceramics with the geometries and production volumes that can be produced by 3D printing [50]. Ceramics are very susceptible to minor defects, and the additive nature of 3D printing leads to many minor defects. For this reason, most of the current applications of 3D printed ceramic parts are geometries where porosity is an asset. Therefore, a possible application of 3D printed ceramic specimens is scaffolding for biomedical applications since they can support tissue growth, which is particularly useful for bone repair [51].

Another example would be its use as lattice substrates for different catalytic processes since ceramics can withstand very high temperatures and different electrochemical environments [52], and the complex geometries enhance the efficiency of the catalysis [53]. Finally, research into the application of ceramic 3D printed parts for patient-specific dental prostheses is being investigated but not widely used since the surface finish and mechanical properties are often far from optimal [54]. The melting temperature of ceramics is remarkably high, which makes it exceedingly difficult to perform direct 3D printing of ceramics. And even though the direct shaping of ceramics is possible, slurries, pastes and highly filled composites are usually prepared as feedstocks to be used in different additive manufacturing techniques [55]. A successful feedstock formulation and processing benefit from Chemical Engineering knowledge and expertise since the ingredients of these concentrated suspensions should be carefully selected and mixed under the appropriate conditions so that the feedstocks can be 3D printed and the additives removed in subsequent chemical steps without damaging the shape. Examples of 3D printed ceramic specimens are shown in Figure 3.

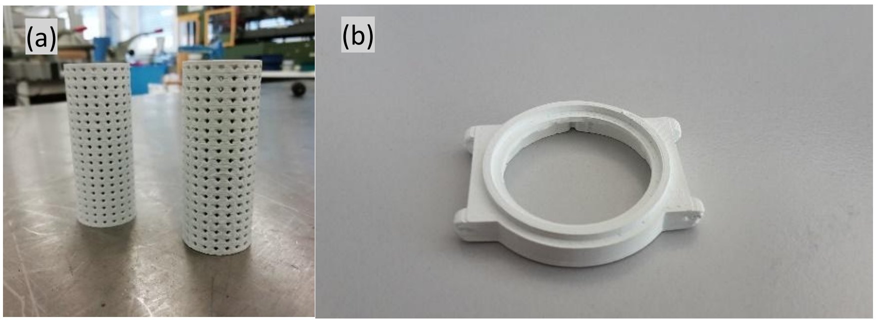

*Figure 3. Examples of 3D printed products made from ceramics: (a) monolithic support structures for plasma discharge catalysis, and (b) prototype of a watch casing.*

The need to reduce the used material and labour, and to increase construction speed, has led researchers to investigate and develop 3D printing of concrete. It has been demonstrated that 3D printing of concrete can be used to construct street furniture [56] and houses [57]. However, the widespread use of 3D printed concrete structures is still not a reality due to a lack of a regulatory framework for expedient approval and limited reinforcement options, which require resorting to unreinforced masonry or the manual application of the reinforcement [58]. A unique mix is needed to give concrete the required flowability to deposit it as strands and the solidification rate so that the shape is retained as the layers are deposited. Chemical Engineering knowledge is beneficial when designing the concrete mix and preparing it before deposition when mass transfer and chemical reactions need to be controlled to obtain suitable rheological properties for 3D printing.

The advantages of 3D printing (e.g., reduced mass, complex geometries that can enhance part consolidation, and heat and mass transfer) combined with the properties of metals (e.g., high strength, thermal resistance, high thermal and electrical conductivities) make 3D printed metal components desirable to many industries. One industry that is keen on developing, implementing, and certifying 3D printed metal parts is the aerospace industry, since mass reduction while maintaining functionality is crucial for reducing the operational costs of these vehicles. Also, compared to other industries, parts for the aerospace sector are usually fabricated at low production volumes. Examples of 3D printed metal parts include components used in liquid rocket engines (e.g., combustion chambers, propellant injectors, fuel pumps, thrusters, fuel nozzles, and nozzle liners) [59], hinge brackets, cabin bracket connectors, bodies of CubeSats, satellite solar panel deployment mechanisms, and satellite sandwich panels [60]. Other industries where low production volumes and high geometry complexity are needed include energy generation, medicine, speciality electrical machines and jewellery. In the energy generation sector, metal 3D printing is used to repair and manufacture turbine blades, heat exchangers, and airfoils [61]; while, in the healthcare sector, metal 3D printed parts are used as parts for medical devices, scaffolds, dental and orthopaedic implants [62]. Metal 3D printed parts are also being investigated to produce more efficient electrical machines such as cores, rotors, cooling channels, coil windings, heat exchangers, and motor housings [63]. Finally, the jewellery industry is currently producing unique designs from different precious (e.g., gold and platinum) and non-precious metals (e.g., titanium and steel) using direct metal 3D printing [64] or indirectly by producing casting cores in polymers or sand bound by polymers [65]. Examples of metal 3D printed products are shown in Figure 4.

As with the other materials discussed here, 3D printing of metals greatly benefits from knowledge in Chemical Engineering since the flow properties of powders or molten metals, as well as heat transfer, need to be controlled during the printing process to achieve high-quality metal specimens. Also, metal oxidations or unwanted reactions with carbon or nitrogen when using organic additives need to be controlled or eliminated to keep the desirable properties of the metal alloys selected for the different applications mentioned above.

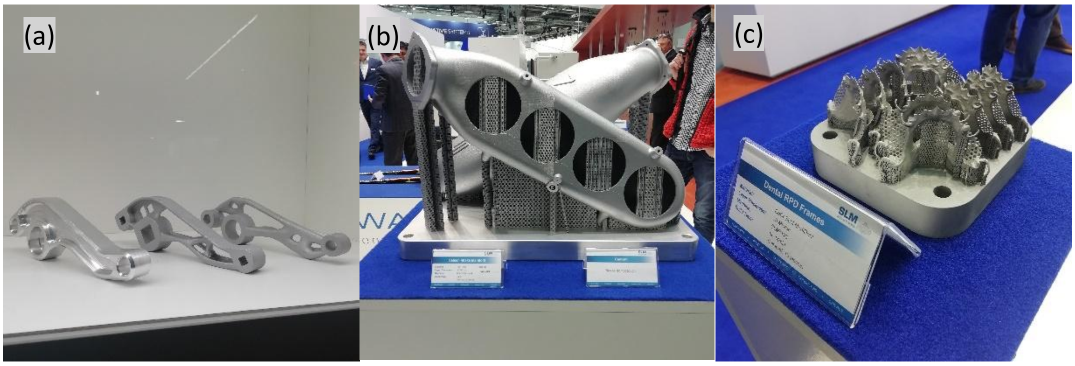

*Figure 4. Examples of 3D printed product made from metal: (a) brackets made by generative design to minimize weight without sacrificing functionality; (b) component of an engine housing; and (c) dental removable partial denture frames.*

In many current applications, 3DP represents a quick method of obtaining a functional part that, in many instances, can be produced by traditional methods (i.e., injection moulding, casting, and extrusion); therefore, the full potential of 3DP is not fully utilized. 3DP does not only represent a new manufacturing route for these materials but would also allow the product to gain enhanced properties [22]. For example, improving the electrochemical performance of batteries in terms of increased power and energy density by designing and printing complex interconnected electrodes [66]. Other examples can include the fabrication of bioinspired functionally graded structures with enhanced mechanical properties, which will be extremely difficult to fabricate by non-additive technologies [67].

# 3. ... to the inside... mostly

In the previous section, the strongest points of 3D printing were outlined: creating unique and/or complex-shaped objects as a function of material nature. However, how many things can we think of that are as unique and complex as the human body? It is not surprising, then, that one of the main lines of development for this technology is in medicine and tissue engineering. Replicating complex structures from every part of the organism is already extremely challenging. If one also considers the peculiarities of individuals, their disease or injury, each scenario in this field is one of a kind. Under these conditions, it is evident that technology with the characteristics of 3D printing is instrumental.

For example, its layer-based nature makes it an exciting option for replicating the different layers of human skin. Moreover, various portable printing devices have been developed for this purpose, enabling rapid in situ skin repair. Advances in cartilage bioprinting, replicating different areas of cartilage depending on depth, are also very promising. Given the importance of cartilage structures and their inability to regenerate, the bioprinting of cartilage with appropriate mechanical and functional properties would be a breakthrough. And this might not be so far, as being avascular and aneuronal, this type of tissue ‘evades’ some of the biggest challenges faced by 3D bioprinting. The development of 3D printed vessels is crucial to create vessels independently and for the proper vascularisation of the rest of the bioprinted tissues. And, of course, considerable progress has already been made in this regard, both by direct and indirect printing (using sacrificial materials that are subsequently removed to leave free channels) and with both conventional and coaxial nozzles. The primary difficulty lies in creating smaller vessels and hierarchical, branched vascular networks with functionality comparable to native vascular tissue. Improved vascularisation, as discussed above, would significantly contribute to the success of bioprinting other tissues, such as bone tissue. In addition to being highly vascularised, bone tissue has stiffness and mechanical performance that vastly differ from other human tissues. For this reason, it is necessary to resort to materials such as metals, ceramics [68] or bio-glasses, different from those commonly used to replicate all other tissues (mainly hydrogels) [69].

With the progressive improvement of bioprinting of different tissue types, the goal of creating complete organs from the patient's cells is getting closer and closer [70]. The successful bioprinting and implantation of solid functional organs is a vast technological and clinical challenge, but it could be a true milestone in the history of medicine.

However, while all these examples already represent incredible advances, there is another tissue whose replication sounds like science fiction: nerve tissue. Many of the most dramatic traumas and diseases we face are of neurological origin. Can we imagine being able to print a functional brain, connect it to a body and load our memories and ideas into it? (by connecting a pen drive or from the cloud?). Of course, the road to that end would be very long and could not be travelled by 3D printing alone but would require many other innovations. But without going to such extremes, being able to manufacture nerve tissue, even with only part of the capabilities of the original, could drastically change the lives of many people; and bioprinting has a good chance of being essential for this [71].

It is common for any engineered tissues to use scaffolds designed to support cells and facilitate their proliferation. Cells can be placed on (or in) the scaffold structure for culture [72]. Generally speaking, the external geometry of a scaffold should mimic that of the tissue to be repaired, while its internal structure should be highly porous to allow for cell growth and movement, as well as to facilitate the transport of nutrients into the scaffold and the removal of metabolic wastes out of the scaffold. On the other hand, regarding the mechanical properties of a scaffold, it is necessary to consider that these will change as the cells and tissue grow and that, in general, the mechanical strength of the combined construction of scaffold and regenerated tissue should be similar, throughout the process, to that of the tissue being repaired. Finally, the biological properties of a scaffold will have to be adequate to support cell growth and functions (such as cell adhesion, proliferation, and differentiation) and tissue regeneration without adverse effects on the host system [73]. Nowadays, most scaffolds are manufactured by conventional techniques such as freeze-drying or electrospinning. Electrospinning allows very thin filaments (in the order of nm) to be obtained, resulting in structures with high porosity but small pore sizes. However, electrospinning has some limitations, such as the difficulty of encapsulating living cells, the problem of creating three-dimensional structures, and the time required to do so. This and other conventional techniques provide only relative control over the structure morphology. In contrast, 3D printing is unlikely to create structures of such small dimensions, but it does offer reproducible control over the structural properties of the scaffolds. Other advantages are the simplicity of the process, the ability to create complex three-dimensional structures that mimic those of natural tissues, and the possibility of incorporating living cells [74]. One way of harnessing the strengths of each technique has been the development of hybrid bioprinting-electrospinning systems. In fact, there are already commercial models that combine microextrusion-based, droplet-based, light-based, or microfluidics-based bioprinting with electrospinning accessories, even within the range of low-cost bioprinters [75].

However, scaffold-free bioprinting techniques are also being explored. Removing the support on what to seed the cells makes the process more difficult in some respects and more accessible in others. After all, a foreign element is introduced to the cells with the scaffold. Compatibility must be ensured for the scaffold used and the decomposition products after completing its function. Scaffold-free techniques provide the cells with an environment more like the one inside the organism and greater freedom to grow and multiply without hindrance [76]. The environment in which the culture takes place is essential for the cells to thrive. This environment is usually achieved by bioreactors in which oxygen and nutrients are supplied to the cells, waste products are removed, and optimal tissue-specific conditions (such as mechanical stimulation in the case of muscle or cartilage) are created. In the end, a bioreactor simulates, as closely as possible, the environment where cells would be found inside the organism. This is like the idea of in-situ bioprinting, where bioink is printed directly on (or into) patient's body. In-situ bioprinting can be done by handheld devices (such as the one previously discussed for skin bioprinting) with fully automated printing systems or with hybrid solutions of human-controlled robotic-assisted bioprinting systems. The development of these techniques would help overcome obstacles, such as the insertion and adaptation of externally cultured tissues, as well as providing a rapid response to emergencies [77].

Until now, tissue engineering has been considered only in regenerative medicine. Indeed, it is true that this is its main application, but it is not the only one. Thus, 3D printing is also involved in the food sector. Cultured meat may become a real solution to the problems associated with meat consumption by an ever-growing world population. On the one hand, it could curb the enormous environmental impact of today's livestock industries. On the other hand, it would solve the ethical problem of animal slaughter. Moreover, this strategy applies not only to meat products but also to vegetables. Plant cells can be incorporated into printing materials to produce 3D printed products that resemble plant tissues [78]. After growing meat and vegetables, post-printing can help to make the resulting textures more 'natural' to consumers and improve the acceptability of 3D printed food. Beyond that, in a future where two-thirds of the world is expected to be urban areas [79], it seems that cell culture in bioreactors will necessarily take over from traditional agriculture and livestock farming. Many consumers may be reluctant to consume such products. However, options that were once practically residual in society, such as vegetarianism or veganism, are proliferating. Thus, this trend may be the vehicle for accepting cultured meat. In this context, 3D printing appears as a way to control the content of protein, fat and other nutrients while giving a more conventional appearance that reduces consumers' perception of unnaturalness [80].

The role of 3D printing in the food sector does not end there, far from it. Many more foods have already been 3D printed. 3D food printing (3DFP) has often been of interest as a commercial attraction because of its novelty. This 'surprise effect' is waning over time, and 3DFP has also been finding those applications where its use can have real added value. As in many cases, the production of customised products is one such application, sometimes for purposes that may be considered frivolous or inconsequential, but that nevertheless have a role to play in our lives. Birthday cakes, food with messages, and eye-catching shapes are things that, for the most part, already existed but which required more time and specific skills, are now within reach of anyone. However, in other situations, 3DFP can do much more for us than brighten our day. Many diseases require specific nutrition as part of their treatment or management. Allergies and intolerances, swallowing or digestive problems, celiac disease, Crohn's disease, diverticulitis, or irritable bowel syndrome are examples of conditions where nutrition plays a crucial role, and the possibility of customising foods could result in a significant improvement in the quality of life of patients [81]. Indeed, this can also be done without using a 3D printer, but 3DFP can make it easier. And that, in difficult situations, can be very important.

In any case, it is not only people with illnesses who could benefit from the advantages of the 3DFP to produce healthy products. It could also be a way to promote children's intake of fruit and vegetables by making foods with shapes and colours that may be more attractive to them [82,83]. Both the US Navy and NASA have launched their projects for the development of 3D printing systems for the preparation of meals on demand, customised to meet the energy and nutritional needs of each individual, which can also be prepared from their components separately and, thus, prolong the shelf life of foods in long-duration missions [84]. Even outside of specific populations, it could significantly change the lives of the whole community. Already today, a great deal of information is available from anyone. Purchases, location, training items and even digitalised medical records can be used to estimate individual's nutritional needs and automatically adjust the composition of meals based on this data [81,85]. In addition, 3DFP allows the creation of foods with structures that reduce their fat, sugar, and salt content and control their textural properties [83,86].

Even though virtually every aspect of our lives is now digitised, the way we cook and prepare food has remained virtually unchanged over the last few decades. Of course, there are new and better appliances that simplify some processes, but not enough to speed up cooking as much as our lifestyles have. This situation has led us to rely on convenience and fast food, to the detriment of our health in the short, medium, and long term. We are all aware of this problem, but we often do not have the time, money, or the desire to prepare something more elaborate. For this reason, a fundamental paradigm shift in food preparation could significantly improve our health and quality of life. 3D food printing has the potential to achieve a new level of automation in food preparation while maintaining (or even improving) the health benefits of traditional foods [87].

The ability to make food more palatable could also help adopt new eating habits, such as making meals from what are now food by-products, trying to meet the needs of a growing world population and doing so in a sustainable way [83].

Something similar could be said about the pharmaceutical industry. 3DP could also become a handy tool when it comes to processing medicines or foods for particular medical purposes that partially or even wholly replace other forms of drug administration, especially for chronic patients who are obliged to take large amounts of medication daily or for those who have difficulty swallowing tablets or low-viscosity soluble preparations [88].

In these cases, obtaining gel-type foods with colours, flavours and shapes that make them more attractive and palatable, as well as with a high content of active ingredients, would make it much easier and more pleasant to comply with long-term treatment. However, to exploit the full potential of 3DP, whether, in conventional food, clinical nutrition, or pharmacology, it is essential to develop more advanced printing systems to obtain more complex products that can genuinely compete with those processed by other methods.

Multi-material printing, in-situ gelling, coaxial printing, and mixing printing are some explored avenues for this purpose. For instance, Diañez et al. [88,89,91] designed and manufactured a new mixing device (Figure 5) to be adapted to a 3D printer controlled by its firmware allowing the continuous and automatic in situ mixing of (at least) one powder and one liquid feed. This device can be used as an automatic, software-controlled mixer to obtain thickener mixtures for patients with impaired swallowing physiology with precise proportions. In addition, more complex mixtures containing nutrients, drugs, or even colouring and/or flavouring agents can be prepared by using additional feeds. Lion et al. [93] developed a novel dual material hot-melt inkjet 3D printing system, which allows for precise control of multi-material solvent-free inkjet printing. This technology reduces the need for time-consuming exchanges of printable inks and expensive post-processing steps. With this printer, they showed the potential for the design of printed dosage forms for tailored drug release, including single and multi-material complex 3D patterns with defined localised drug loading, where a drug-free ink is used as a release-retarding barrier. Davis et al. [94] and Khaled et al. [95] addressed the current challenge of using multiple 3DP techniques to develop patient-specific, controlled-release formulations in a single-step process, providing a considerable leap in delivering tailored medications at the point of care, by eliminating the extensive formulation steps involved in other processes.

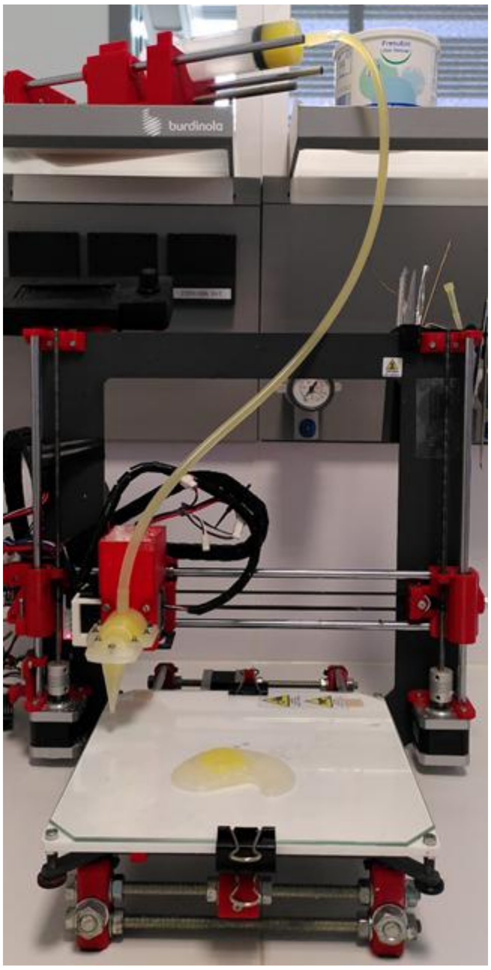

*Figure 5. Modified 3D printer and 3D printed a simulated fried egg made with thickened milk and orange juice (Adapted from ref. [83])*

To conclude this section, it is logical that one might think that all these aspects of the 3D printing technology seem to be more the domain of doctors, biologists, or nutritionists. In addition, it appears to be more related to mechanics and electronics, focusing on the design of increasingly sophisticated printers. So, what is the role of a chemical engineer? Well, it turns out that soft materials are the protagonists in tissue engineering, food technology, pharmacology, and, ultimately, everything that is designed to end up inside our bodies (liquids too, but those get along worse with 3D printing). Those materials that flow strangely, that are somewhere in between solid and liquid (i.e., viscoelastic), when a degree up or down dramatically changes their behaviour. Indeed, a significant temperature change is more normal, but with flow rate? How narrow is the place through which it passes? These are the ones chemical engineers get on well with, those where rheology plays a key role. Ideally, the material should flow without blockings or instabilities during printing but be consistent enough to hold its shape up afterwards. Often, yield stress and shear-thinning will help in this task. However, cells do not withstand shear well; and the material will not only be subjected to shear but also extensional flow. How will this affect their survival? Neither many nutrients nor drugs can tolerate high temperatures. We cannot expose our organism to crosslinkers or initiators that can be toxic. So gelling, phase changes or curing must be chosen carefully because there are (quite a few) occasions when the optimal conditions for printing are not optimal for the product or, instead, for the application. As 3D printing is a relatively immature technology, it is natural that much of the research has focused on the process itself: what does the material have to be like for the process to work well? Without losing sight of all that has been learned in answering that question, another question becomes more important: how does the process have to be for the product to be helpful? The printing process affects the rheology of the product, its shape, its appearance and even its composition. As in any production process, processing must be optimised so that all aspects meet the specifications required for its final use. It is excellent news that knowledge is also being generated in this regard [96]. As a result, the adaptation of 3D printing to new applications is becoming increasingly efficient and immediate.

## 4. Future directions: what to expect?

The relationship between Chemical Engineering and 3DP is not apparent to many chemical engineers. Many opinion pieces from as recent as 2020 [97] and 2022 [98] on the future of Chemical Engineering do not mention 3DP as one of the future endeavours of Chemical Engineering. This perspective is slowly changing, and opinion pieces from 2022 mention 3DP [99]. However, it is essential to highlight how Chemical Engineering will change 3DP in the future and vice versa.

The first area where 3DP is changing Chemical Engineering is in education. The scientific and technological future is directly linked to the education students of all ages receive, and 3D printing is not only revolutionizing the way products are designed and manufactured but also changing students' learning experience at various educational levels. Lecturers in architecture and engineering were early adopters of 3D printing primarily for the fabrication of models. However, it was observed that 3D printing is a powerful tool that can increase student and teacher engagement, facilitate learning, facilitate the understanding of scientific and mathematical concepts, improve the attitude towards science and technology subjects, and inspire creativity. 3D printing in different engineering disciplines can be used for very different purposes. For example, mechatronics students are tasked with building their own 3D printers to implement their knowledge of electronics and programming, while mechanical engineering students are asked to 3D print components of machines and perform experiments to understand concepts of hydro and aerodynamics. It has been observed that including 3D printing in the curriculum can improve the attitude towards different engineering subjects [100]. For example, in a Chemical Engineering program, it has been reported that combining project-based learning with 3D printing helped students to perform better when learning subjects that are perceived to be far from the core subjects of Chemical Engineering, for example, statics and dynamics [101].

Based on the results observed at the university level, 3DP has been extended to elementary and high schools (K-12). For example, 3D printed models are used in elementary school classes to explain geometric concepts and atomic structures and learn about extinct species with replicas of fossils. By teaching the 3DP process, students developed skills in creativity, technical drawing, product design and development, and later, how to apply 3DP to solve real word problems such as the design and fabrication of prosthetic devices [100]. However, pedagogical experts warn that the introduction of 3D printing can sometimes lead to frustration, physical fatigue, mental exhaustion, tedium, and occasional panic among the students. To counteract these adverse effects, a well-trained, enthusiastic, motivated, and organized teacher is needed [102]. It is safe to say that 3D printing will continue to be used in education in the future by looking at the positive outcomes presented in the literature.

If future professionals include 3DP in their toolbox, it will undoubtedly help this technology consolidate its position at the industrial level and in more domestic environments. And not just to consolidate, but to grow, of course. In fact, it is already happening. 3D printing using stimuli-responsive materials has originated a new term, “4D printing (4DP)”, which refers to the ability of these materials to alter their appearance and shape predictably after they are 3D printed, being the time the fourth dimension [103]. These materials are responsive to temperature, humidity, electric current, magnetic fields, pH, ionic strength, and light changes. Therefore, 4DP provides additional functional capabilities and performance-driven applications in all domains, such as aerospace, automotive, biomedical, electronics, acoustics, architecture, energy, and fashion. Applications include adaptive mechanisms, products, garments that respond to different environmental stimuli, and robot-like actuation without relying on complex electro-mechanical-chemical devices [104].

The most common 4D printed materials are shape memory polymers (SMPs). SMPs can recover their original shape after being deformed into a secondary shape. This memory effect occurs when a polymeric geometry transitions between its glassy and rubbery state. However, shape memory behaviour does not occur in all polymers since it depends on their structure and morphology, which, in turn, is influenced by their chemistry and processing conditions [105]. SMPs are networks consisting of molecular switches and fixing points. The switches are stimuli sensitive, whilst the fixing points determine the permanent shape of the network. The fixing points can be covalent bonds or intermolecular interactions [106]. Examples of SMPs that are melt/sinter processable include copolymers of polyurethane or polyesters, such as thermoplastic polyurethane (TPU) and polylactic acid (PLA). Examples of SMPs that are 3D printable by photopolymerization include poly(ethylene glycol)diacrylate (PEGDA), N-isopropylacrylamide (NIPAAm), and various methacrylate-based copolymers [107]. Some applications of 4D printed SMPs are heat-responsive grippers [108], valves [109], and occluders to treat cardiovascular diseases [110]. Other polymeric systems can be prepared to be responsive to moisture absorption. Thus, by swelling and shrinking in a controlled manner, these materials have been proposed to be used in architectural applications [111].

Metal 4DP requires the use of shape memory alloys (SMAs). SMAs are metallic alloys that can exist in at least two different phases and attain at least two different crystal structures. Temperature changes can be used to recover their initial shape after being deformed. This behaviour is because, at different temperatures, different crystalline structures are more stable. For example, the martensite structure is stable at lower temperatures, while at higher temperatures, the austenite structure is more stable. The recovery can be in one or two ways, meaning that the alloy can remember one or two shapes due to their different compositions and thermomechanical treatments applied [112]. Besides heat, magnetic fields can trigger the shape recovery in certain alloys by twin boundary motion or magnetic-field induced phase transformation [113]. The most common type of SMA is nickel-titanium (NiTi) alloys, which can be shaped by powder bed fusion technologies and can have applications as dental braces or stents [114]. Other 3D printable SMAs include Cu-Al-Ni [115] and Cu-Zn-Sn [116]. Another way to obtain shape-changing metallic objects is to fabricate bi-metallic objects with metals having dissimilar thermal expansion coefficients (e.g., Ni and Cu); these systems could be used, i.e., for high-temperature automatic switches [117].

Besides shape-memory materials, other materials that can be considered capable of undergoing 4DP are self-healing materials. There are two types of self-healing materials, intrinsic and extrinsic. Intrinsic self-healing materials have dynamic bonds, such as metal-ligand or hydrogen bonds, and are generally gels or elastomers that facilitate molecular diffusion. Extrinsic materials have healing components in microcapsules or vascular networks. Consequently, they can be more rigid since the healing occurs when the healing agents are released after the damage has occurred. Not all self-healing materials are 3D printable, but researchers are working to make them 3D printable while retaining their self-healing capabilities. Intrinsic self-healing elastomers [118] and hydrogels [119] have been 3D printed using extrusion for sensing and soft robotic applications. On the other hand, extrinsic self-healing polymers have been printed by vat photopolymerization using a UV curable resin containing solvent-filled microcapsules [120]. Being able to 3D print self-healing materials adds flexibility to the type of products that could be created, but commercially viable applications are still yet to come.

As mentioned above, 4D printing can fabricate dynamic structures with adjustable shapes, properties, or functionality. According to Momeni et al. [121], 4D printing is the art of combining science with engineering technology. The scientific aspect of 4D printing is related to fundamental research into developing new smart materials, stimuli, and mathematical modelling. From the engineering aspect, the 4D printing process enables innovative and fascinating applications that can hardly be achieved with conventional manufacturing processes.

However, 4D printing has its limitations in terms of printing techniques, materials used, and design techniques of the structures. These limitations open enormous scope for the future, as more smart materials may be discovered along with new and more efficient printing technologies. Overcoming these limitations poses an exciting challenge to Chemical Engineering. 4D printing will revolutionise the manufacturing and designing of products in the future. It will lower the capital requirement, reduce marketing time, make products easily transportable, and reduce the size of products, thus bringing a new and efficient business model [104].

# 5. Concluding Remarks

*At its simplest, Chemical Engineering is the science of converting one thing into another* [122]. If 'one thing' is a digital design and 'another' is a real object, we have the basic principle of 3DP. The link between 3DP and Chemical Engineering is undeniable; both can benefit from each other. A recurrent statement among academic staff is that "Chemical Engineering is everywhere". It has something to contribute to all —or almost— phenomena in the world around us (indeed, professionals from other disciplines have the same feeling about their areas of knowledge, and no doubt they are not wrong either). Knowledge in Chemical Engineering will continue the development of better materials and devices for 3D printing, while 3D printing can be used to train better chemical engineers and to solve other problems faced in Chemical Engineering. It can be said that Chemical Engineering and 3D printing can be a powerful duo to find solutions to some of the most pressing challenges currently being faced by humanity.

The following table (Table 1) is intended to summarise how Chemical Engineering should be (and indeed is) deeply involved in 3DP and its development to get all it has to offer.

*Table 1. Summary of potential contributions of Chemical Engineering and fields of application for different 3DP technologies*

| **Technique** | **Chem Eng contribution** | **Tools** | **Fields** |
|---|---|---|---|
| Material Extrusion - MEX | Heat transfer, material flow and pressure drop, phase changes, chemical and physical gelation, new printable materials (plastic, metal, ceramics, concrete, gels, and fluids) | Rheology, CFD, mixing, thermomechanical analysis | Building and fabrication, food and pharmaceutical, bioengineering, biomedicine, aerospace, and industrial applications |

| | | | |
|---|---|---|---|
| Vat photopolymerization - VPP | Viscosity of resins, crosslinking degree and kinetics, new printable materials (low viscosity and high performance, eco-friendly and biocompatible) | Rheology, optical analysis, thermomechanical analysis, UV, or visible light radiation | Medical and dental models, orthodontic devices, industrial applications, bioengineering, adhesives, and coatings |
| Material jetting -MJT | Newtonian and complex fluids, surface tension, contact angle | Rheology, CFD, surface properties and wettability, thermomechanical analysis | Medical and dental models, visual prototypes, industrial tooling, electronics |
| Powder bed fusion – PBF | Powder flow, surface tension, contact angle, heat transfer, new printable materials (thermoplastic composites, metal alloys, ceramics) | Powder rheology, optical analysis, thermomechanical analysis | Aerospace applications, industrial applications, optical frames, orthopaedic implants |
| Direct Energy Deposition - DED | Powder flow, heat transfer, flow of Newtonian fluids | Powder technology, optical analysis, thermomechanical analysis | Large aerospace construction and industrial, multi-material fabrication, in-situ repair |
| Binder Jetting - BJT | Powder flow, surface tension, contact angle, interparticle interactions | Powder technology, thermomechanical analysis | Casting patterns, industrial moulds, aerospace applications, prototypes, jewellery |
| Sheet Lamination - SHL | Heat transfer, surface property modification, adhesive development | thermomechanical analysis, surface chemical analysis | Visual prototypes, aerospace, and industrial applications. |

Throughout this text, we have tried to emphasise the critical role that Chemical Engineering should play in the future of 3DP, as we strongly believe it should. However, we cannot finish without recalling that, like most outstanding achievements, this cannot be done on our own. The development of 3DP must be approached interdisciplinary, bringing together the knowledge, views and efforts of many disciplines and minds. Only then will it become the powerful tool it has the potential to be. Therefore, we can take advantage of 3DP as a starting point for interdisciplinary learning about the significant challenges facing our society today. Thus, also providing significant changes in 21st-century education.

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