

Article

Green Process Engineering as the Key to Future Processes

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Abstract: Growing concern for the environment, increasing stringent standards for the release of chemicals into the environment and economic competitiveness have led to more environmentally friendly approaches that have resulted in greater pollution prevention via waste reduction and efficiency maximisation. Green process engineering (GPE) is an important tool that could make significant contributions in the drive toward making hazardous and wasteful processes more sustainable for the benefit of the economy, environment and society. This article highlights the guidelines that could be used by scientists and engineers for designing new materials, products, processes and systems. Few examples of current and future applications of GPE, particularly in the areas of biofuels, supercritical fluids, multi-functional reactors and catalytic processes, have been presented.

Keywords: biofuels; catalytic processes; environmentally benign process; green applications; green engineering principles; green process engineering (GPE); supercritical fluids (SCF); propylene carbonate; dimethyl carbonate; epoxides

1. Introduction

It is impossible to imagine modern life without the products manufactured by industries. These products are used in everyday aspects of life, including agriculture, construction, transportation, electronics and well-being. However, their productions generate waste, release toxic chemicals, increase greenhouse emissions and greatly affect human health and the environment. As such, these

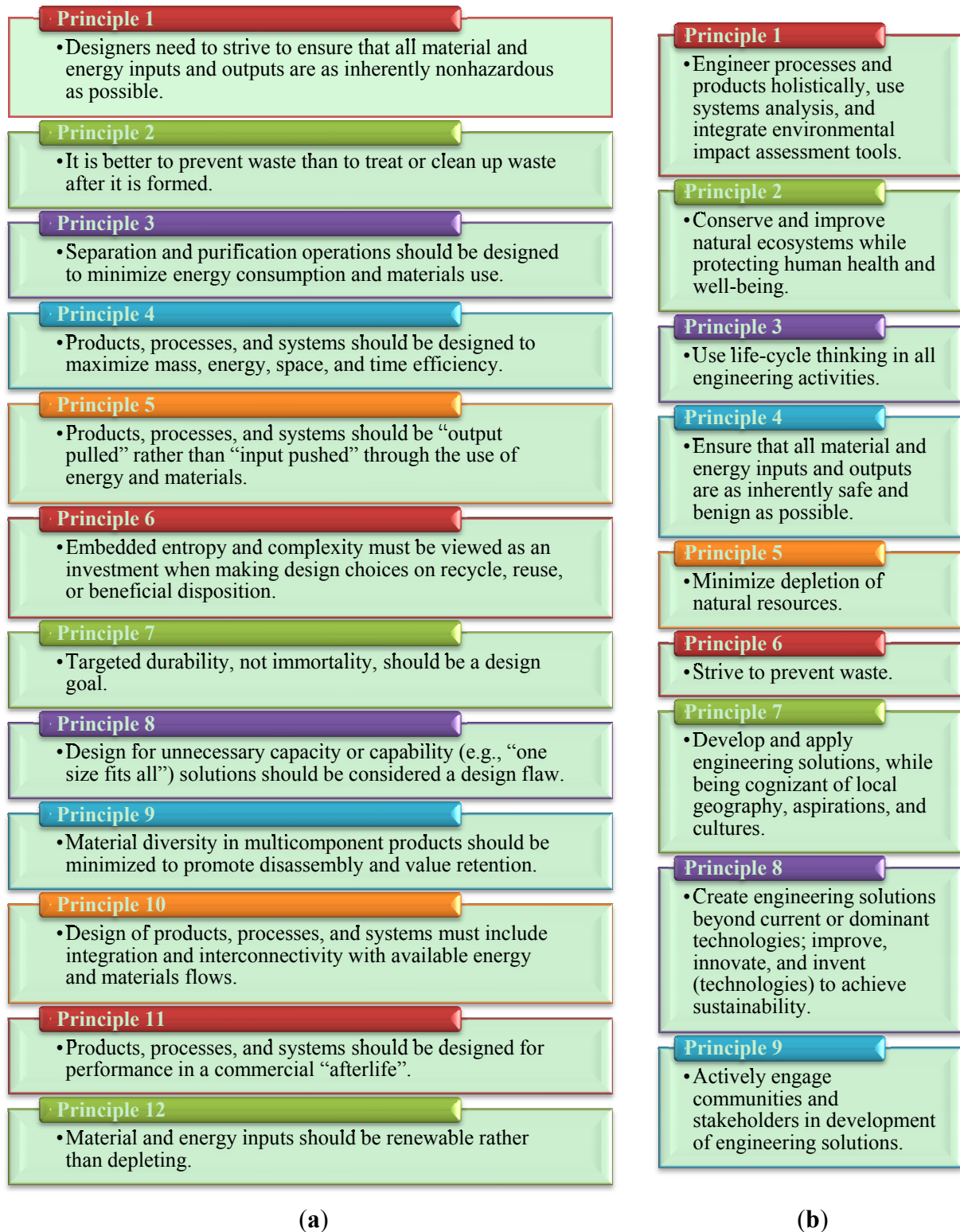
concerns are driving new priorities that have emphasis on being “green”, ranging from products to processes and technologies. Engineers and scientists from diverse fields are leading the way to solve these issues and challenges. Thus, green engineering has the capability to support and foster this innovation. One of the goals of the modern green process engineering (GPE) community is to design, develop and commercialise industrial processes that are sustainable and economically feasible, whilst minimizing the impact of chemical processes on human health and the environment. GPE is defined as, “the design, commercialization, and use of processes and products, which are feasible and economical while minimizing (a) generation of pollution at the source and (b) risk to human health and the environment. Green engineering embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product [1]. In the past, the objective of process engineering was to minimise product cost and increase profitability without assessing the long-term impacts on the planet and human health. Hence, engineers and scientists should carefully make technical decisions that could have significant impact on the environment. These decisions can lead us either in the direction of sustainability or contribute further to the growing problems. Hence, there is a greater need for engineers and scientists to come together for a common vision of saving the planet by providing new greener technologies and products in an environmentally friendly manner.

1.1. Issues and Challenges of Green Process Engineering

As we move to 2014, our society is faced with challenges in the sustainability of our current technological and lifestyle systems. There are enormous global environmental concerns, including energy and fuels, food, transportation, construction, water access and use, pollution and ecological destruction. The current and future goals of process engineering are therefore not only to sustain and reduce the cost of products, but simultaneously reduce the impact on the environment and on human health. In other words, today’s process engineering has moved towards green process engineering (GPE). As such, the biggest challenge is to find innovative solutions that are based on environmentally benign design and manufacturing, to avoid the generation of waste or pollutants, to keep the product cost affordable with growing demands, to increase the capability of products to be recycled or reused and with the ultimate goal of introducing significant environmental improvements. Most companies are on a sustainability mission, where parameters, such as the utilization of non-depletable resources, the reduction of global-equivalent greenhouse gases emissions and the reduction of energy costs (by utilizing renewable energy resources), are considered important environmental and social targets [2]. However, in terms of fully adopting a sustainable process, there are other factors to be considered, including suitable market conditions, effective economical regulations and social acceptance defined by product demands. To improve industrial sustainability at the process level, the principles of green engineering provide a tangible framework to address the growing concern of human health and the environment and also provide a suitable guide for green process engineering. Its emphasis is on process, system and product optimisation. Anastas and Zimmerman [3] have outlined twelve principles of green engineering that are summarised in Figure 1a. Similarly, at the first conference on “Green Engineering: Defining the Principles” held in Florida in 2003, nine principles of green engineering were developed and are presented in Figure 1b. These principles provide a framework for scientists

and engineers to use in designing processes and products within the boundary conditions set by society, business and government, which are guided by important parameters, such as costs, safety, demand, performance and environmental impact [4]. It integrates and couples the most important elements on product optimisation, processes and systems [5].

Figure 1. (a) The twelve [3] and, **(b)** nine [4] principles of green engineering.



In 2012, the U.K. Engineering and Physical Sciences Research Council (EPSRC) announced four new engineering projects that aim to help the U.K. in developing lightweight, novel, easily recyclable, with a longer lifetime, materials and clean contaminated land for reclaiming valuable metals [6]. These projects are: (i) CLEVER (Closed Loop Emotionally Valuable E-waste Recovery); (ii) Cleaning Land for Wealth (CL4W); (iii) EXHUME (Efficient X-sector use of Heterogeneous Materials); and (iv) CORE (Creative Outreach for Resource Efficiency).

Thus, as noted, many industrial and academic sectors are considering greener and cleaner alternative routes. Green engineering applications are extremely broad and include almost every industry. These applications can be generally grouped into the following categories: renewable power energy [7], process optimisation [8], environmental monitoring [9] and the development of green products and technologies [2]. In this paper, we will focus on green processes, examine how industry is moving towards this direction and highlight the challenges chemical and process engineers are currently facing. A mini review of a selection of implemented processes, such as the utilization of supercritical fluids, continuous hydrothermal processes and a few important catalytic processes, that have had direct impact on the field of green engineering are discussed in the following section.

2. Applications of Green Process Engineering (GPE)

2.1. Production of Biodiesel and Biofuels

Currently, the majority of the world's energy is supplied through petrochemical sources, coal and natural gas. However, depleting fossil fuels, increasing energy demand from various sectors, global warming, environmental pollution due to the widespread use of fossil fuels and price fluctuations make petroleum-based energy unreliable. Therefore, it is increasingly necessary to develop renewable energy resources to replace the traditional sources.

Biodiesel has recently attracted enormous interest as an alternative and environmentally friendly fuel source. Biodiesel exhibits characteristics that are similar to traditional diesel fuel. In addition, the flow and combustion properties of biodiesel are similar to petroleum-based diesel [10]. Biodiesels have the following advantages over diesel fuel: they produce less smoke and particulates, have higher cetane numbers, produce lower carbon monoxide and hydrocarbon emissions, are biodegradable and non-toxic and provide better performances in engine lubricity compared to low sulphur diesel fuels. Hence, it could be used as a substitute for diesel fuel.

Abbaszaadeh *et al.* [11] have compared different current biodiesel production technologies, including blending of vegetable oils, micro-emulsions, pyrolysis and transesterification reaction. The preferred method for the production of biodiesel is generally prepared from the transesterification of triglycerides. The most common sources of triglycerides are first generation biofuels, such as edible virgin vegetable oils, and second generation biofuels, such as animal fats and used cooking oil (UCO). Most of the current biodiesel (>95%) is prepared from first generation agricultural crops [12]. The use of food sources for biodiesel production could have serious consequences on the food supply chain. Hence, UCO is considered to be an attractive feedstock for biodiesel production, since it does not put pressure on food supply, helps in recycling the UCO and is significantly cheaper than virgin oils. However, UCO must go through a pre-treatment process before it can be used for the production of

biodiesel [13,14]. Alcohols, such as methanol, ethanol and butanol, have been used for the transesterification reaction [15,16]. However, it is considered that short chain alcohols, such as methanol and ethanol, give a stable product and higher conversion, compared to long-chain alcohols [17]. The transesterification reaction can be acid-catalysed [18], alkali-catalysed [19] or enzyme-catalysed [18,20,21]. A number of authors have reported biodiesel production in terms of composition, properties and specification [22], the effect of different catalysts on biodiesel production [23], biodiesel production using enzymatic transesterification [24] and waste cooking oil [25,26].

A comparison of an immobilised enzyme (Novozyme 435) with an ion exchange resin (Purolite D5081) for the pretreatment of used cooking oil (UCO) for biodiesel production was reported by Haigh *et al.* [18]. A 94% conversion of free fatty acids (FFA) was obtained using Purolite D5081 compared to FFA conversion of 90% with Novozyme 435. On the other hand, it was reported that there are side reactions associated with Novozyme 435, which result in the formation of more fatty acid methyl esters (FAME) and FFA. However, it was stated that Novozyme 435 uses a low optimum methanol to FFA ratio of 6.2:1, instead of the very high methanol to FFA ratio, *i.e.*, 98:1, required by Purolite D5081 for optimum FFA conversion. Jachuck *et al.* [27] reported an energy efficient continuous production of biodiesel from methanol and sodium hydroxide using an intensified narrow channel reactor module and canola oil as a feedstock. A triglyceride conversion of 98% was reported within 3 min at 60 °C, 80 psig and 1% catalyst loading.

To eliminate the drawbacks of first and second generation biofuels, including the issue of sustainability, the third generation of biofuels, such as microalgal oil, is regarded as the best route for biodiesel production, as it is independent of food sources [12,28,29]. During the process of photosynthesis, algae efficiently store solar energy and sequester CO₂, easing climate change caused by the emission of greenhouse gases [29]. In addition, algae could grow 7–31 times faster than palm oil plants, and 50% of their weight consists of oil [28]. Pfromm *et al.* [30] studied the economics of biodiesel from algae using the principle of conversion of mass and concluded that algal biodiesel could be produced sustainably with the exception of natural gas to produce nitrogen-based fertiliser in the long term. Overall, the commercialization of algae to biodiesel during initial stages will depend on the support of the government [31,32]. A number of reviews on biodiesel production using microalgae as feedstock has been published [33,34].

A number of publications have reported the production of biodiesel from algal oil using a two-step process, *i.e.*, acid esterification followed by base transesterification. [35,36]. Using a two-step process, a 90.6% yield of biodiesel was achieved at optimum conditions using *Enteromorpha compressa* algal oil [36], while 100% conversion of triacylglycerols (TAG) and FFA was achieved using *Scenedesmus* sp. algal oil [35]. Krohn *et al.* [37] reported the production of biodiesel using a supercritical fixed bed continuous flow process using algae (*N. oculata*) as a feedstock with 85% efficiency. A single-step process of converting wet algal biomass (Inoculum: *Nannochloropsis* sp.) to biodiesel using supercritical methanol was reported by Patil *et al.* [38]. Similarly, a single-step method using a wet lipid extraction procedure (WLEP) was conducted to extract 79% of transesterifiable lipids present in wet algal biomass (84% moisture) via acid and base hydrolysis [39]. The single-step process looks promising, as it eliminates the need for drying and extraction of algal biomass and yields faster reaction times. Martin and Grossman [40] conducted experiments for the production of biodiesel using

different technological routes and concluded that for algal oil, the optimised route for biodiesel production is an alkali-catalysed process, while for waste cooking oil, heterogeneous catalysed transesterification is regarded as the optimum process for biodiesel production.

As of now, the production of biodiesel is much less compared to traditional fuels to make a significant impact on the fuel market. In comparison to petroleum-based fuel, biodiesel has poor cold flow properties, therefore, having a tendency to gel or solidify at low temperatures, and possesses low volatility, high pour and cloud points, higher NO_x emissions and incomplete combustion. In addition, the cost for biodiesel is not competitive compared to petroleum-based fuel and requires special management for transportation and storage. However, engineers and scientists are putting significant efforts into improving the current technology of biodiesel production, so as to reduce the greenhouse gases and to meet the needs of current and future fuel demands.

2.2. Green Synthesis of Organic Carbonates from Carbon Dioxide

One of the requirements for a sustainable environment in designing a green chemical process is the utilization of renewable raw materials. Carbon dioxide (CO₂) emissions have increased to unsustainable levels in the atmosphere, which has led to climate change. The reduction of CO₂ emissions has therefore become a global environmental challenge. Organic carbonates, such as propylene carbonate (PC) and dimethyl carbonate (DMC) have been widely used as intermediates in the synthesis of chemicals, pharmaceuticals and fuel additives [41–45]. Organic carbonates are generally synthesised using homogeneous catalysts, toxic raw materials, including phosgene and *iso*-cyanates and solvents [45–50]. Hence, there is an urgent need for an environmentally benign green process for the synthesis of organic carbonates from CO₂ by using a heterogeneous catalyst and eliminating the use of toxic chemicals and solvents. Several methods have been developed to design a stable and reusable heterogeneous system by immobilised or grafted ionic liquids and salts into solid materials, such as polymers [51,52], a molecular sieve MCM-41 (Mobil Composition of Matter No. 41) [53,54], magnesium oxide (MgO) [55,56] and silicon dioxide (SiO₂) [57,58]. These heterogeneous catalysts showed good catalyst activity and selectivity for the cycloaddition reaction of organic carbonate synthesis, but failed in terms of catalyst reusability.

Adeleye *et al.* [59] synthesised PC in a Parr high pressure reactor using several heterogeneous catalysts, including ceria doped zirconia (Ce-Zr-O), lanthanum oxide (La-O), lanthana doped zirconia (La-Zr-O), ceria and lanthana doped zirconia (Ce-La-Zr-O) and zirconium oxide (Zr-O), and without using a solvent. High propylene oxide (PO) conversion and yield of PC were reported at 170 °C, 70 bar CO₂ pressure and 10% catalyst loading using the Ce-La-Zr-O catalyst. Reusability studies revealed that the Ce-La-Zr-O catalyst could be used several times without any significant decrease in PC yield.

Similarly, Saada *et al.* [60] have used heterogeneous catalysts, such as ceria-zirconia doped graphene (Ce-Zr-graphene) catalyst, for the synthesis of DMC from CO₂ in the presence of 1,1,1-trimethoxymethane (TMM) as a dehydrating agent and without using a solvent. The results for the synthesis of PC and DMC look promising as a future greener process. From the environmental, economic and human health point of view, solvent-free heterogeneous catalysis is the process route of the future for eliminating the shortcomings of the current process of organic carbonate synthesis.

2.3. Production of Commercially Important Epoxide Building Blocks

Epoxides are valuable building blocks for organic synthesis, particularly for the production of commercially important products for pharmaceuticals, plastics, fragrances, food additives, paints and adhesives [61–64]. The conventional methods for the industrial production of epoxides employ either stoichiometric peracids or chlorohydrin as an oxygen source. However, both methods have a serious environmental impact, as the former produces an equivalent amount of acid waste, whilst the latter yields chlorinated by-products and calcium chloride waste. In addition, there are safety issues associated with the handling and storage of peracids. Hence, there is a strong need for cleaner catalytic epoxidation methods that use safer oxidants and produce little waste.

Over the years, soluble compounds of transition metals have been used as efficient catalysts in alkene epoxidation [65,66]. A notable industrial implementation of homogenous catalysed epoxidation is the Halcon process [67]. However, homogenous catalysed systems suffer from several industrial difficulties, including corrosion, deposition of the catalyst on the wall of the reactor and difficulties in the separation of the catalyst from the reaction mixture, which may lead to product contamination [68]. As such, alternatives have been considered. These new routes include developing a greener epoxidation process by utilizing a heterogeneous catalyst and a benign oxidant, such as *tert*-butyl hydroperoxide (TBHP), as it is environmentally benign, safer to handle and possesses good solubility in polar solvents. There has been a considerable amount of publications on polymer supported alkene epoxidation catalysts, such as Fe, Ni and Co [69], Ru [70], Ti [71], Mn [72], Mo [73] and Cu [74]. Additionally, polymer supported molybdenum catalysts have been reported to be effective for alkene epoxidation using alkyl hydroperoxide as the oxygen source [75–83].

A number of authors reported a novel and greener solvent-free process for alkene epoxidation using environmentally benign *tert*-butyl hydroperoxide (TBHP) as an oxidant [84,85]. In this process, polybenzimidazole supported molybdenum complex (PBI.Mo) and a polystyrene 2-(aminomethyl) pyridine-supported molybdenum complex (Ps.AMP.Mo) were used as catalysts for the epoxidation of alkenes. During the epoxidation reaction, *tert*-butanol is also formed as a co-product, and hence, this is termed as an atom-efficient process. Furthermore, *tert*-butanol can be efficiently recycled through hydrogenolysis and oxidation [86]. Recently, continuous epoxidation of 1-hexene with TBHP using the Ps.AMP.Mo catalyst has been conducted in an RDC (Reactive Distillation Column) [87,88] and FlowSyn reactor [89,90].

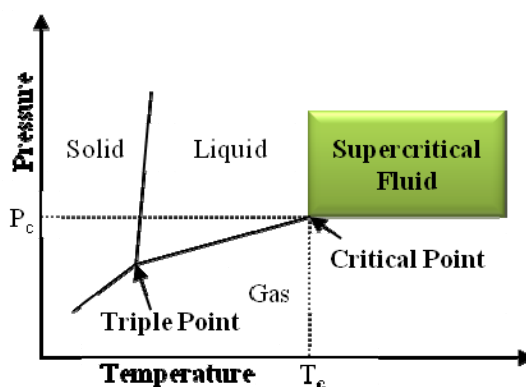
Continuous flow reactions in a FlowSyn reactor (Figure 2) have shown substantial benefits, including increased selectivity, scalability and reproducibility, and therefore, they have enormous potential as a process alternative for carrying out liquid phase chemical reactions [91–94] compared to experiments conducted in a classical batch reactor. The reactor is equipped with a stainless steel column packed with catalyst, two HPLC pumps, a control interface, SquirrelView software and a data logger supplied by Grant Instruments. Recently, epoxidation experiments conducted in a FlowSyn reactor achieved 95% conversion of TBHP and ~82% yield of 4-vinyl-1-cyclohexene 1,2-epoxide at 353 K and a 5:1 feed mole ratio (FMR) using Ps.AMP.Mo catalyst [90].

Figure 2. Continuous FlowSyn flow reactor experimental set-up.

2.4. Green Chemical Processing Using Supercritical CO₂ (SC-CO₂)

A supercritical fluid (SCF) is defined as a material that is used in a state above the critical temperature and critical pressure (Figure 3) where gases and liquids can coexist [95–97]. They exhibit unique properties that are different from those of either gases or liquids under standard conditions. SCF has a higher diffusion coefficient, lower viscosity (very similar to the gas phase) and lower surface tension than a liquid solvent and improved mass transport properties. SCF properties can be tuned dramatically by small changes in pressure, especially when the critical parameters are being approached [98].

Figure 3. A simplified phase diagram for a pure phase substance illustrating density changes from liquid to gas. P_c and T_c are the critical pressure and temperature, respectively. P_c and T_c are the defining boundaries on a phase diagram for a substance. Beyond these points, the fluid is supercritical, with unique physical and chemical properties between gases and liquids.

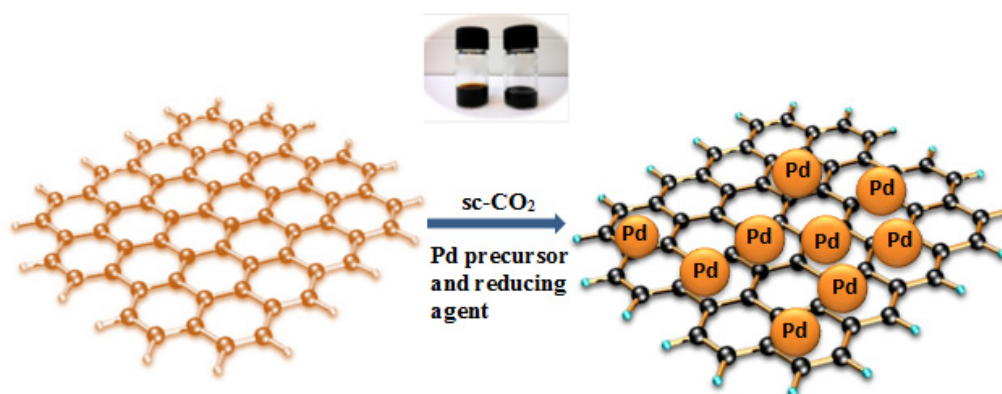


The increased interest in SCFs is driven by the ability to easily modulate their properties (via altering the pressure and temperature) and, more importantly, their potential to substitute toxic organic solvents [95,99]. Conventional synthetic processes use volatile organic solvents that are flammable, toxic, generate large amounts of waste and, consequently, are non-sustainable. Dictated by

the changes in legislation on waste solvent production and emissions and the significant increased costs of their waste disposal, many industrial sectors have moved towards cleaner and greener chemical manufacturing routes.

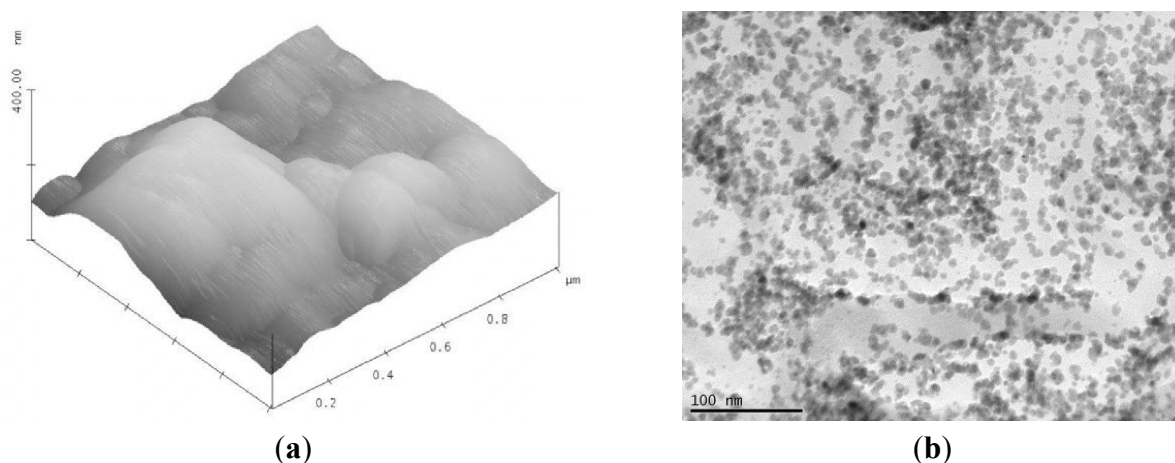
The substitution of the organic solvents by SCFs (e.g., carbon dioxide or water) offers significant improvements in the chemical and environmental fields. As such, supercritical carbon dioxide (sc-CO₂) offers relatively low critical parameters ($T_c = 31.1\text{ }^{\circ}\text{C}$, $P_c = 7.38\text{ MPa}$), non-toxicity, non-flammability, recyclability and is a by-product of the industrial synthesis of ammonia [100]. Furthermore, it leaves no residue, as the solvent removal is done easily via the decompression of CO₂. As a result, the number of applications in various areas, including industrial scale-up production, has increased dramatically. These include nutrition, such as coffee bean decaffeination, pharmaceutical and polymer processing [99,101–103] of compounds, such as hyperbranched copolyesters [104], polycarbonates [105] and polyurethane [106], cleaning applications in the area of microelectronics, medical instrumentation and metallic surface cleaning, textile processing and dyeing of natural fibres, such as cotton, cellulose fibres and some synthetic materials [107,108], offering optimisation in the economical, energy reduction and waste aspects of this technology [109,110], chromatography and materials synthesis [111–114], such as metallic Janus silica particles [115], palladium (Pd) nanoparticles [116] or the treatment of LiFePO₄ cathode materials [117], in addition to the fabrication of semiconductor devices [118]. Recent scientific reports have utilised sc-CO₂ for the synthesis of graphene-related materials, including exfoliation of graphite to make graphene [119], polystyrene/functionalised graphene nanocomposite foams [120], platinum (Pt) [121] or platinum-ruthenium/graphene catalysts [122] for methanol oxidation and cell or silver-graphene antibacterial materials [123]. Our group employed an innovative approach for synthesizing graphene-inorganic nanoparticles *via* the utilization of sc-CO₂, which allows us to homogeneously grow and disperse various nanoparticles onto graphene [124,125]. This is because of the high diffusion rates, zero surface tension and low viscosity; the SCF can rapidly transport and homogeneously deposit a range of materials onto a sample matrix very efficiently. In a typical experiment, graphene (synthesised using the chemical exfoliation method), a Pd precursor and the reducing agent were placed in the reactor with sc-CO₂, (as shown in Figure 4), leading to the formation and homogenous dispersion of Pd nanoparticles onto graphene.

Figure 4. A schematic representation for the synthesis of Pd-graphene nanocomposites using sc-CO₂.



The Pd-graphene ratio was varied, and the properties of the nanocomposites were studied. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of homogeneously dispersed Pd nanoparticles onto graphene materials are shown in Figure 5. This is a promising strategy for designing, synthesizing and developing next-generation functional novel nanomaterials with a broad range of applications, where the simplicity of the reactor design offers great possibility for the production of graphene-based nanocomposite materials.

Figure 5. (a) Atomic force microscopy (AFM) images and (b) transmission electron microscopy (TEM) images of Pd-graphene nanocomposites.



2.5. Continuous Hydrothermal Flow Synthesis (CHFS)

Like sc-CO_2 , supercritical water ($\text{sc-H}_2\text{O}$) has attracted tremendous interest amongst academia and industry [126]. The critical parameters of $\text{sc-H}_2\text{O}$ (374 °C and 22.1 MPa) are higher than those for sc-CO_2 (31.1 °C and 7.38 MPa). In the supercritical state, water solvent properties, such as the density, viscosity and dielectric constant, change drastically in comparison to ambient water [95]. Conventionally, due to the high dielectric constant, ambient water easily dissolves polar compounds [127]. However, near the critical phase, the dielectric constant of water is greatly reduced, and therefore, it has the ability to dissolve non-polar compounds. Furthermore, the lower density and viscosity values of water at its supercritical state mean higher diffusion and, consequently, faster reaction rates, provided that mass transfer is the rate controlling step of the process. The density, viscosity and dielectric constant of $\text{sc-H}_2\text{O}$, as with most SCF properties, can be controlled by fine-tuning the pressure and temperature of the fluid. $\text{Sc-H}_2\text{O}$ with unique tuneable properties provides an excellent medium for the synthesis of various highly crystalline nanoparticles [128].

In the manufacture of materials, hydrothermal (superheated or $\text{sc-H}_2\text{O}$) syntheses can offer many advantages over conventional preparation methods, e.g., lower synthesis temperatures and relatively less processing steps [129–131]. The vast majority of hydrothermal synthesis tends to be conducted in batch reactions, which are time consuming and allow little or no control over the final product properties. Following the pioneering research of the Arai group in Japan [132], continuous hydrothermal flow reactors were developed [133–136]. The process is considered green, since it uses water rather than organic solvents. The basic process involves mixing a flow of superheated or $\text{sc-H}_2\text{O}$ with a flow of an aqueous solution of metal salts to give the rapid precipitation and growth of

well-defined particles [137,138]. The composition and certain particle properties, such as size and morphology can be modulated by controlling the ratios of the metal salt feed, the pressure, the temperature of mixing and the presence of a pH or redox modifiers [131,137,139]. Sc-H₂O provides a rapid nucleating and crystallizing environment within a hydrothermal flow reactor, which facilitates the accelerated synthesis of highly crystalline nanomaterials. The mechanism of the production of nanomaterials is generally explained in terms of: (i) the kinetics of the reaction; (ii) the solubility of the metal oxide; and (iii) the hydrodynamics around the mixing point. Near to or in the supercritical conditions, the rate of the hydrothermal reactions increases, and the solvation of metal oxides are extremely low. Consequently, such hydrothermal reactions are associated with high supersaturation levels, very rapid nucleation, high dehydration and low growth rates, which lead to the precipitation of fine particles. Further, the reaction engineering of the reactor, including the shape and the direction of the mixing point, influence the particle size and the particle size distribution of the final product. Commonly, the mixing of water and metal feeds is usually carried out in a tee union mixer. In the nozzle reactor, the water is injected downwards using a pipe-in-pipe design [133,136], whereas the side injection of water has been reported to produce smaller particles. Recently, a new mixer design was reported, where the metal salt feed and auxiliary were mixed well and then split into two streams before entering the reactor through two inlets, where they meet sc-H₂O, forming nanoparticles [140]. In all cases, the synthesis of uniform reproducible nanoparticles has been successfully achieved. To conclude, continuous hydrothermal synthesis has been proven to be an excellent medium for the synthesis of nanomaterials. In such processes, control over particle properties, such as the size and composition, is easily achievable. Moreover, continuous hydrothermal systems offer the ability to carry out synthesis in a high-throughput mode, enabling the discovery of new materials [139,141,142]. Additionally, large-scale production is also reported [143,144].

2.6. Supercritical Water Oxidation (SCWO) Process

Supercritical water oxidation utilises the unique properties of sc-H₂O, such as the high diffusivity, low density and remarkable mass transport properties, for the destruction of various toxic and hazardous wastes streams, such as paints, oils, pharmaceutical wastes, chemical warfare agents and contaminated soil [145–149]. The addition of an oxidant, such as hydrogen peroxide or oxygen, is often required. The destruction efficiencies of supercritical water oxidation (SCWO) are reported to be very high (99.99%). At supercritical conditions, various organic compounds, such as chlorinated organic compounds or nitro-compounds, are destroyed to more environmentally friendly compounds, such as chloride ions and nitrates, respectively [150]. However, this process is associated with technical drawbacks, such as corrosion and salt precipitation, and, as such, is limited to the selection of a suitable wastewater and correctly designed reactors that satisfy a selection of criteria for successful operation, including an energy recovery system for the economically feasible implementation of this technology [151].

2.7. Green Process Using Biphasic Catalysis

Most of the industrial processes rely on catalysis, such as chemical, pharmaceuticals, materials, polymers and energy. In the case of homogeneous catalysts, where the catalyst is in the same phase as

the reactants, they offer numerous advantages for optimizing catalytic systems [152]. However, homogeneous catalysts suffer from many drawbacks, including difficulty in separating the catalyst particles after the reaction, which could increase the overall product cost. The concept of biphasic catalysis, which could possess high activity and reusability, has attracted considerable interest [153]. One such example of the biphasic catalytic process is the Ruhrchemie/Rhone-Poulenc commercial process [154]. In a biphasic catalysis system, a homogenous catalyst is modified to dissolve in a particular solvent, e.g., Solvent A, and the reactants are dissolved in another solvent, e.g., Solvent B. During the course of the reaction, the reactants, catalyst and Solvents A and B are vigorously stirred to form a single phase in which the reaction can take place. As soon as the reaction is completed, the reaction mixture is cooled down, resulting in phase separation and can be easily separated by simple decantation. Since the catalyst and product are in separate phases, this helps in removing the catalyst from the reaction mixture, and it could be recycled several times without any problems. Yu *et al.* [155] investigated the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as the oxidant and metal dodecanesulfonate salts as the catalysts and found that ~100% selectivity could be achieved by the principle of biphasic catalysis. Recently, the application of biphasic catalysis for hydrogenation of cinnamaldehyde to hydrocinnamaldehyde has been reported, wherein 100% selectivity of cinnamaldehyde to hydrocinnamaldehyde has been achieved [156].

3. Conclusions

Engineering strategies have a direct significant impact on the environment. These approaches can either add to growing environmental concerns or direct us towards sustainability if the right tools and options are selected. As such, green engineering is an effective approach, which offers guidance and support towards the direction of sustainable processes, products and systems, whilst reducing the risks to humans and the environment. The “greening” of the industry with the introduction of processes that provide adequate environmental protection is a key component for the future sustainable growth of our society. To implement this vision, new approaches have been developed. These include the utilisation of greener supercritical fluids, catalysis, continuous flow processes for the synthesis of a broad range of materials or the conversion of carbon dioxide to a value-added chemical. Overall, the examples represented here aim to be green in terms of processing with cleaner solvents, avoiding multiple step reactions and lowering the energy requirements, in addition to providing materials with improved properties. To conclude, driven by fast developing social and economic factors, the greening of the industry is the key to our future, where the motivation and efforts of chemical and process engineers have introduced attractive and ecological changes via changes in chemical processes. However, there still are challenges ahead, and much has to be achieved for the “greening” of chemical processes.

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Conflicts of Interest

The authors declare no conflict of interest.

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