Some novel aspects of green process engineering

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KEYWORDS
Catalytic processes, environmentally benign process, green applications, green engineering principles, green process engineering, supercritical fluids.

ABSTRACT
Green process engineering (GPE) is an approach to make a hazardous and wasteful process more sustainable. The implementation of a wide range of innovative and effective green process technologies over the years has led to more environmentally friendly approaches that have resulted in greater pollution prevention via waste reduction and efficiency maximisation. This paper highlights some novel applications of green process engineering, particularly in the areas of supercritical carbon dioxide and catalytic processes, including the guidelines utilised in designing a green process, following twelve principles of green engineering.

INTRODUCTION
One of the missions of modern green engineering community is to design and develop sustainable and economically proficient processes whilst giving adequate protection to the environment. Green process engineering (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 UK, the first systematic attempts to control the polluting effects of the industrial revolution were made by the Alkali Acts in the 19th Century (2). However, the modern “green” revolution dates back in the 60’s and linked to the book of Rachel Carson’s Silent Spring in 1962. But it was not until 1972 that we saw the introduction of legislation which addressed pollution of water and land (Deposit of Poisonous Wastes Act 1972). Consequently, the scientific community started to explore new or improved engineering approaches that reduce or eliminate the utilisation or production of hazardous materials with environmental impact. Such environmental impacts are the results of the following factors: the consumption of raw materials, manufacture, processing and consequently released emissions including the toxicity potential, energy consumed, and the waste generation. As this concern about the magnitude of the associated environmental footprints increases, engineers, and particularly chemical and process engineers, will face new challenges, in a way that processes should be both economically and environmentally sustainable. As such many industrial sectors are considering greener and cleaner alternative routes that reduce the pollution at the source. For instance, the twelve principles of green engineering provide frameworks on how green process engineering should be guided (3). It integrates and couples the most important elements on product optimisation, process and systems. Additionally, the choice of solvent is an important parameter in making synthetic processes “greener”. For instance, supercritical fluid processing has accelerated rapidly and being considered as a green process solvent (4). Another fundamental area of interest that fits the aims of green engineering is that of catalysis. It is a very broad area and is considered as an environmentally benign process covering heterogeneous and homogenous catalysis. A few of the important catalytic processes that have had direct impact in the field of green engineering are discussed in this paper.

GREEN ENGINEERING PRINCIPLES
There was a need to develop guidance for green engineering principles due to the environmental concern. When a consumer no longer requires a particular product, (i) the product should be either reusable (as with old furniture), (ii) remanufacture (as with copier machines or automobile alternators), (iii) recycle for the same use in a “closed loop” (as with asphalt pavement), (iv) recycle into a lower valued use (as with plastics formed into park benches), (v) incinerate (as with burning paper to reclaim energy), (vi) landfill (as with most municipal solid wastes) or (vii) discard directly to the environment (as with littering or dumping into the ocean) (5, 6). The first four options (i-iv) are part of green engineering principles (7).

Anastas and Zimmerman (3) have outlined twelve principles of green engineering. These are summarised in Table 1. Similarly, as reported by environmental protection agency (EPA), US, more than 65 engineers and scientists developed nine principles of green engineering (8). The preliminary principles
forged at the first conference on “Green Engineering: Defining the Principles” held at Florida in 2003 were intended for engineers to use as guidance in the design or redesign of products and processes within the constraints dictated by business, government and society such as cost, safety, performance and environmental impact (8). The developed nine principles of green engineering are given in Table 2.

“Chemical engineering tools for supporting green engineering” has been reported by Allen (9). The tool could help analyse technologies to evaluate options that support green engineering goals. The above mentioned principles and chemical engineering tools that supports green engineering shows that while there is not universal agreement about the precise objectives of green engineering, most of them suggested reduction in the energy use, reduction in the material use, reduction emissions and to consider about entire supply chains i.e. life cycles (9).

A team of engineers and scientists assembled by the AIChE identified five core sustainability metrics for chemical processes (10) that are summarised in Table 3. These metrics correlate very well with the general guidelines identified in the green engineering principles, i.e. to use less energy, to use less raw materials and to generate less waste. For many commodity chemicals, the benchmarks have been developed by AIChE and the values of indices have been calculated for industry standard flow sheets (9). Engineers can compare their designs with the developed benchmarks. With a set of measurable performance indicators, the next step in the process of green engineering would be to evaluate alternative designs. The fundamental concepts of life cycle considerations and inherency i.e. the first principle of green engineering should be strived by designers and engineers to integrate at every opportunity (3). Chiu and Tzeng (11) defined a number of criteria and strategies that need to be evaluated in green engineering industry. Contreras and Bravo (12) have suggested what needs to be done during plant design and operation design stages to make them green. They also recommended some ideas on how to tackle research and development activities on key environmental issues.

GREEN ENGINEERING (GPE) APPLICATIONS

Green Chemical Processing using Supercritical CO\(_2\)

A supercritical fluid is a material used in a state above the critical temperature and critical pressure (see Figure 1), where gases and liquids can coexist (4). They show unique properties that are different from those of either gases or liquids under standard condition. An increase in pressure at constant temperature results in a region where gas and liquid can coexist. The pressure at which these two states coexist is called the critical pressure, and the temperature at which this occurs is called the critical temperature. Beyond these points, the fluid is supercritical with unique physical and chemical properties between gases and liquids.
in an increase in density values and a corresponding increase in solvating power. Temperature variation (at constant pressure) is a more complex process, e.g. a temperature increase results in a decrease of density. Furthermore, the process is associated with a concomitant increase in the vapour pressure of the solute. Consequently, optimisation of the subsequent increase in pressure of the supercritical fluid solvent power is required. Moreover, a supercritical fluid has a higher diffusion coefficient, lower viscosity (gas-like), and lower surface tension than a liquid solvent, as well as enhanced mass transport properties [13-16]. Supercritical fluid properties can be modified dramatically by small changes in pressure, especially when the critical parameters are being approached. At below critical temperature gas and liquid coexist together. As the pressure or temperature is increased, the density difference between two phases becomes less distinctive. At the critical point, a homogenous single phase is observed. The main factors influencing the increased interest in the use of supercritical fluids are their potential to replace toxic organic solvents and the simplicity of optimising their properties by altering the pressure and temperature. More conventional chemical reactions using volatile organic compounds are associated with the toxicity, production of large amounts of waste, flammability and non-sustainability. Taking into consideration the fact that legislation on waste solvent production and their emissions has tightened considerably and consequently, the cost of disposing of this waste has greatly increased, many companies have started to consider greener and cleaner chemical synthesis routes. The replacement of organic and toxic solvents by supercritical fluids (such as carbon dioxide or water) offers a great advantage in the chemical and environmental fields. In particular, supercritical carbon dioxide (sc-CO₂) has attracted the most interest due to the relatively low critical parameters (critical temperature, T_c = 31.1°C, critical pressure, P_c = 7.38 MPa), non-flammability, non-toxicity, recyclability [4]. It is chemically inert and it is a by-product of industrial chemical synthesis process (the major source being ammonia synthesis). Moreover, the solvent removal is performed easily by venting out CO₂ via decompression, which leaves no residues. Over the years, the number of applications in a variety of fields, including large scale productions has increased significantly. These include pharmaceutical and polymer processing, nutrition such as coffee bean decaffeination, cleaning, textile processing and drying, chromatography and materials synthesis [16-18]. Beckman [13] have made commentaries on the use of CO₂ as a “green solvent” for a number of commercial applications including textile dyeing, polymer processing and microelectronics processing. Although the equipment needed to use supercritical carbon dioxide is expensive, this disadvantage is clearly outweighed by the benefits of greener and cleaner chemical processes and, consequently, a greener environment.

**Rapid Expansion of Supercritical Solution (RESS) process**

In the RESS process, the reactant is initially solubilised in a supercritical fluid at a desired temperature and pressure, followed by rapid depressurisation of the system across a nozzle in a chamber at atmospheric pressure causing an extremely rapid nucleation of the product reaction parameters such as rate of depressurisation, temperature, injection distance and precursor solubility influence the particle size, morphology and crystallinity [14]. Often the materials are collected into aqueous solution containing surface protecting agents, such as poly(N-vinyl-2-pyrrolidone) or reducing agents, such as sodium borohydride to produce stabilised monodisperse particles with a narrow particle size distribution including Ag, CdS, TiO₂, various polymeric and pharmaceutical compounds such as ibuprofen [14-16]. However, there are limitations to the technique due to the low solubility of various polymers in supercritical fluids.

**Supercritical Anti-Solvent (SAS) process**

The CO₂ solubility limitations are often overcome by using the supercritical anti-solvent (SAS) synthetic process. In SAS process the substance is first dissolved in an organic solvent such as acetone, dichloromethane, dimethyl sulfoxide. The solvent mixture (which is entirely miscible with supercritical carbon dioxide) is then introduced into sc-CO₂, across a nozzle where it extracts the solvent and acts as an anti-solvent for the solute resulting in the precipitation of particles. In this process, the introduction of the supercritical fluid into a solution leads to a decrease in solvent power in which the solute is dissolved, therefore forcing the precipitation or crystallisation of a compound due to expansion of the liquid when supercritical carbon dioxide is introduced. The separation of CO₂ and organic solvent can be easily achieved by means of decompressions. Mainly this technique is employed for synthesis of various pharmaceutical compounds such as insulin, polymers and other compounds including fullerene.

**Supercritical Fluid Deposition (SFD)**

Recently, supercritical fluid deposition (SFD) has emerged as a potentially effective deposition technique due to the highly tenable properties (density, viscosity, dielectric constant) [18]. Additionally because of its high diffusion rates and zero surface tension and low viscosity, the supercritical fluid can rapidly transport and homogeneously deposit a range of materials onto a sample matrix. This method has been utilised for deposition of a wide range of nanomaterials, including Pt, Pd, Au, and Rh, on polymer substrates [18]. Our group has employed an innovative approach for synthesising graphene-inorganic nanoparticles via utilisation of supercritical CO₂ which allows to be homogeneously grown and dispersed onto graphene (as shown in Figure 2) [19].

**Biodiesel and Biofuels production**

Biofuels play an important role as an alternative to fossil fuels. Biodiesel exhibits characteristics that are analogous to traditional diesel fuel. On the other hand, the flow and combustion properties of biodiesel are similar to petroleum based diesel [20]. Hence, it could be used as a substitute for diesel fuel. Biodiesel is prepared typically from transesterification of triglycerides. Methanol is the preferred choice of alcohol for biodiesel production due to its low cost. Ethanol and bioethanol could also be used as cost-effective alcohols if they are produced from the wasted crops.
[i.e. crops that are lost during various stages of farming, storage and transportation]. The most common sources of triglycerides are virgin vegetable oils, animal fats and waste cooking oil. The dependence of food sources for biodiesel production could have serious consequences on food supply. Hence, waste cooking oil to produce biodiesel is considered to be the best route for biodiesel production, since it does not put strain on food supply and helps in recycling the waste cooking oil and supports green engineering principles. Waste cooking oil, however, requires pre-treatment before it can be used for biodiesel production [21]. The alcohol and the catalyst used for biodiesel production should be essentially anhydrous, since the presence of water in the feedstock could promote the hydrolysis of alkyl esters to free fatty acids (FFA). Biodiesels have major advantages over diesel fuel; they produce less smoke and particulates, have higher cetane numbers, produce lower carbon monoxide and hydrocarbon emissions and are biodegradable and nontoxic. Conversely, depending on the sources of feedstock, they present other technical challenges such as low volatility, high pour points, high cloud points and high cold filter plugging temperatures, elevated NOx emissions and incomplete combustion. There is also a major concern regarding the unfavourable cold flow properties of biodiesel as it tends to gel (freeze) at lower temperature, thus affecting the driveability of biodiesel vehicles. Current biodiesel production is not sufficient to make a considerable impact on fuel market and driveability of biodiesel vehicles. Current biodiesel production is considered as an important process technology that decreases emission of greenhouse gases and reduces the current and future dependence on fossil fuels.

**Greening of alkene epoxidation**

Epoxides are key raw materials or intermediates in organic synthesis, particularly for the production of a wide variety of chemicals such as pharmaceuticals, plastics, paints and adhesives. The batch production of epoxides often uses peracids including peracetic acid and m-chloroperbenzoic acid. The employment of peracids for alkene epoxidation is not an environmental friendly synthesis since equivalent amounts of acid waste are produced. In addition, there are safety issues associated with handling and storage of peracid. Hence, there is a strong need for cleaner catalytic epoxidation methods that employ safer oxidants and produces little waste. Over the last few decades, soluble compounds of transition metals have been used to catalyse alkene epoxidation with good activity and product selectivity. However, homogeneous catalysed systems suffer from numerous industrial problems including corrosion, deposition of the catalyst on the reactor wall and high chance of product contamination due to difficulties in separation of the catalyst from the reaction mixture. Due to the recent concern for environmentally safer chemical processes, more and more attention has been focused on developing greener and efficient epoxidation process employing a heterogeneous catalyst and a benign oxidant. Polymer supported molybdenum complexes have been shown to be effective for alkene epoxidation with alkyl hydroperoxide as oxygen source [22]. In this novel and greener process an efficient and selective polybenzimidazole supported molybdenum complex (PBI.Mo) and a polystyrene 2-(aminomethyl) pyridine supported molybdenum complex (Ps.AMP.Mo) have been used as catalysts for the epoxidation of alkenes. This process is solvent-free and uses environmentally benign tert-butyl hydroperoxide (TBHP) as an oxidant. On the other hand, tert-butanol is also used as a co-product during epoxidation and hence this process is atom efficient. Oku et al. [23] reported that tert-butanol can be efficiently recycled in the Sumitomo process through hydrogenolysis and oxidation. Hence, for the above mentioned reasons, this process is considered greener and follows green engineering principles. The remarkable catalytic performance of these catalysts has been realised in continuous epoxidations of cyclohexene, limonene and α-pinene employing TBHP as the oxidant. Very high conversion of TBHP to cyclohexene oxide (>98%) and 100% selectivity towards cyclohexene epoxide was achieved during epoxidation of cyclohexene in the reactive distillation column (RDC). This study confirmed that this new process is about 50% more energy efficient than the conventional processes.

**One-Pot Multistep Reactions**

One-pot multistep reactions are very attractive since they significantly lower the cost of the synthetic routes, by reducing the number of purification and separation steps, as well as reducing the amount of waste and solvents. Abu-Rezig et al. [24] reported one-pot dehydration and hydrogenation reactions in the presence of two catalysts. One of the catalysts was palladium that was doped with magnetic nanoparticles so that it could be magnetically separable, while the other catalyst was separated after the reaction by simple filtration. The magnetically separable palladium-based catalyst was reused for carbylation of iodoarenes. The application of these types of synthesis is limited since the catalysts used in these reactions have to be compatible with each other. Bhat et al. [25] reported multi-component one-pot synthesis of β-acetylamino ketones by the reaction of aldehydes, enolisable ketones, acetonitrile and acetyl chloride at room temperature in the presence of environmentally friendly, reusable and inexpensive zeolite Hβ as a catalyst.

**Biphasic catalytic process**

Baker and Tumas [26] reported that in case of homogeneous catalysts, where the catalyst is in the same phase as the reactants offer numerous advantages for optimising catalytic systems. However, the difficulty in separating the catalyst particles after the reaction increases separation and overall cost of the product. Biphasic catalytic process such as Ruhrchemie/Rhone-Poulenc commercial process could provide solution to this problem [27]. For reactions using biphasic catalyst, a homogeneous catalyst is tailored to dissolve in a particular solvent, e.g. solvent A and the reactants are dissolved in another solvent, e.g. B. At reaction conditions, catalyst, reactants and solvents A and B form a single phase in which the reaction takes place. As soon as the reaction is completed, the reaction mixture is cooled down, resulting in phase separation. Since the catalyst and product are in separate phases it helps in removing the catalyst from the reaction mixture. One of the applications of biphasic catalysts is the hydroformylation reaction. In hydroformylation of higher molecular weight olefins using conventional method, the separation of the catalyst from the produced aldehydes was found to be difficult and expensive. This drawback was successfully overcome with the application of biphasic catalyst.

**Green process using iron catalyst**

Drugs are generally synthesised using platinum based catalysts such as palladium, rhodium and ruthenium. These catalysts are very expensive that adds to the total cost of the product. On the other hand, they are toxic. Hence, they are required to be separated from the product using expensive purification methods. Iron catalyst could be the solution for the above mentioned drawbacks of platinum based catalysts even though iron is considered to be a base metal of low catalytic activity as compared to highly active platinum metal catalysts. The highly active iron catalyst was prepared by attaching an organic molecule to the ferrous state of the iron [28]. The prepared complex iron catalyst was highly active and similar in structure to highly active platinum metal catalysts. It was reported small amount of the complex iron catalyst was used to synthesise a large amount of alcohol product and the process is called asymmetric transfer hydrogenation.
CONCLUSIONS

The technical decisions made by scientists have direct significant impact on the environment. Such decisions can either direct towards sustainability or add to the growing environmental concerns. As such, green engineering provides guidance and support towards the direction of sustainable products, processes and systems whilst giving adequate environmental protection. The "greening" of the industry with introduction of processes which have a reduced impact on environment and human health is a key component for the sustainable growth of our society. To implement this vision, new approaches have been developed including utilisation of supercritical fluids, which facilitate cleaner production routes and catalytic processes that aim to avoid multiple step reactions and lower the energy requirements. The examples represented here revealed general efforts and motivations of chemical and process engineers in introducing attractive and ecological changes in methodologies aimed at "greening" the industry, which are purely driven by the fast developing social and economic factors.

REFERENCES


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