1. Introduction

In the pursuit towards attaining sustainability, arrays of greener pathways are being carved to address the needs of the diverse chemical universe. The evolving area of green and sustainable chemistry envisions minimum hazard as the performance criterion while designing new chemical processes. Green Chemistry is defined as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products” [1]. Sustainable processes are being sought to explore alternatives to conventional chemical syntheses and transformations. Among several thrust areas for achieving this target includes: the utility of alternative feedstocks, preferably from renewable materials or waste from other industries; unconventional efficient reaction conditions and eco-friendly reaction media to accomplish the desired chemical transformations with minimized by-products or waste generation, and ideally avoiding the use of conventional volatile organic solvents, wherever possible. Other avenues for achieving this objective are to explore the generation of efficient catalytic processes, particularly magnetically retrievable nano-catalysts [1–4]. In addition to greener synthesis, the recyclability and reuse aspects for catalytic systems are extremely significant particularly when it boils down to the use of endangered elements and precious catalysts. Several friendlier applications in catalysis have been advanced via magnetically recoverable and recyclable nano-catalysts for oxidation, reduction, and multi-component condensation reactions [1–4] and this has made a terrific impact on the development of green chemical pathways [1]. The greener preparation of nanoparticles has been exemplified via the use of vitamins B1, B2, C, and tea [5] and wine polyphenols [6], beet juice [7] and other agricultural residues which function both as reducing and capping agents. This avoids the need to deploy toxic reducing agents, such as borohydrides or hydrazines and empowers simple and aqueous green synthetic methods to produce bulk quantities of nano-catalysts without the requirement for large amounts of insoluble templates [8].
The desired ultimate approach may encompass alternative activation methodology, such as photocatalysis, mechanochemical mixing, ultrasonic- and microwave-irradiation [9]. Additionally, the strategy has to follow “benign by design” principles and make an effort to utilize renewable resources whenever feasible [10].

Numerous newer strategies have been advanced in recent years namely, reactions under mechanochemical mixing [11]; solvent-free conditions [12,13], use of supported reagents and the alternate heating and activation methods that utilize microwave (MW) [14–16], and ultrasonic irradiation [17] for expeditious syntheses. These techniques have circumvented some of the problems associated with inefficient heating. Ball-mill processing, envisioned as a solid-state size reduction process, can be easily scaled up and has been used in material science, paint industry, and for environmental remediation. Mechanochemical solventless processing of molecules that prevents the use of toxic metals and solvents is gaining acceptance [11]. While ultrasonic irradiation enhances the chemical reaction and mass transfer via the process of acoustic cavitation [17], MW irradiation provides the “in-core volumetric” and selective heating of polar and ionic chemical entities [14]. The selective absorption of microwaves by polar intermediates in a multiphase system could replace any phase transfer reagent, reminiscing the observed acceleration of chemical reactions which is common place in case of ultrasonic irradiation [18]. This is borne out by several experimental observations which are consistent with the proposed mechanistic postulation; the polar transition state of the reaction is favored by MW irradiation due to the dielectric polarization nature of MW energy transfer [14]. Newer findings on these topics, especially involving eco-friendly reaction media such as water and polyethylene glycol (PEG), when used in conjunction with photo activation, MW and ultrasonic irradiation, and/or mechanochemical means under solvent-free conditions, may help achieve sustainable pathways for chemical synthesis and transformations, including the production of novel nano-catalysts.

2. The Present Issue

I am deeply honored to be the guest editor of this thematic issue which includes two reviews, two communications and three papers (see the content list). I am grateful to the several leaders in these areas and would like to place on record my thanks to these illustrious contributors. I am equally thankful to many reviewers who have helped me to evaluate and critique these manuscripts with substantial improvements. I appreciate Prof. Dr. Takayoshi Kobayashi/Editor-in-Chief of Applied Sciences, for inviting me to guest edit this special issue and staff of the Applied Sciences Editorial office who supported the entire process.

This issue provides access to several articles encompassing the sustainable theme. The first review article by Díaz-Álvarez and Cadierno [19] describes elegant applications of glycerol, a non-toxic, non-hazardous, non-volatile, biodegradable, and recyclable liquid that is generated as a byproduct in the manufacture of biodiesel fuel from vegetable oils. Due to its unique chemical and physical properties and its easy availability, glycerol has emerged as an economically viable and safe solvent for organic synthesis including nanomaterials. Further, glycerol can be used as a hydrogen source in metal-catalyzed transfer hydrogenation for a variety of organic compounds [19]; the utility of glycerol as solvent and reducing agent has tremendous future potential. The second review article describes the fastest growing segment of a group of catalysts that bridge the homogeneous and heterogeneous
catalysis. Magnetically recyclable nano-catalysts and their use in aqueous media for the development of sustainable organic synthesis methodologies are summarized [20]. Water is the ideal medium to perform the chemical reactions with magnetically recyclable nano-catalysts, as this fusion adds tremendous value to the overall benign reaction process development. The review highlights recent developments in the use of water and magnetically recyclable nano-catalysts for an array of organic reactions namely reduction, oxidation, condensation, and several cross-coupling reactions. Continuing on the same theme, Hojo et al. describe a water-based MW-assisted solid-phase synthesis using Boc-amino acid nanoparticles which enables a rapid solid-phase reaction of nanoparticle reactants on the resin in aqueous medium [21]. The syntheses of Leu-enkephalin, Tyr-Gly-Gly-Phe-Leu-OH, and model peptide with difficult sequence such Val-Ala-Val-Ala-Gly-OH, has been described using water-based MW-assisted protocol with Boc-amino acid nanoparticles.

Lalevée et al. summarize the green technologies pertaining to the photopolymerization area wherein the use of visible light sources (Xe and Hg-Xe lamps, diode lasers), soft irradiation conditions (household lamps: halogen lamp, fluorescence bulbs, LED bulbs), sunlight exposure, development of very efficient photo initiating systems and use of renewable monomers are highlighted [22].

Adhering to the principles of green chemistry, Anastas and Wool, describe a series of materials that are prepared by curing acrylated epoxidized soybean oil (AESO) and dibutyl itaconate (DBI) or ethyl cinnamate (EC) comonomers to provide examples of thermosets with a high proportion of bio-based carbon [23]; the comonomers are representative of cellulose-derived (DBI) or potentially lignin-derived (EC) raw materials.

Representing the use of alternate energy activation, Nogueras et al. have synthesized new 1,3-diaryl-5-(1-phenyl-3-methyl-5-chloropyrazol-4-yl)-4,5-dihydropyrazole derivatives under ultrasonic irradiation conditions in ethanol or methanol/glacial acetic acid mixture [24]. Hydrazines and several chalcone-like heteroanalogues, accessed from 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde, are used and the method provides numerous advantages over current methodologies such as shorter reaction times (2–20 min), simple work-up procedure, and good yields.

Mack and co-workers have described the utility of mechanochemical (ball milling) approach in the solvent-free synthesis of 2-aminothiophenes via the Gewald reaction [25]. Utilizing high speed ball milling conditions, the Gewald reaction could be accomplished using only a catalytic amount of base, and the desired results are achieved under aerobic conditions. The salient features highlight the use of thermal heat in tandem with the mixer/mill which significantly increases the rate of reaction.

In conclusion, the special issue of Greener and Sustainable Chemistry highlights various strategies that can be adopted to address the pollution preventive measures promoting the use of energy efficient reactions that utilize benign and bio-renewable raw materials in a relatively safer reaction media, thus encompassing the Principles of Green Chemistry.

**References**


**Biographical Sketch**

Prof. Rajender S. Varma was born in India (Ph.D., Delhi University 1976). After postdoctoral research at Robert Robinson Laboratories, Liverpool, UK, he was faculty member at Baylor College of Medicine and Sam Houston State University prior to joining Sustainable Technology Division at US Environmental Protection Agency in 1999. He has over 40 years of research experience in management of multi-disciplinary technical programs ranging from natural products chemistry to therapeutics and development of environmentally friendlier alternatives for synthetic methods using microwaves, and ultrasound etc. Lately, he is focused on greener approaches to assembly of nanomaterials and sustainable applications of magnetically retrievable nano-catalysts in benign media. He is member of the editorial advisory board of several international journals and published over 400 scientific papers and awarded over 14 US Patents.