

Green chemistry in Brazil*

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Abstract: The philosophy of green chemistry has been very well received in Latin America's research and development programs. In this review we describe the green chemistry contributions of Brazilian research groups over the last three years.

Keywords: alternative energy sources; alternative solvents; biocatalysis; biofuels; biomass; catalysts; energy; green chemistry; ionic liquids; nanomaterials.

The development of products and green processes is one of the most important challenges of the present society. In the last 20 years, green chemistry has an increasingly important role in various sectors, be it in academia, industry, regulatory agencies as well as other governmental organs all over the world [1]. It is no coincidence that during Rio+20, the United Nations Conference on Sustainable Development, which took place in Brazil on 4–6 June 2012, treated various principles of green chemistry considering that the scientific undertaking plays a central part in delivering green economies that meet the challenges of sustainable development and poverty eradication [2].

In Brazil several activities involving the concepts of green chemistry have been carried out since the middle of the 1990s [3]. However, the first reviews appeared only in 2000 [4]. The book *Green Chemistry in Latin America* was published in 2004, in the Green Chemistry Series from IUPAC and INCA, edited by Tundo and Rossi [5]. This book contains 18 chapters written by research groups from different countries, such as Argentina, Brazil, Costa Rica, El Salvador, Mexico, Uruguay, and Venezuela, demonstrating that the philosophy of green chemistry was very well received in Latin America's research and development programs.

The concepts of green chemistry began to be disseminated faster, whether in academia, government, or industrial sectors. The group Clean Organic Synthesis, from the Federal University of Pelotas (RS) created WWVerde, a web site containing information about green chemistry [6]. Similarly, in 2006, the chemistry department of the Federal University of São Carlos promoted its 26th Summer School [7], which focused on green chemistry and with the participation of national and international researchers and lecturers in the field. In January 2007, the first Summer School in Green Chemistry was held at the Institute of Chemistry of the University of São Paulo (USP) [8]. In November of the same year, the first Brazilian Workshop on Green Chemistry was held in Fortaleza, where the Brazilian Network on Green Chemistry was created. Its main objective is to be one of the central institutions to promote technological innovation for national companies, with the support of the scientific community and governmental agencies.

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In 2009, the first book in Portuguese containing the concepts of green chemistry was edited by Corrêa and Zuin [9]. In the same year, the project Sustainable Education and Environmental Development in Latin American started, sponsored by IUPAC and coordinated by Profs. Patricia Vazquez and Vânia Zuin. The aim of this project was to disseminate the green chemistry philosophy in all Latin American countries.

In 2010, the Center of Management and Strategic Studies (CGEE) launched the book *Green Chemistry in Brazil: 2010–2030* [10]. In 2012, the United Nations Conference on Sustainable Development was held in Rio de Janeiro. The Rio+20 declaration was titled “The Future We Want”. The book *Contribution from Brazilian Postgraduate Studies to Sustainable Development: Capes at Rio+20* was also launched by the Coordination for the Improvement of Higher Education Personnel within the Ministry of Education, whose central purpose was to reinforce the necessity of new green products and process studies in Brazil [11].

The 4th International IUPAC Conference on Green Chemistry (ICGC-4) took place in Foz do Iguaçu, Brazil, from 25 to 29 August 2012. ICGC-4 happened under the auspices of IUPAC and the Brazilian Chemical Society (SBQ) [12], with the theme “Exchanging experiences towards a sustainable society taking care of natural resources in their socio-economic development”, expressing the main aim to transform the conference into a possibility to experience the scientific and the environmental dimensions towards a greener and ethical life all over the world. ICGC-4, with around 600 participants from up to 40 countries of all continents, brought together the ICGC series history, all the areas of chemistry and their related fields, as well as its sectors as academia, industry, government, and chemistry societies worldwide.

In this review we describe the contribution of the Brazilian research groups in green chemistry in the last three years. For the period of 2010–2012, according to the Web of Science database (Thomson Reuters), more than 200 scientific papers were published. The main areas are analytical chemistry and organic synthesis, with 68 and 83 publications, respectively. These publications employ several green chemistry concepts, but the most common is the use of alternative energy, especially microwave irradiation, corresponding to 69 % of the total.

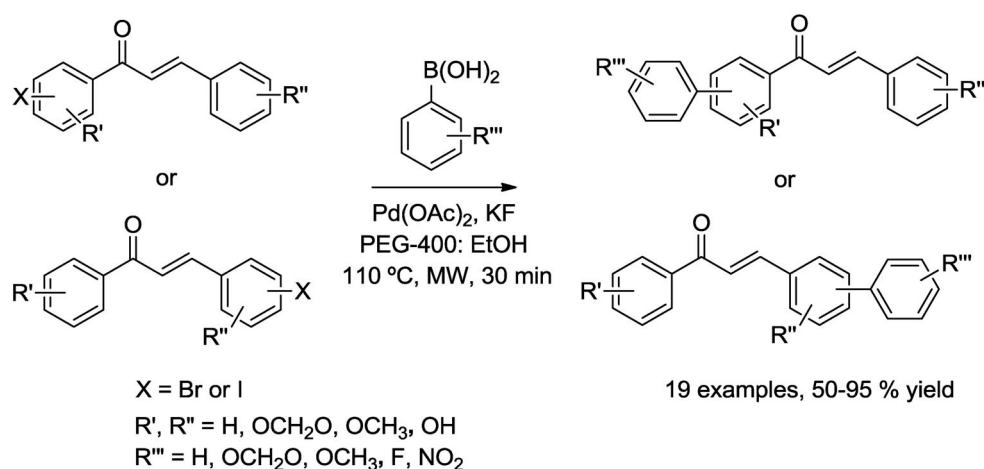
Considering the different aspects of the green chemistry, some publications, selected with the aim to present the state of the art of this field in the country, will be discussed in more detail.

ALTERNATIVE ENERGY SOURCES

Microwave applications have expanded from the original use of the industrial-type multiple-mode microwaves in drying and food processing to more analytical-type applications, including digestion and extraction of samples [13]. Expansion into other areas of chemistry includes synthetic organic work such as peptide synthesis, inorganic work, pharmaceutical research, polymer chemistry, and even nanoparticle synthesis. Microwave irradiation has already proven its value as a tool within the chemistry community, pushing reactions to completion more rapidly than previously possible and opening doors to perform novel transformations [14]. Recent efforts have focused on translating microwave batch reactions to a high-temperature continuous-flow format (“microwave-to-flow” paradigm) [15].

An eco-friendly, efficient, and versatile approach for the Suzuki coupling reaction of chalcones (Scheme 1) and coumarins with arylboronic acids with low catalyst loading using nontoxic polyethylene glycol (PEG) as a solvent has been reported [16]. The reaction conditions employed include an economically cheap and stable catalyst, Pd(OAc)₂, microwave irradiation as a source of energy, and short reaction times.

Mendes et al. reported a new and versatile approach to synthesize SnO₂ nanocrystals (rutile-type structure) using the microwave-assisted hydrothermal method. The exploration of novel synthetic methodologies that control both size and shape of functional nanostructure opens new avenues for the functional application of nanomaterials [17].

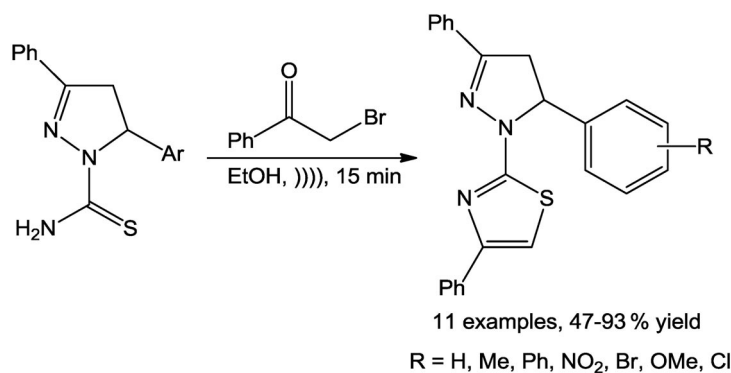


Scheme 1 Microwave-assisted cross-coupling reaction of chalcones.

Microwave-assisted procedures are well-established strategies currently used in routine analysis for different sample preparation steps, such as drying, extraction, and digestion. Mesko et al. described a focused microwave-induced combustion (FMIC) as a sample preparation technique [18]. The main advantage of FMIC is the possibility to digest relatively higher sample masses, up to 1500 mg, using diluted nitric acid solution as absorbing medium. In addition, as a result of higher sample mass the relative standard deviation was lower than those obtained by other procedures. The proposed procedure was suitable for determining elements otherwise extracted with difficulty in botanical samples, such as aluminum, iron, and calcium.

Another important alternative energy for chemical processes is the ultrasound. Sonochemistry, the chemical effects and applications of ultrasonic waves, aims to reduce energy consumption, and increases product selectivity. Applications of ultrasound have been reported in fields such as materials science, polymer chemistry, medical applications, drug and gene delivery, nanotechnology, food science and technology, water and wastewater treatment, degradation of environmental contaminants, reactor design, anaerobic digestion, and synthetic applications [19].

A rapid and cleaner procedure for the synthesis of a series of 2-(3,5-diaryl-4,5-dihydro-1*H*-pyrazol-1-yl)-4-phenylthiazoles under ultrasonic irradiation in ethanol has been described (Scheme 2) [20]. In comparison to conventional methods, the main advantages of this procedure are the significant decrease of reaction time and improvement of yields.



Scheme 2 Synthesis of thiazole derivatives under ultrasound.

More recently, mechanochemical reactions have been described. Milling can be carried out in a variety of ways; the simplest is the laboratory mortar and pestle. This hand-milling process can provoke a large number of mechanochemical reactions, which do not require the surpassing of a high-energy barrier. Ball mills are used when higher energy is involved and when the milling time requires hours or even days [21].

Asseli and co-workers investigated the hydrogen sorption properties of 3Mg–Fe and 2Mg–Fe compositions prepared through high-energy ball milling under hydrogen pressure. After reactive milling, the 2Mg–Fe sample is mainly constituted of Mg_2FeH_6 phase, nonetheless, unreacted α -Fe phase is still present in the powder [22]. As a consequence of the incomplete reaction of the metallic elements with hydrogen, the measured hydrogen gravimetric density was only 3.5 wt %, representing an abundance of 65 wt % of Mg_2FeH_6 . In the case of the 3Mg–Fe sample, the Mg_2FeH_6 – MgH_2 nanocomposite was successfully synthesized and the α -Fe phase was kept to a minimum, resulting in a higher hydrogen gravimetric density of 5.2 %. Enhanced hydrogen sorption properties were observed for the 3Mg–Fe sample in comparison to the 2Mg–Fe one.

FLOW CHEMISTRY

In flow chemistry, a chemical reaction is run in a continuously flowing stream rather than in batch production. There is a growing interest in using flow chemistry in both discovery and process research laboratories within the pharmaceutical, agro, fine chemical, petrochemical, and fragrance industries [23]. The main advantage of continuous-flow processing is the ease with which reactions can be scaled, without the need for re-optimization, through the operation of multiple systems in parallel (numbering-up, scaling-out) or related strategies, thereby readily achieving production-scale quantities [15].

Rocha and co-workers reported an overview of the evolution of flow analysis towards green analytical chemistry by means of replacement of hazardous chemicals and the trend towards waste minimization [24]. This development has been successfully accomplished without hindering the analytical features that could impair analyte determination. Indeed, better analytical performances have been achieved in some circumstances, as the improvement in sensitivity, which makes time-consuming and not environmentally benign preconcentration steps unnecessary. In this sense, the potential of flow approaches such as multicommutated flow analysis (MCFA), sequential injection analysis (SIA), and multisyringe flow injection analysis (MSFIA) as well as the use of immobilized reagents were described in the literature.

Ingenious strategies such as reagentless procedures, green analyte extraction and sample clean-up, and the reuse of chemicals have been feasible using flow systems. A recent trend is the development of miniaturized procedures coupling all the stages of sample processing (including sample treatment and preconcentration) with minimal waste generation. It is a general-use strategy, and the devices have allowed the implementation of well-established methods without significant impact on the environment.

Monoacylglycerols are nonionic, highly hydrophobic surfactants that have been used as controlled release systems for drugs. Souza and co-workers reported a comparative study on the esterification reaction catalyzed by lipase between 1,2-*O*-isopropylidene glycerol and free fatty acids derived from palm oil refining (acid residue) under batch and continuous-flow conditions using the surface response methodology for optimization of reaction conditions. The results show that both batch and continuous-flow conditions can lead to the desired product in short reaction time and high yield (70–95 %), but the use of packed-bed reactors shows higher efficiency when compared to batch reactors [25].

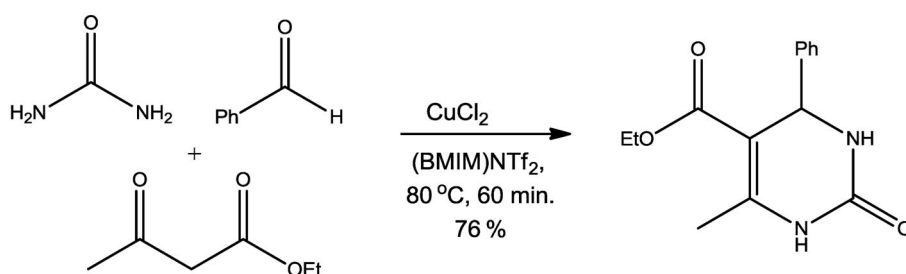
ALTERNATIVE SOLVENTS

Four directions towards green solvents have been developed: (i) substitution of hazardous solvents with ones that show better environmental, health, and safety properties, such as increased biodegradability

or reduced ozone depletion potential; (ii) use of “bio-solvents”, i.e., solvents produced with renewable resources such as ethanol produced by fermentation of sugar-containing feeds, starchy feed materials, or lingo-cellulosic materials; (iii) substitution of organic solvents either with supercritical fluids that are environmentally harmless (e.g., the use of supercritical CO_2); or (iv) use of ionic liquids that show low vapor pressure, and thus less emission into the air [26].

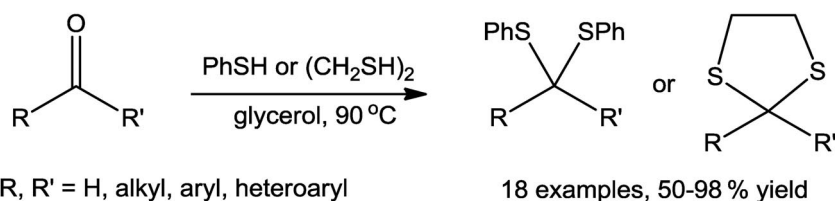
Ionic liquids, a special group of classical molten salts, are widely used in various fields of science and sit at the center of various green industrial innovation processes, where they play important roles in material extraction, reactive catalytic supports, spatial devices, and biotransformations [27].

Ramos et al. described the use of common Lewis acids supported in imidazolium-based ionic liquids as the catalysts to promote the three-component Biginelli reaction. The ionic liquid effect and the reaction mechanism were studied employing nuclear magnetic resonance, electrospray ionization mass spectrometry, and theoretical calculations. The results showed that the ionic medium plays a fundamental role in the synthesis of dihydropyrimidinones due to the stabilization of the charged intermediates proposed in the mechanism. When conducted in an ionic liquid as solvent, the reaction mechanism is more complex than in other Lewis-acid-catalyzed Biginelli reactions (Scheme 3) [28].



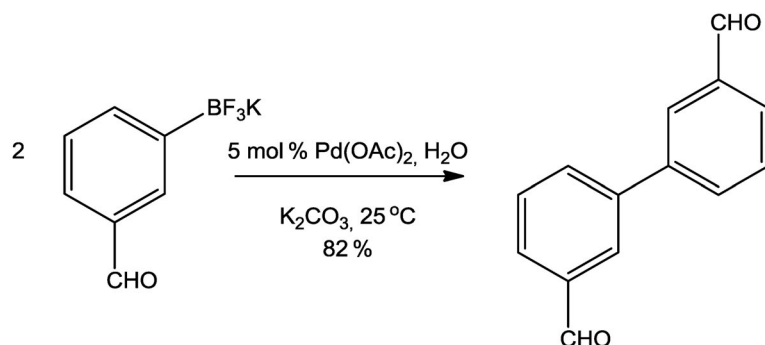
Scheme 3 Synthesis of dihydropyrimidinones in ionic liquid.

Perin et al. described the use of glycerol as an efficient and a recyclable solvent in the thioacetalization of aldehydes and ketones (Scheme 4). The catalyst-free reactions were carried out using glycerol at 90°C and the corresponding thioacetals were obtained in good to excellent yields. Glycerol was recovered and utilized for further thioacetalization reactions [29].



Scheme 4 Thioacetalization of aldehydes and ketones in glycerol.

The homocoupling reaction between potassium aryl trifluoroborates containing different functionalities promoted by a catalytic amount of $\text{Pd}(\text{OAc})_2$ was described by Oliveira and co-workers (Scheme 5) [30]. The methodology uses water as a solvent under aerobic conditions to give the corresponding biaryl compounds in good yields.



Scheme 5 Homocoupling reaction in water.

CATALYSIS

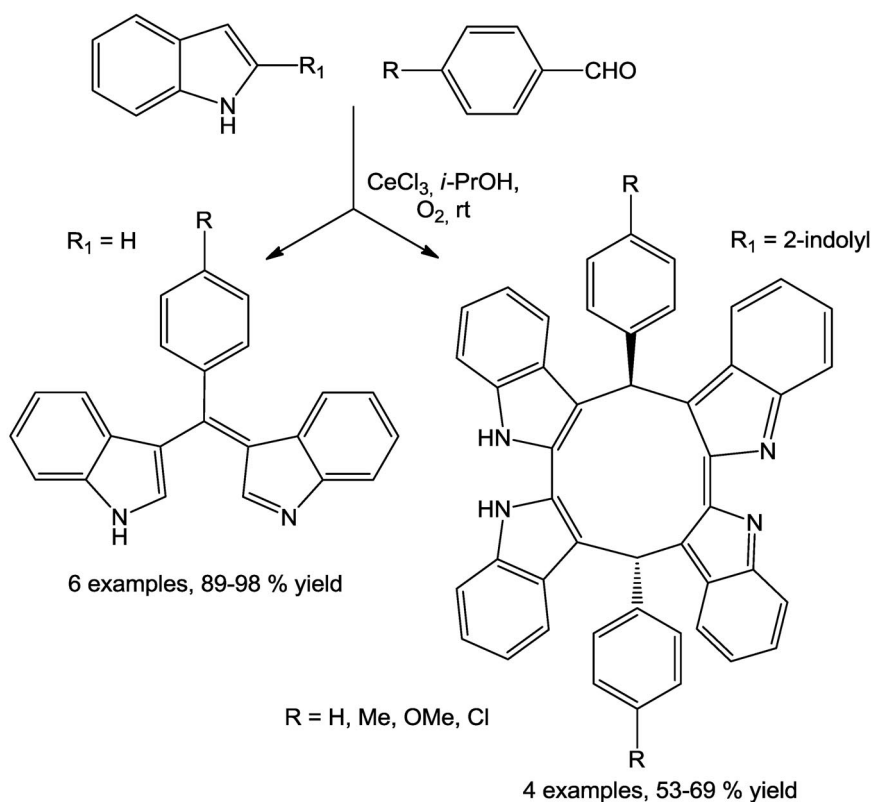
The waste generated in the manufacture of organic compounds consists primarily of inorganic salts. This is a direct consequence of the use of stoichiometric inorganic reagents in organic synthesis, particularly in fine chemicals and pharmaceuticals manufacture. The solution to the waste problem could be the substitution of antiquated stoichiometric methodologies with green catalytic alternatives that are more atom and step economic, and, consequently, have lower E factors [31].

Indoles and benzaldehyde derivatives undergo an efficient one-pot smooth condensation and a further atmospheric-pressure aerobic dehydrogenation with CeCl_3 in *i*-PrOH, to be able to afford the corresponding oxidized bis(indol-3-yl) methanes (Scheme 6). Also, the use of 2,2'-bisindole as the heterocyclic precursor provides cyclic tetra(indolyl)dimethane derivatives, which further undergo partial oxidation to the related calix-shaped macrocycles, carrying an all *cis*-1,3,7-cyclodecatriene core and supporting a 2,2'-biindolylidene moiety. The syntheses of these high value-added compounds are simple and could be performed at room temperature under mild, neutral, and green conditions [32].

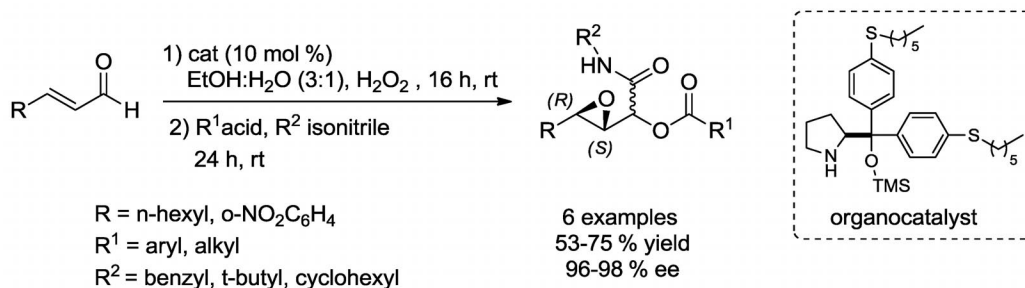
Asymmetric organocatalytic multicomponent reactions have been used in the synthesis of enantiomerically enriched molecules. A very convenient strategy for the synthesis of highly functionalized epoxides was developed by combining an asymmetric organocatalytic epoxidation and the Passerini three-component reaction [33]. This process was carried out employing an α,β -unsaturated aldehyde which was oxidized with H_2O_2 and 10 mol % of a diarylprolinolsilyl ether as organocatalyst, followed by condensation with isocyanides and benzoic acids in EtOH/ H_2O as a solvent. The new organocatalyst showed high activity in an environmentally friendly solvent system (Scheme 7).

Schulz et al. reported the soot oxidation activity of metallic iron nanoparticles under real diesel engine conditions [34]. Particulate matter was sampled at distinct temperatures, using fuels containing ferrocene. The results indicated an 80 % reduction of accumulated particulate matter using fuels doped with 50 ppm ferrocene at a temperature of 460°C . The transmission electron microscopy analysis of the particulate matter revealed that soot agglomerates with and without the presence of Fe showed a similar morphology and that the average diameter of Fe nanoparticles is 10 nm. The use of ferrocene-doped diesel fuels increases the speed of particulate matter oxidation significantly, enabling the filter to self-regenerate at the average temperature of the exhaust gases. Moreover, 500 ppm of sulfur in fuels does not reduce the catalytic activity of Fe nanoparticles in particulate matter oxidation.

Nanocatalysts possess several advantages over conventional catalyst systems; however, isolation and recovery of the nanocatalysts from the reaction mixture is not easy [35]. Conventional filtration is inefficient because of the nano size of the catalyst. This limitation hampers the economics and sustainability of these nanocatalytic protocols. To overcome this limitation, the use of magnetic nanosupports has emerged as one of the best solutions; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. In addition, control



Scheme 6 Condensation of indoles and benzaldehyde derivatives followed by aerobic dehydrogenation catalyzed by CeCl_3 .



Scheme 7 Organocatalytic asymmetric tandem epoxidation/Passerini reaction.

of their properties, including size, shape, morphology, and dispersity, which can mimic the nature, makes it possible for scientists to carefully design the materials that are specifically needed for a specific application.

As commonly known, enzymes are highly efficient catalysts extensively employed in biotechnology. Among the many challenging aspects in this area, enzymes are yet difficult to obtain and purify, which makes them extremely expensive [36]. Therefore, the industrial use of such expensive biocatalysts suffers from the lack of efficient recovery processes. As a very promising strategy, superparamagnetic nanoparticles based on magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) have been recently employed as supporting materials for enzymes, exhibiting striking characteristics, such as large surface

area, mobility, and high mass transference. Additionally, they can be easily recovered by applying an external magnetic field. Moreover, the use of such superparamagnetic nanoparticles represents an effective green chemistry approach, since it prolongs the lifetime of the biocatalyst through the successive recovery cycles.

A new silylant agent 3-(*N,N'*-dicyclohexylguanidine)-propyltrimethoxysilane (GPMS) was prepared straightforwardly in high yield by the simple reaction between 3-aminopropyltrimethoxysilane and dicyclohexylcarbodiimide. This new organosilane containing the basic dicyclohexylguanidine group covalently attached on silica gel is an efficient heterogeneous catalyst for the production of biodiesel. Conversions up to 98 % were obtained for soybean oil methanolysis at 353 K for 3 h. This catalytic system was transposed to a semi-pilot scale in a continuous-flow reactor and resulted in 44 % conversion. The calculated activation energy of the methanolysis in this continuous system indicated that the reaction is probably under mass-transfer limitations [37].

BIOMASS AND BIOFUELS

Long before the invention of the term “green chemistry” as currently known, Brazil has been developing biofuels from renewable biomass. In 1931, ethanol made from sugarcane was already used for energy purposes, but only in 1975, when the National Alcohol Program (Proálcool) was launched, did alcohol effectively become the vanguard of the use of biofuels. For years and to the present day, Brazil remains the largest producer of biofuels in the world. To give an idea of the size of this program, in 1986 ethanol-powered cars accounted for 96 % of vehicles sold in the country. Throughout those 35 years, the use of ethanol, to replace or be mixed with gasoline, promoted an economy over 1.2 billion barrels of oil equivalent.

The progress that is being sought is currently focused on methodologies to enhance the production of second-generation ethanol—which has the raw sugarcane bagasse—the waste and the use of the fermentation process in order to reduce the final cost of biofuels.

The program Bioenergy from the São Paulo State Research Foundation (BIOEN-FAPESP) aims at articulating research and development using academic and industrial laboratories to promote the advancement of knowledge and its application in areas related to bioenergy production in Brazil [38]. More recently, ethanol itself is becoming a platform for the production of new chemicals and supplies for new and old materials. For example, Braskem is producing green ethylene from ethanol to produce green polyethylene [39]. This is a technology that is already in operation, and much of this material is being produced from a renewable source.

In fact, sugarcane biorefineries, besides producing materials such as sugar, ethanol, and polyhydroxybutyrate, can expand their production using several renewable feedstocks to produce biofuels and high-value biobased chemicals [40].

The performance of adsorbents prepared by green processes and based on solid residues arising from biodiesel production has been analyzed by Nunes and co-workers [41]. The adsorbents studied for the removal of cationic dyes from wastewaters or even other matrices was produced by microwave thermal activation. The adsorption capacity increased in comparison to the adsorbent obtained by thermal processing of the same residue in a conventional oven, showing that microwave processing is an attractive alternative for adsorbent production, given the significant reduction in processing time (decreased from 60 to 3 min). Both the removal efficiency and the removal capacity decreased with an increase in temperature, pointing towards the exothermic nature of the removal process, adequately explained by the Freundlich model, which provided the best fit for equilibrium data, indicating heterogeneous adsorption.

EDUCATION

The principles of green chemistry at the higher education level, especially in the organic chemistry area, have been the object of increasing interest in Brazil [42]. The possibility to introduce green chemistry into the curriculum of undergraduate chemistry courses, in a transversal manner—in a number of their regular disciplines—can increase a student's ability to think critically about the chemistry contents, as well as the risks associated with the engine of this specific field and the relationship of the science, technology, and social (STS) dimensions [43].

Most of the papers propose experiments using a Brazilian context or topic, for instance, focusing on biomass or biofuels [44,45], as is the case of the quantitative analysis of bioethanol and its blends with gasoline by using solvatochromic dyes [46]. The students have tested two approaches: (i) use of a solvatochromic dye, followed by determination of fuel composition from plots of the empirical fuel polarity vs. its composition; (ii) use of an ethanol-soluble dye, followed by determination of the blend composition from a Beer's law plot; the former proved to be much more convenient. All the papers show the students' appreciation of the usefulness of chemistry by working with "real" samples from their daily lives which include the awareness and understanding of green chemistry principles.

CONCLUSIONS AND PERSPECTIVES

The contribution of the Brazilian research groups in green chemistry has increased considerably in the last few years. The main area observed is organic synthesis, and the most common green chemistry concept employed is the use of alternative energy specially microwave irradiation, corresponding to 69 % of the total papers. Some investigated topics are of special interest in Brazil, as are the cases of energy subjects: biofuels (biodiesel and ethanol), synthesis, analysis, additives, and antioxidants of/for biofuels [11].

In fact, Brazil has a very favorable condition in terms of biomass as a source of energy and raw materials for chemical industry, besides accumulated considerable expertise in the production of biofuels on a large scale, especially concerning ethanol from sugarcane [47]. Nowadays, there are different sectors involved in the research, development, and innovation activities considering the Brazilian specific conditions and potentialities in green chemistry. In this context, governmental induction actions have been very effective in supporting the research and training of professionals, especially through postgraduation programs.

Recently, FAPERJ, the Rio de Janeiro State Financial Research Foundation, launched the first call for specific support research, development, and innovation of chemical products and processes in green chemistry. The technical and scientific merit of the projects were focused on originality and its adherence to green chemistry theme, primarily following the guidelines outlined in the document "Green Chemistry in Brazil 2010–2030" from the CGEE [10]. The approved projects mainly focused on organic synthesis, followed by biomass and biocatalysis, which has a similar tendency observed in the distribution of the green chemistry publications Brazilian per area of knowledge from 2010 to 2012.

As can be observed, there are several conjugated actions promoting green chemistry in Brazil, reflected by the increasing number of published scientific papers, contributing to introduce national demands and issues related to scientific and technological innovations in this field.

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