

Research Article

Modified Fats by Heterogeneous Catalysis: Changes on the Way to Green Chemistry

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Abstract: Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of contaminants. Within this approach, heterogeneous catalysts have proven to be a promising alternative to replace homogeneous catalysts. This study aimed to investigate the feasibility of using heterogeneous catalysts in the production of modified fats by chemical interesterification reaction. The mesoporous molecular sieves such as MCM-41 and SBA-15 modified with basic organic molecules may be promising catalysts for this reaction due to its surface area and pore size suitable for access of triacylglycerol molecules to their active sites and possess activity in reactions involving the production of carbanions as reaction intermediates.

Keywords: Chemical interesterification, molecular sieves, sustainable chemistry

INTRODUCTION

Almost all segments of chemistry industry, from the production of simple commodities to complex syntheses of drugs, are responsible for waste generation leading to great environmental impact.

Indiscriminate waste generation and its effects on various ecosystems have been discussed worldwide. The Stockholm Conference on the Human Environment (1972) was the first major step in respect to environmental legislation (Passos, 2009). Since then, the chemical industry has been strongly requested to improve technologies to minimize waste generation and to create environmental management policies, such as the ISO 14000 series, containing technical requirements for environmental management capable of auditing certification, registration, or self-declaration (Martini Jr and Gusmão, 2009).

In this scenario, the sustainable chemistry or green chemistry stands out, aimed at developing new products and/or chemical processes to reduce or eliminate environmental impacts generated by the current technologies (Silva *et al.*, 2005). The twelve principles of green chemistry have elaborated several pathways on sustainability, including the preference to less toxicity reagents or derived from renewable sources, the use more selective reactions to avoid the generation of undesirable products, besides the use of catalysts that can be easily recovered and reused.

Recently, studies on green chemistry mainly involve the replacement of homogeneous by heterogeneous catalysts. The latter has the major

advantage of using simple unit operations to remove it from the final product, such as filtration techniques. These catalysts stand out for not being corrosive when compared to the homogeneous catalysts. Many studies assessing the solids base catalysts in chemical reactions have been published since the 1990s, for example, potassium fluoride (Corma *et al.*, 1997), metal oxides, zeolites (Gamallo, 2001), hydrotalcites and amino groups stabilized on silica gel (Cauvel *et al.*, 1997), clays, alkali metal carbonates and alkaline earth metals (Corma *et al.*, 1998).

Similarly, the food industry may be ready for this new scenario. A citation made by Ernest Reimerdes during the Congress of Food Technology of the Association of Agriculture of Germany, in 1994, summarizes this concern:

“The food industry is getting ready for the future. The world population growth, the new markets in underdeveloped and developing countries and the consumption habits of industrialized countries are increasing demands. For the food industry, it is increasingly important to offer high quality products with nutrition and health claims and production compatible and safe for the environment.”

This study aims to present a brief review of the technologies used in the food industry for the production of modified fats and to investigate an alternative to replace the conventional catalysts currently used in this process by heterogeneous catalysts. Such substitution can match this type of reaction to the world reality, in respect to the use of cleaner technologies, as it will significantly reduce the

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impact caused by neutralization and separation steps of conventional catalysts of the final reaction products.

GREEN CHEMISTRY

The green chemistry was created during the second half of the 20th century and was defined as chemistry faced in developing new products and/or processes that will eliminate fully or partially the environmental impacts caused by humans, focused on the principles of a sustainable development (Horvath and Anastas, 2007). This requires a new approach on developing new technologies or improving the conventional ones, in order to generate fewer wastes, whether solid, liquid or gaseous. Besides the environmental benefits, the use of the principles of green chemistry generates savings with storage and treatment of waste and prevents costs with decontamination and payment of court awards (Tundo *et al.*, 2000; Anastas and Eghbali, 2010).

Historically, the United Nations Conference on the conservation and use of resources held in 1949 in the United States appears as the first report of concern about the environmental pollution, accelerated by the intense industrial development. Later, in 1968, both the Biosphere Conference and the Meadows report have questioned the paradigms on economic development, which was as a tool to pressure world leaders on environmental issues. Furthermore, it played a decisive role in the Stockholm Conference in 1972, which contained the bases of environmental laws and the concepts of sustainable development, which, in early 1980, were considered official documents such as the World Wildlife Fund (WWF), International Union for Conservation of Nature (IUCN) and the United Nations (UN). Then, new ideas and concepts have emerged, aimed at waste reduction and waste management practices (Farias and Favaro, 2011).

Thus, over the years, a consensus on key issues and basic principles of green chemistry was created. The twelve points for the implementation of green chemistry in an industry or institution and/or chemistry research center are the following (Anastas and Warner, 1998):

Prevention: It is cheaper to prevent toxic waste than to treat them after they are produced. The generation of low value-added product and the energy loss during the process is considered waste, which can affect the environment in different ways. The environmental acceptability of a manufacturing process may be evaluated for its environmental impact factor (E-factor), as reported by Sheldon (2007), which is defined as the weight ratio of the residue generated by the desired product (kg waste/kg of product).

Atom economy: Synthetic methods should be developed to incorporate all reactants in the final product. This concept was introduced by Trost (1991) to maximize the utilization of foodstock so that the final product contains the same number of atoms of the

reactants. It is defined as the ratio between the molecular weight of the desired product and the molecular weight of all reactants used.

Secure synthesis: Synthetic methodologies should be developed to use and generate substances with little or no toxicity to human health and the environment (Prado, 2003). Many reactions used in organic synthesis, including cycloaddition, rearrangements and coupling reactions are well known and considered very efficient reactions. However, new reactions, such as cascade reactions and CH activation have been used to minimize the degree of toxicity of reagents and products. For example, the CH activation appears as a promising alternative for the coupling reactions in which halo compounds are used due to their high reactivity. Stuart and Fagnou (2007) coupled two aromatic compounds selectively, without the need for any activation or activating groups. These examples evidence the important role of the CH activation in the advance of green chemistry.

Development of safe products: Products that do not harm the environment after use should be developed. Knowing the properties of a molecule with direct impact on the environment and the changes it can cause to the biosphere is essential for sustainable development. In recent decades, a considerable number of toxicology publications is found in literature, focused on studies of quantum mechanics modelling related to the structure, properties and functions of a given molecule. Voutchkova *et al.* (2011) developed guidelines for the development of low toxicity chemicals in aquatic environment for four kinds of seaweed products by using molecular modeling calculations. The properties of the molecules studied include water solubility, size, shape and molecular orbital energy.

Decrease of solvents and auxiliary substances: The use of auxiliary substances such as solvents, cleaning agents and drying agents need to be avoided. When used, these substances must be innocuous or easily reused. Generally, conventional solvents present problems related to toxicity, corrosivity, flammability, volatility and solubility. In addition, reuse requires energy costs for purification and distillation processes. For being used in large amounts, these substances are responsible for a considerable portion of the waste generated during the process (Anastas and Eghbali, 2010). Given this scenario, some alternatives have been suggested such as no solvent systems (Guo *et al.*, 2014), water (Joó and Kathó, 2010), ionic liquids and supercritical fluids (Jessop, 2011).

Energy efficiency: The environmental and economic impacts caused by the energy generation in a chemical process must be considered. The energy lost in a process is considered waste. It is necessary to develop

processes to be performed at room temperature and pressure. Reductions of the energy barrier of a reaction or alternative reagents that allow milder reaction conditions are required. Alternative energy sources such as wind, thermal and solar energy should also be considered (Anastas and Eghbali, 2010).

Use of renewable feedstocks: The use of biomass as raw material should be prioritized in the development of new technologies and processes. The use of renewable sources was strongly driven by the search for alternatives to the consumption of oil and its derivatives. For many years, lignin was the major solid waste generated by the paper industry, being incinerated to produce energy for the industry itself. In recent years, new applications have emerged for lignin, including raw material for the production of humic acid and vanillin and as a dispersant and additive (Agbor *et al.*, 2011). Oils and fats also play an important role as renewable raw materials in various applications, with emphasis for biodiesel production (Biermann *et al.*, 2011).

Reduction in derivatives: Derivatization is a technique widely used in organic synthesis and analytical chemistry. This operation be minimized or avoided, once the reaction steps require additional reagents and consequently may produce undesirable byproducts. At the end of the last century, a new concept called non-covalent derivatization was employed as an alternative to conventional derivatization, which is dependent on intermolecular interactions rather than covalent bonding (Taylor and Warner, 1993).

Catalysis: Catalysis can improve the efficiency of a reaction by lowering its activation energy, increasing selectivity, besides preventing the use of reagents in stoichiometric amounts, which generates economy with energy reductions, lower use of raw materials and waste generated. The use of catalysts (as selective as possible) should be chosen instead to stoichiometric reagents (Anastas and Eghbali, 2010).

Use of degradable product: Chemicals must be designed for biocompatibility. After use, they should not remain in the environment, so they must degrade into innocuous products. Some chemical structures as halogenated radicals, branched chains, tertiary amines and quaternary carbons are resistant to degradation and should be avoided. The use of compounds whose structure can be degraded by degradative enzymes should be prioritized. Currently, the biopolymers have been widely assessed as alternative to conventional polymers (Tome *et al.*, 2011).

Real-time analysis for pollution prevention: Monitoring and controlling the methodologies in real time within the process should be taken into account.

The formation of toxic substances must be monitored prior to generation.

Safer chemistry for accident prevention: Substances and their use in a chemical process should be chosen to minimize the risk of accidents, such as releases, fires and explosions.

Food industry has a direct interest in several productive chains and plays a prominent role in various economic activities. However, the food production chain has recently been recognized worldwide as inefficient in terms of decreasing the large amount of waste generated and accumulated (Gunders, 2012). In this approach, the United States is the largest waste generator. Food production in this country consumes 10% of the energy generated, requires 50% of its territory for cultivation and 80% water available for consumption; however, 40% of food production is lost. Furthermore, 25% of the water used along with a large amount of chemicals is responsible for most of the liquid waste generated. It is worth mentioning that the generation of methane from food decomposition in landfills represents 16% of all methane emissions in that country (Gunders, 2012). In Europe, less than 90 million tons of food waste is produced each year, 38% of which are directly produced by the food industry. In 2012, the Food and Agriculture Organization of the United Nations (FAO) estimated that up to a third of food intended for human consumption was wasted each year worldwide (Pfaltzgraff *et al.*, 2013).

TECHNOLOGIES FOR FATS MODIFICATION IN THE FOOD INDUSTRY

Lipids, along with carbohydrates and proteins, are a major food constituent. It is water-insoluble organic molecules with different functions in living organisms, such as energy reserve, thermal and physical protection of internal organs, carriers of vitamins A, D, E and K, hormone synthesis and cell membrane constituents (Dubois *et al.*, 2007; Kouba and Mourot, 2011). In addition, lipids provide pleasant flavor to food, which is a determining factor for consumers (Karleskind, 2003; Gurr *et al.*, 2002).

Lipids are presented mostly in the form of triacylglycerols, whose composition and distribution of fatty acids defines its physical properties (Karupaiah and Sundram, 2007; Venkatachalam and Sathe, 2006). With the purpose of adapting the lipids to a particular product, many processes have been developed in the food industry to modify the composition and distribution of fatty acid chains in triacylglycerol molecules for use in various foods (Hammond and Glatz, 1988; Gunstone, 1999; Castro *et al.*, 2004; Ribeiro *et al.*, 2007; Pinho and Suarez, 2013). Among the technologies used for the production of modified fats, the partial hydrogenation, fractionation and chemical interesterification of oils and fats have stood out.

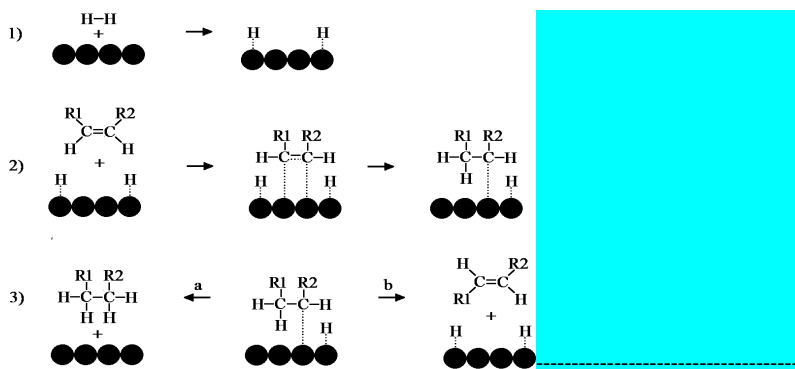


Fig. 1: Mechanism involved in the partial hydrogenation of vegetable oils. Adapted from Pinho and Suarez (2013)

Partial hydrogenation: The partial hydrogenation of oils and fats is a chemical reaction that adds hydrogen atoms across the carbon-carbon double bonds of the unsaturated fatty acids of the raw material, yielding modified fats industrially able to replace saturated fats. adsorbs the reagent on its surface, occurring partial disruption of the double bond ($C = C$) of unsaturated fatty acid and HH hydrogen bonding, forming an intermediate organometallic complex, followed by addition reaction and desorption of the final product. Under operating conditions such as high temperatures, slow agitation, low pressures and high concentrations of catalyst, the hydrogenation reaction becomes selective for fatty acids with higher degree of unsaturation (Pinho and Suarez, 2013).

As an advantage, this process yields fats with adequate plasticity for the production of solid and semi-solid fats used in the manufacture of margarine and other foods. In addition, partial hydrogenation considerably reduces the number of double bonds, which increases their thermal and oxidative stability (Pinho and Suarez, 2013).

During the process, the unsaturated fatty acids that have not undergone hydrogenation are converted to their more stable isomers, i.e., *trans* isomers, whose consumption has been of concern once the hydrogenated fats have been widely introduced in many foods (Merçon, 2010). Although the partial hydrogenation has provided technological advances, the physiological effects of *trans* fats obtained by this process are much more damaging when compared to saturated fats, increasing the risk of cardiovascular disease and cancer (Stender and Dyerberg, 2004; Mozaffarian *et al.*, 2006, 2009).

Fractionation: In the fractionation of oils and fats, the triacylglycerols are separated into fractions of different melting point and compositions, once the vegetable oils have a melting temperature range as a function of their constituents (Centenaro *et al.*, 2008; Parmentier and Fanni, 2000). The process consists in the partial crystallization of the oil, followed by separation of the solid (stearin) and liquid (olein) fraction by filtration (Parmentier and Fanni, 2000). The resulting fractions directly depend on the characteristics and operating

In this process, vegetable oil is introduced into a reactor where the solid catalyst (nickel) and hydrogen gas are added under agitation at temperatures ranging from 120 to 150°C. Figure 1 illustrates the mechanisms involved in the hydrogenation process. The metal catalyst conditions, while the separation efficiency of the liquid phase influences the quality of the solid fraction.

The dry fractionation process involves fat homogenization and selective crystallization of the high-melting-point triacylglycerols that are dependent of temperature, time and agitation to crystals formation, followed by filtration. This leads to a separation of stearin fraction with a high content of saturated fatty acids and olein fraction with a high content of unsaturated fatty acids. In the homogenization process, the fat is heated to a temperature above its melting point and cooled slowly in the next crystallization step, in which the triacylglycerols molecules, in constant motion, are close to each other and increasingly attracting molecules until the crystals formation and stabilization. In the last step, the crystals are separated by filtration (dry method) or by centrifugation (wet method) (Centenaro *et al.*, 2008).

Dry fractionation is currently used in the manufacture of a wide range of oils and fats to remove most of the saturated compounds by increasing the content of unsaturated fatty acids, as mentioned earlier, or by obtaining fractions with special rheological properties. As an example, there is chicken fat, which is a semisolid fat in its natural state with good nutritional properties when compared to other fats of animal origin. Its dry fractionation results in a greasy solid fraction with physical characteristics similar to those of lard and tallow (Arnaud *et al.*, 2004).

Chemical interesterification: Chemical interesterification has emerged as the most viable alternative to partial hydrogenation process because it enables the production of modified fats only by the redistribution of the fatty acids on the triacylglycerol molecule, without being subjected to chemical modifications. Thus, the fatty acids remain unchanged, but their redistribution occurs on the triacylglycerol molecules by changing the triacylglycerols composition (Petrauskaitė *et al.*, 1998). In this process, metal

alkylates or metallic sodium is used as homogeneous catalysts. These are introduced into the reaction mixture free from moisture at temperatures ranging from 90 to 110°C and low pressures for a time interval that can vary from 30 min to 2 h. After this time, water is added to inactivate the catalyst and terminate the reaction (Sreenivasan, 1978).

A disadvantage of chemical interesterification is that the catalysts are extremely prone to inactivation by water and free fatty acids, as well as by peroxides, carbon dioxide and oxygen. In addition, these catalysts are highly toxic and reactive, requiring special care of storage and handling. Another disadvantage is the need for subsequent reaction steps such as neutralization and successive washings with water, necessary for inactivation and separation of the catalyst (Rozenaal, 1992).

The use of bases as homogeneous catalysts in industrial processes usually cause serious problems related to equipment corrosion and environmental pollution. Generally, the separation of homogeneous catalysts from the reaction medium is a very costly step. Alkali amounts above the stoichiometric quantities may form highly polluting residues during neutralization.

HETEROGENEOUS CATALYSTS

The efficiency of the chemical processes can be increased according to the principles of the green chemistry. In the case of catalysts, they are used not only to accelerate the reaction, but also to increase the selectivity and specificity of a given reaction product, thereby reducing the amount of undesirable products to be discarded. However, when these catalysts are used in homogeneous phase, further steps are required after the reaction to remove the catalyst from the final product, often causing destruction of the catalyst and increasing waste generation (Prado, 2003). There are also many reports on problems related to corrosion of equipment due to the use of these catalysts (Dabdoub *et al.*, 2009).

The heterogeneous catalysis has been presented as an alternative for this type of problem. Catalysts supported on solid matrices with high surface area (such as silica gel and mixed oxides, for example) have many advantages over the homogeneous catalysts, as follows: Easy separation of the catalysts from the reaction medium (usually occurring by simple filtration), regeneration and reactivation capacities, higher activity and selectivity, non-corrosive, higher thermal stability and versatility once they can be used in numerous reactions. Thus, these catalysts have advantages both from a technical and environmental point of view, which are very important factors in choosing a production process.

When making use of heterogeneous catalysis, it is of fundamental importance to assess the extent and the manner of attaching the catalyst on its support. Problems such as decreased activity or contamination of the final products can occur by leaching of these catalysts by the reaction medium. Faced with these

problems, several studies have presented methods for immobilization of catalysts on inert supports (Di Serio *et al.*, 2010). Among these, the sol-gel process in the presence of driver agents has been highlighted to obtain mesoporous solids. The advantage of this method is the possibility of the synthesis of high purity materials, under conditions similar to the reaction environment. Furthermore, incorporation and immobilization of active components in the solid matrix are relatively simple and can even be done during the synthesis of the material (called synthesis functionalization) or after its preparation (so-called post-modification). These mesoporous materials exhibit high surface area, a fundamental characteristic in the catalytic processes (Lafond *et al.*, 2002).

CHEMICAL INTERESTERIFICATION VIA HETEROGENEOUS CATALYSIS

Two mechanisms are involved in the chemical interesterification reaction in homogeneous phase: the attack on the carbonyl and the Claisen condensation (Fig. 2). Although these are two distinct mechanisms, it is worth emphasizing that they are different paths to achieve the same chemical species as reactive intermediate: the carbanion glyceroxide (Marangoni and Rousseau, 1995).

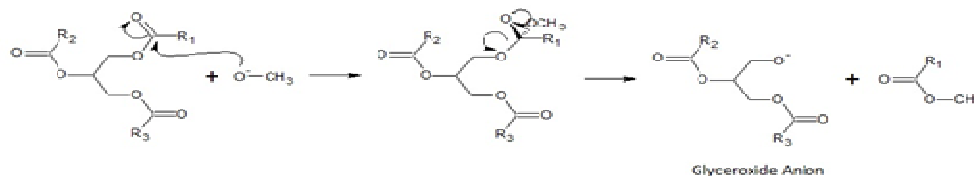
Carbanions are important organic intermediates in various reactions of industrial interest in fine chemicals, including drug synthesis reactions, dyes, perfumery, etc. They are formed by proton abstraction from a C-H bond by a base (March, 1990). In most industrial processes involving these reactions, inorganic or organic bases are used as homogeneous catalysts and the use of greater amounts of these bases is needed to maintain the medium under alkaline conditions (Ono, 2003).

Some examples of organic reactions using carbanions as intermediates are: isomerization of alkenes and alkynes, hydrogenation, amination, hydrocycle dimerization, aldol condensations, Michael addition, Knoevenagel condensation, conjugate addition of alcohol and cyanoethylation. Among these, the aldol condensation is very important because it involves the formation of carbon-carbon bonds and generally results in molecules with more complex structures than the reactants (Ono, 2003).

The use of bases as homogeneous catalysts in industrial processes usually lead to serious problems related to equipment corrosion and environmental pollution (Dabdoub *et al.*, 2009). Generally, the separation of the homogeneous catalysts from the reaction medium is a very expensive step. The use of bases above the stoichiometric amounts generates highly polluting residues formed by the neutralization of these compounds. The replacement of homogenous catalysts by base solids that act as heterogeneous catalysts is a cleaner technology for the production of interesterified fat that avoids these problems.

CHEMICAL INTERESTERIFICATION

Initiation: Carbonyl attack mechanism:



Initiation: Claisen mechanism:

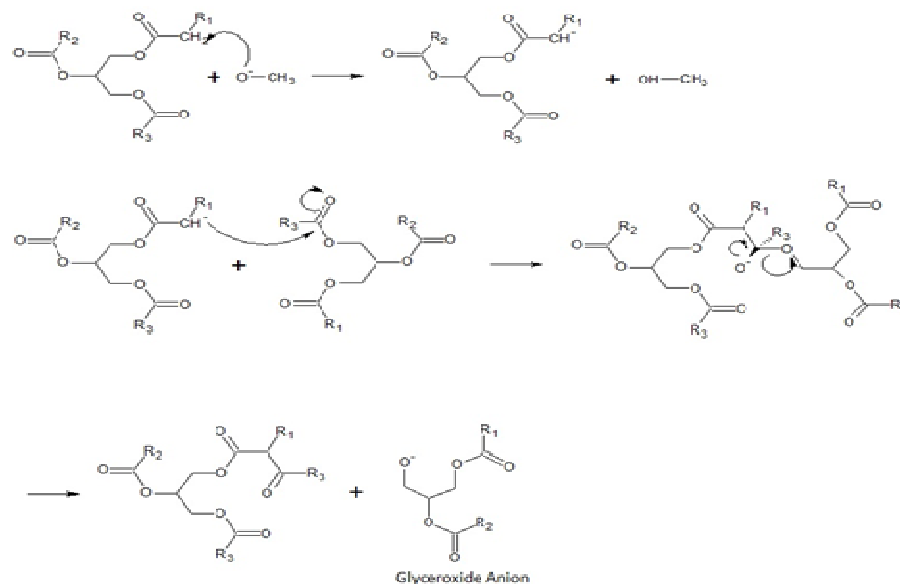


Fig. 2: Chemical interesterification mechanisms. Adapted from Marangoni and Rousseau (1995)

Beck *et al.* (1992), scientists of the Mobil company discovered a new family of materials called M41S, being formed by two major phases: MCM-41 and MCM-48. These mesoporous materials have a pore size distribution ranging from 20 to 100 Å with a very narrow distribution with respect to the pores diameter. These structures are composed primarily of silica and have high specific surface area (over 1000 m²/g). Some authors have reported the possibility of producing MCM-41 samples with a well-defined and controlled pore diameter in the range 20-70 Å, only by changing the synthesis conditions (Corma *et al.*, 1997).

Due to its high surface area, mesoporous molecular sieves such as MCM-41, MCM-48 and SBA-15 can be used as supports for anchoring basic oxides and organic molecules with basic properties, like amines and hydroxide quaternary ammonium salts (Choudary *et al.*, 1999; Xie and Qi, 2013). In addition, there are reports on literature about the generation of basic properties of these materials, with aluminum in its structure by isomorphic substitution (Wang *et al.*, 2006) and the use of compensation cations with high ionic radius (Oliveira *et al.*, 2009). These samples should have basic properties and high surface area, with great potential for application as heterogeneous catalysts. The control of the pore diameter, combined with the possibility of

producing materials with different basicity levels should allow adjustment of the properties of these solids to catalyze diverse types of reactions that require different basicity levels or involving molecules of different kinetic diameters.

Thus, the possibility to synthesize M41S molecular sieves to act in the interesterification reaction of fats and oils is quite feasible, since their active sites can be achieved by molecules with large kinetic diameters, such as the triacylglycerols and with basicity similar to the conventional catalysts, thereby allowing a cleaner technology for the production of modified fats free of trans isomers.

CONCLUSION

The development of new processes or the improvement of conventional ones should focus not only on the final product but also in the reduction or complete elimination of potentially hazardous by-products to the environment. The great challenge of the millennium is to make the principles of the green chemistry routine in the chemical industries.

Heterogeneous catalysts have been widely used to replace homogeneous catalysts because they avoid equipment corrosion and are more active and selective,

reducing the formation of undesirable byproducts. Furthermore, the heterogeneous catalysis significantly reduces the generation of industrial waste due to no need of further steps for catalyst separation and product purification, since they can also be reused.

The use of heterogeneous catalysis in the production of modified fats by chemical interesterification can be a reality within the environment of the green chemistry, since various catalysts with basic activity have been successfully tested in reactions involving the formation of carbanions as reactive intermediates. However, the synthesis of catalysts with high specific surface area and pore size should be investigated so that molecules such as triacylglycerols can access their active sites, which can be obtained using the molecular sieves by sol gel processing.

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