Review

Transesterification of Vegetable Oils: a Review

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A transesterificação de óleos vegetais com metanol, bem como as principais aplicações de ésteres metílicos de ácidos graxos, são revisadas. São descritos os aspectos gerais desse processo e a aplicabilidade de diferentes tipos de catalisadores (ácidos, hidróxidos, alcóxidos e carbonatos de metais alcalinos, enzimas e bases não-iônicas, como aminas, amidinas, guanidinas e triamino(imino)fosforanos). Enfoque especial é dado às guanidinas, que podem ser facilmente heterogeneizadas em polímeros orgânicos. No entanto, as bases ancoradas lixiviam dos polímeros. Novas estratégias para a obtenção de guanidinas heterogeneizadas mais resistentes à lixiviação são propostas. Finalmente, são descritas várias aplicações para ésteres de ácidos graxos, obtidos por transesterificação de óleos vegetais.

The transesterification of vegetable oils with methanol as well as the main uses of the fatty acid methyl esters are reviewed. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidines and triamino(imino)phosphoranes) are described. Special attention is given to guanidines, which can be easily heterogenized on organic polymers. However, the anchored catalysts show leaching problems. New strategies to obtain non-leaching guanidine-containing catalysts are proposed. Finally, several applications of fatty acid esters, obtained by transesterification of vegetable oils, are described.
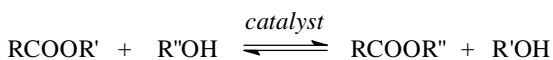
General Aspects of Transesterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Scheme 1)[1]. In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or

base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds[1]. An example is the production of PET (polyethylene terephthalate), which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst (Scheme 2)[2]. Furthermore, a large number of acrylic acid derivatives is produced by transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts[3-6].

If the alcohol and the ester groups are present in the same molecule simple lactones[7,8] or macrocycles[9-10] are formed by an intramolecular transesterification, as shown

$$\text{RCOOR'} + \text{R''OH} \underset{}{\overset{catalyst}{\rightleftharpoons}} \text{RCOOR''} + \text{R'OH}$$

Scheme 1. General equation for a transesterification reaction.
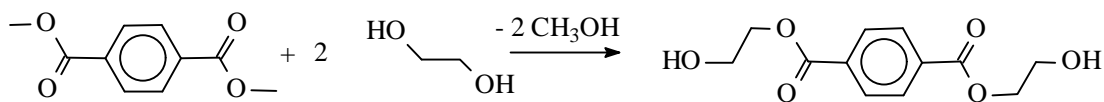
Scheme 2. Transesterification of dimethylterephthalate with ethylene glycol.

in Scheme 3. Further transesterification reactions can be found in the literature, in which metal alkoxides[11-16], aluminum isopropoxide[17-19], tetraalkoxytitanium compounds[20-22] and organotin alkoxides[23,24] are applied as catalysts.

Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol[25,26] (Scheme 4). The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates[26]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification and will be discussed below, based on the type of catalyst used.

Acid-Catalyzed Processes

The transesterification process is catalyzed by BrØnsted acids, preferably by sulfonic[27] and sulfuric acids[26,28,29]. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, tipically, temperatures above 100 °C and more than 3 h to reach complete conversion[30]. Pryde *et al.*[26] showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the
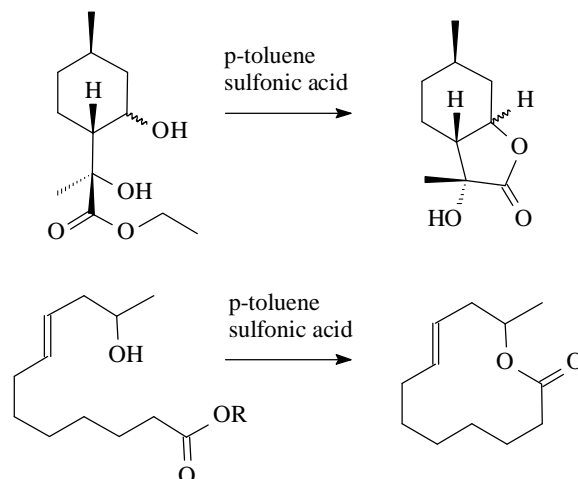
Scheme 3. Examples of intramolecular transesterification reactions, forming lactones or macrocycles.
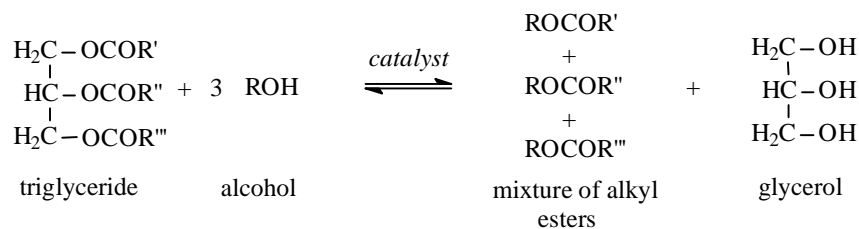
other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Scheme 5, for a monoglyceride. However, it can be extended to di- and triglycerides[31]. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.
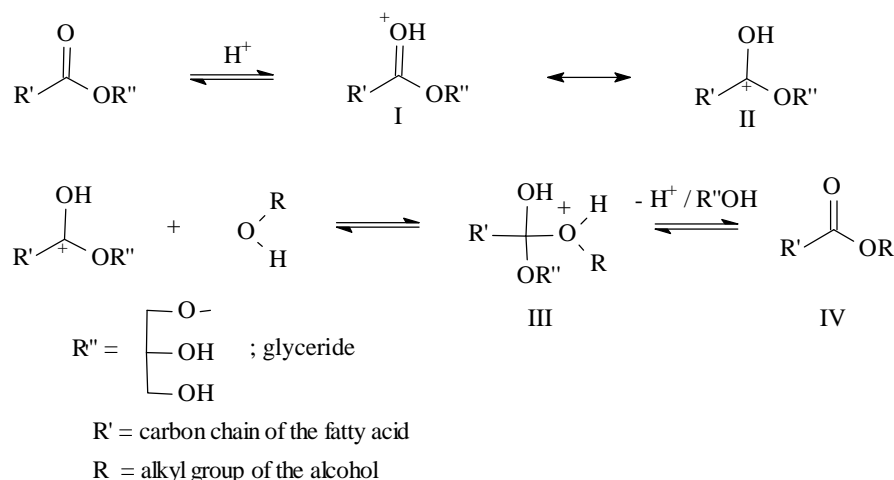
According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.
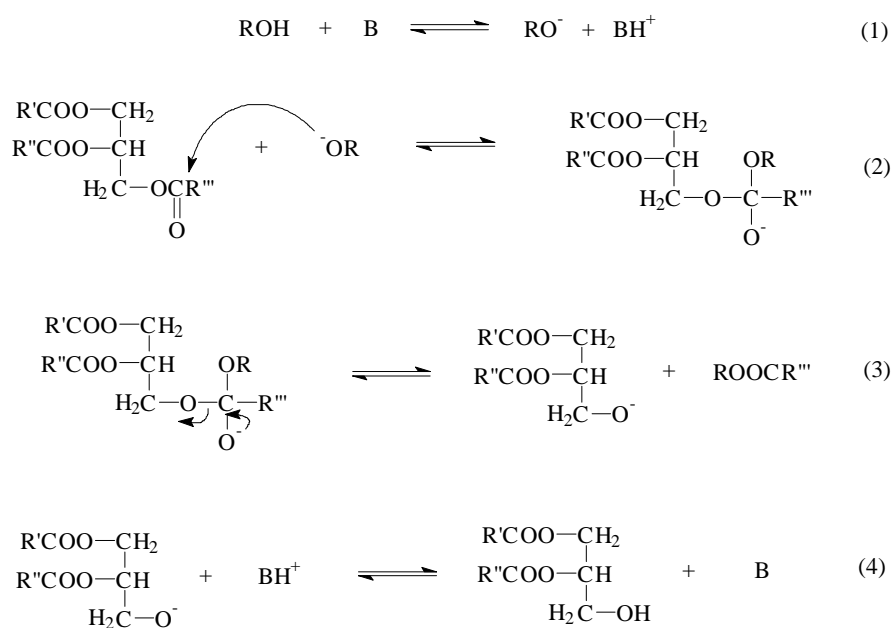
Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction[26,30]. Due

Scheme 4. Transesterification of vegetable oils.

$$R'' = \begin{cases} O- \\ OH \\ OH \end{cases} ; \text{glyceride}$$

R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 5. Mechanism of the acid-catalyzed transesterification of vegetable oils.

$$ROH \;+\; B \;\rightleftharpoons\; RO^- \;+\; BH^+ \tag{1}$$

Scheme 6. Mechanism of the base-catalyzed transesterification of vegetable oils.

to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides[26,30,32] and hydroxides[29,33-36] as well as sodium or potassium carbonates[37-39].

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme 6. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2)[11,40], from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second

molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes[30]. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is pro-

duced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Scheme 7). This undesirable saponification reaction reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions[30].

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation[38]. This can be explained by the formation of bicarbonate instead of water (Scheme 8), which does not hydrolyse the esters.
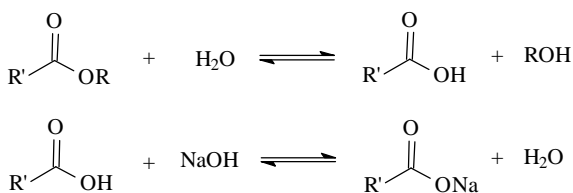
Lipase-Catalyzed Processes

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools[41].

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents[42-48]. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.
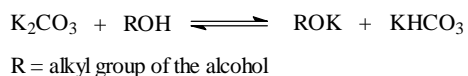
Non-Ionic Base-Catalyzed Processes

In order to obtain milder reaction conditions and to simplify manipulations, a great number of organic bases has been developed and used as catalyst or reactant for organic syntheses. Among these bases, amines such as triethylamine[49,50], piperidine[49], 1,2,2,6,6-pentamethylpi-peridine[49,51], pyridine[49,50,51], 2,6-di-*tert*-butylpyridine[49,51] and 4-dimethyl-aminopyridine[1,52] (DMAP); amidines such as 1,8-diazabicyclo[5.4.0]undec-7-ene[1,49,50,51] (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene[49,51,53] (DBN); guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene[50,54] (TBD), 1,1,3,3-tetramethylguanidine[55,56,57] (TMG), 1,1,2,3,3-pentabutylguanidine[58] (PBG), 1,3-diphenylguanidine[59], 1,2,3-triphenylguanidine[60,61] and amino- and nitroguanidines[62]; triamino(imino)phosphoranes such as *tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2- diazaphosphorane[51] (BEMP) and tris(dimethylamino)methyliminophosphorane[51] (Me_7P), shown in Scheme 9, are frequently used in organic synthesis.

The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied. In a first series of studies, the catalytic activity of some guanidines was compared to that observed using other bases such as the amidines DBU and DBN, and the triamino(imino)phosphoranes BEMP and Me_7P[63]. It was observed that TBD, even if applied at only 1 mol%, produces more than 90% of methyl esters after 1 h. Using the other bases, under the same experimental conditions, the yields were not higher than 66% (Table 1). The order of the catalytic activity is not directly related to the relative basicity of these compounds, since BEMP and Me_7P should be the more efficient catalysts, followed by TBD. However, the guanidines are more active catalysts and the activity follows their relative basicity.

According to the observed results and to the mechanism of the base-catalyzed transesterification (Scheme 6), it seems that the good performance of TBD, when compared to BEMP and Me_7P, is related to its kinetic activity. The catalytic site (unshared electron pair of the $sp^2 N$) of TBD is practically unhindered (Scheme 10), allowing an easy access of the methanol for proton transfer, while the steric

R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 7. Saponification reaction of the produced fatty acid alkyl esters.

$$K_2CO_3 + ROH \rightleftharpoons ROK + KHCO_3$$

R = alkyl group of the alcohol

Scheme 8. Reaction of potassium carbonate with the alcohol.

Table 1. Comparison of the catalytic activity of some guanidines, amidines and triamino(imimo)phosphoranes in the transesterification of rapeseed oil with methanol.

Catalyst	Relative basicity[51]	pKa (CH_3CN)[49]	Yield (%) after 1 h [a]
TBD	150	25.9	91
BEMP	6873	not available	66
Me_7P	4762	27.52	63
MTBD	43.65	25.43	47
DBU	3.4	24.32	32
TMG	0.95	23.30	18
DBN	1	23.79	4.5

a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.
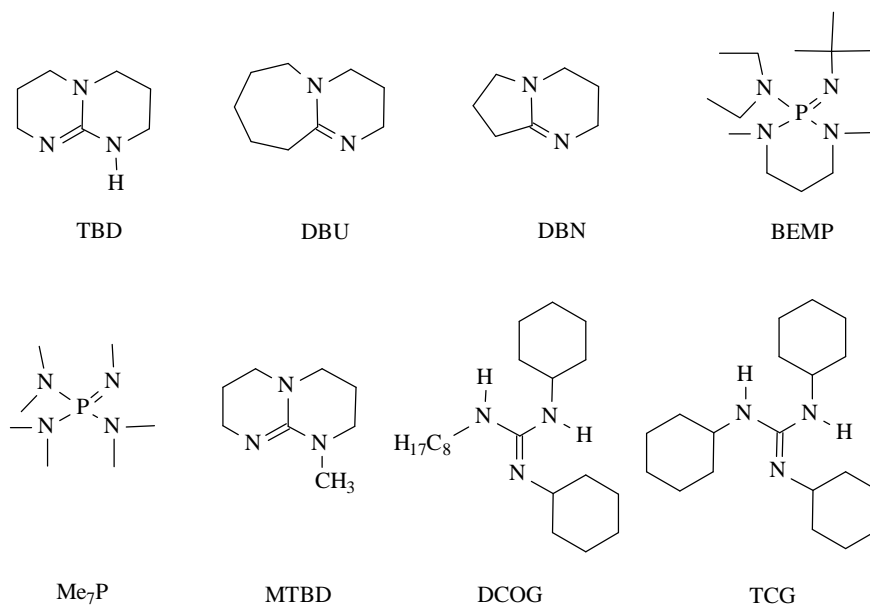
Scheme 9. Molecular structures of some non-ionic organic bases.
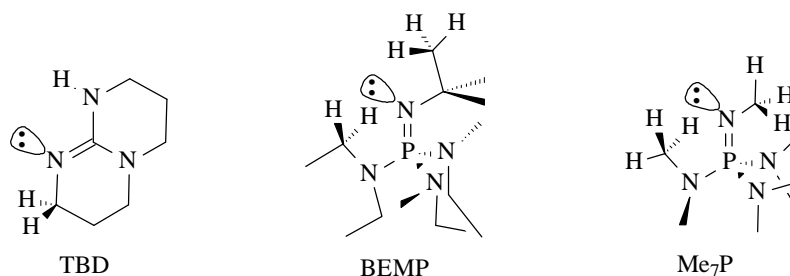
Scheme 10. Steric hindrance of TBD, BEMP and Me$_7$P.

hindrance shown by the triamino(imino)phosphoranes is so significant that they are practically inert to alkylating agents, such as isopropyl bromide, as well as extremely resistant to react with thionyl chloride and thiophosgene[51]. Other bases such as DMAP, pyridine and triethylamine were also tested. However, even at 5 mol%, these amines did not give satisfactory yields. DMAP was the most active within this series, producing only 20% of methyl esters after 1 h.

In a second series of studies, the catalytic activity of TBD was compared to that observed for typical industrial catalysts (*e.g.* NaOH and K$_2$CO$_3$)[37-39]. The results of this study[63] are shown in Table 2. The reaction yields obtained with TBD were close to those observed with NaOH and no undesirable by-products such as soaps (easily formed when alkaline metal hydroxides are used) were observed. When compared to potassium carbonate, TBD was always more active, even at low molar concentrations. Although TBD is less active than sodium methoxide (at only 0.5%, CH$_3$ONa produces more than 98% of methyl esters after 30 min), its use does not require any special condition.

Table 2. Comparison between TBD and the conventional inorganic catalysts.

Catalyst	Yield (%) after 1 h[a]
NaOH (1 mol%)	98.7
K$_2$CO$_3$ (1 mol%)	84.0
K$_2$CO$_3$ (2 mol%)	90.3
K$_2$CO$_3$ (3 mol%)	92.4
TBD (1 mol%)	89.0
TBD (2 mol%)	91.4
TBD (3 mol%)	93.0

a: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 h, 70 °C.

Due to the excellent performance of TBD in the transesterification of vegetable oils, the catalytic activity of other alkylguanidines was also investigated, in order to establish and understand all factors that may affect their catalytic properties. In a third series of studies, the catalytic

activity of several alkylguanidines was compared[64]. TBD was always the most active, however, 1,3-dicyclohexyl-2-*n*-octylguanidine (DCOG), 1,1,2,3,3-pentamethylguanidine (PMG), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,2,3-tricyclohexylguanidine (TCG), also showed a good catalytic performance[64]. The activity order of the catalysts TBD > TCG > DCOG > MTBD > PMG (Table 3) corresponds to their relative base strength, which is increased by structural factors such as number and type of substituents (cyclic or acyclic chain)[51]. The excellent performance of DCOG and TCG is also assigned to the high symmetry of their guanidinium cations, as observed earlier for the symmetric 1,2,3-trimethylguanidine[65].

Results obtained in the transesterification of soybean oil with methanol show that 1,2,3,4,5-pentacyclohexyl-biguanidine (PCBG) is even more active than TCG, as a 82% yield of methyl esters is obtained with PCBG after 1 h, compared to 69% with TCG under the same conditions[66].

Heterogeneously Catalyzed Processes

The advantage of using guanidines in the transesterification of vegetable oils is the possibility to heterogenize them on organic polymers. Schuchardt *et al.* tested principally cellulose and poly(styrene/divinylbenzene), but also polyuretanes and other organic polymers allow the suitable incorporation of guanidines. The heterogenization of guanidines on organic polymers and their use in the transesterification of vegetable oils were described in a patent[67].

The heterogenization of unsubstituted guanidines can be achieved by their reaction with microcrystalline cellulose activated by cyanuric chloride at the C-6 position (Scheme 11). After deprotonation of the guanidinium salt formed, the guanidine-containing cellulose shows a slightly reduced activity, compared to guanidine in homogeneous phase, giving a conversion of 30% after 1 h, when used at 5 mol%[68]. This guanidine-containing cellulose was used in a continuous reactor containing 100 g of the catalyst. An alcohol/oil mixture of 2:1 was pumped at 60 °C with a rate of 0.48 L/h. In the first hour the methyl esters were obtained with high yields and the phase separation was quick[69]. After this, however, the reaction was incomplete and the phase separation difficult. This could be due either to leaching of the catalyst or to its irreversible protonation. As no leaching tests were performed, no definite reason can be given at this point.

Table 3. Transesterification of rapeseed oil with methanol using the most active alkylguanidines as catalysts.

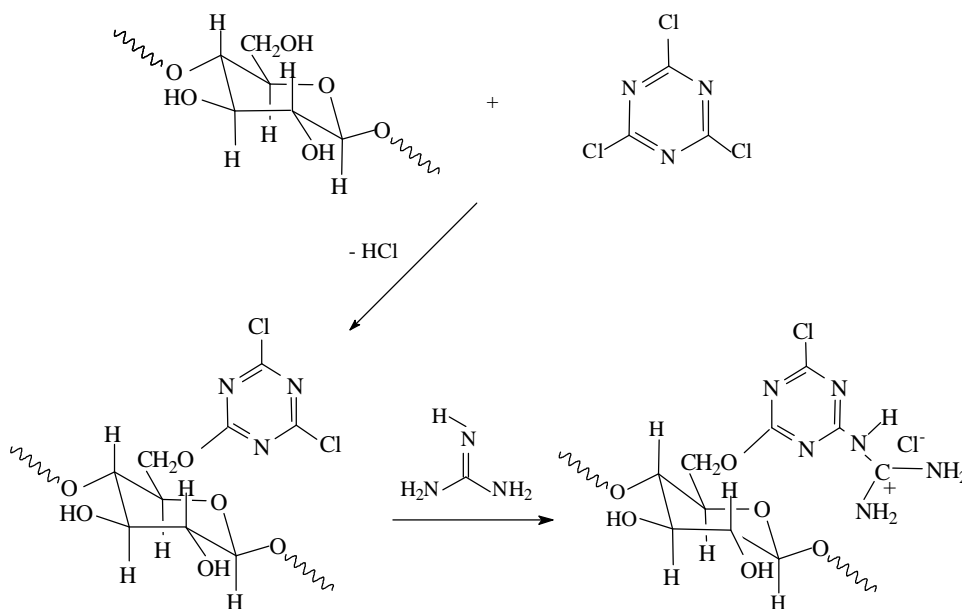| Catalyst	Yields (%) after 1 h[a]		
	1 mol%	2 mol%	3 mol%
TBD	90	91	93
DCOG	74	80	92
TCG	64	91	92
MTBD	47	74	-
PMG	49	67	90

a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.

Scheme 11. Heterogenization of guanidine on activated microcrystalline cellulose.

The catalytic performance of some alkylguanidines heterogenized on different substituted polystyrenes was investigated[70]. The guanidine-containing polymers (Scheme 12) were used in the transesterification of soybean oil with methanol in several consecutive catalytic cycles. The guanidines heterogenized on gel-type poly(styrene/divinylbenzene) with 1 meq Cl/g (polymers I and II) showed a slightly lower activity than their homogeneous analogues but allowed the same high conversions after prolonged reaction times. However, they slowly leached from the polymers, allowing only nine catalytic cycles. The guanidines heterogenized on linear polystyrene with the use of a 'spacer-arm' (polymers III, IV), were less active. Polymer V, which is symmetrically substituted showed an activity as high as polymer I. When another methyl group was introduced (polymer VI) its activity was slightly reduced. Furthermore, all polymers with a 'spacer-arm' suffered substitution reactions during the recycling experiments to form inactive hexasubstituted guanidinium compounds. A summary of the catalytic performance of these polymers is shown in Table 4.

The lower activity of the guanidine-containing polymers I and II, when compared to their homogeneous analogues, is probably due to the hydrophobicity of the polymer chain which reduces the concentration of the methanol at the active sites. However, at prolonged reaction times, the efficiency of the anchored catalysts is practically the same. The use of a 'spacer-arm' (polymers III-VI) was expected to improve the performance of the heterogenized catalyst. However, polymer IV showed the same activity as

polymer II and polymer III was even less active than polymer I[70].

Despite less active than their homogeneous analogues, all polymer-containing guanidines could be reused in several consecutive reaction cycles[70]. However, a loss of activity was observed, mainly due to leaching of the anchored base from the polymers, as mentioned above. Polymers I and II have the guanidine moiety bound to the benzylic CH_2 group of the polystyrene. After the protonation of the base, the electrophilic character of the methylene group is in-

Table 4. Total turnover numbers and turnover frequencies (after 1 h) observed with guanidine-containing polymers in the transesterification of soybean oil with methanol.

Catalyst	total turnover number[a,b] (number of cycles)	turnover frequency $(h^{-1})^c$
I	124 (9)	15
II	118 (9)	12
III	36 (5)	13
IV	30 (4)	12
V	84 (6)	15
VI	42 (7)	14

a: turnover number: mol of products/ mol of catalyst.
b: conditions: 1 eq. of soybean oil, 6.9 eq. of methanol, 5 mol% of base, 70 °C. c: turnover frequency: turnover number/ reaction time.

P = polymer chain
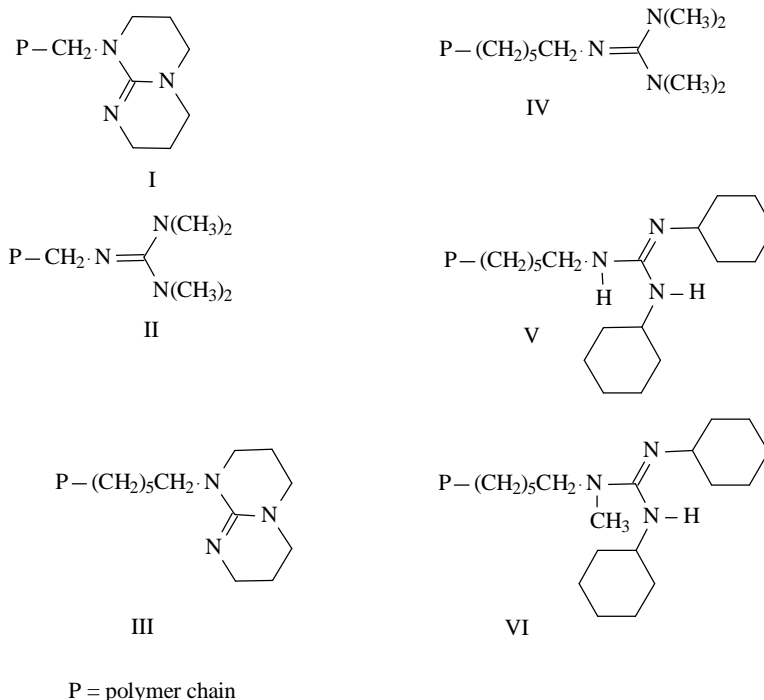
Scheme 12. Molecular structures of some guanidine-containing polystyrenes.

creased, thus becoming more susceptible to nucleophilic attack by methoxide ions present in the reaction medium. This attack results in the removal of the guanidine moiety from the polymer as shown in Scheme 13. The leaching of the guanidines from the other polymers follows a similar mechanism.

For the polymers containing a 'spacer-arm', there is an additional factor that accelerates the deactivation of the supported catalysts. The anchored bases can react with electrophilic functional groups which are further away on the polymer chain, producing inactive hexasubstituted guanidinium compounds[64], as shown in Scheme 14. However, it is possible to deprotonate these hexasubstituted guanidinium compounds, which should give doubly anchored active guanidines whose leaching is less probable.

In order to circumvent the leaching of the guanidines from the polymers, Schuchardt *et al.* encapsulate TCG by the reaction of dicyclohexylcarbodiimide and cyclohexylamine in the supercages of a hydrophobic Y zeolite. The encapsulated guanidine showed a good catalytic activity in the addition reaction of benzaldehyde to acetone[71]. However, its activity in the transesterification of vegetable oils is low (14% conversion after 5 h[72]), as the diffusion of the triglycerides through the channels of the Y zeolite is slow due to steric hindrance.

Fatty Acid Alkyl Esters as Feedstocks for Industry

Fatty acid methyl esters can be transformed into a lot of useful chemicals, and raw materials for further synthesis[73], as shown in Scheme 15. The alkanolamides, whose production consumes the major part of the methyl esters produced in the world, have a direct application as non-ionic surfactants, emulsifying, thickening and plastifying agents, etc[73]. The fatty alcohols are applied as pharmaceutical and cosmetics additives (C_{16}-C_{18})[73], as well as lubricants and plastifying agents (C_6-C_{12}), depending on the length of their carbon chain. The isopropyl esters are also applied as plastifying agents and emollients. However, they can not be produced in a convenient way by esterification of fatty acids, as an azeotrope formed by water and isopropanol avoids the recycling of the alcohol. The fatty acid methyl esters are further used in the manufacture of carbohydrate fatty acid esters (sucrose polyesters), which can be applied as non-ionic surfactants or edible non-calorific oils[74-77], and can be used as an alternative fuel substitute for diesel engines (biodiesel)[28-30, 78-80]. These two applications will be discussed separately.
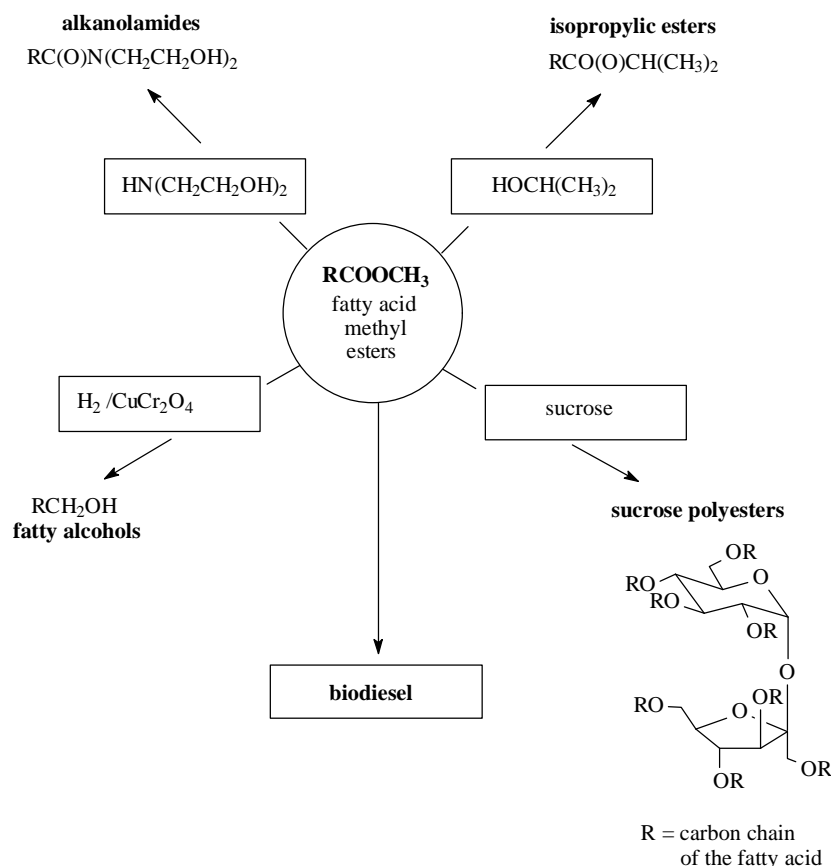
The glycerol also has important applications, in cosmetics, toothpastes, pharmaceuticals, food, lacquers, plastics,
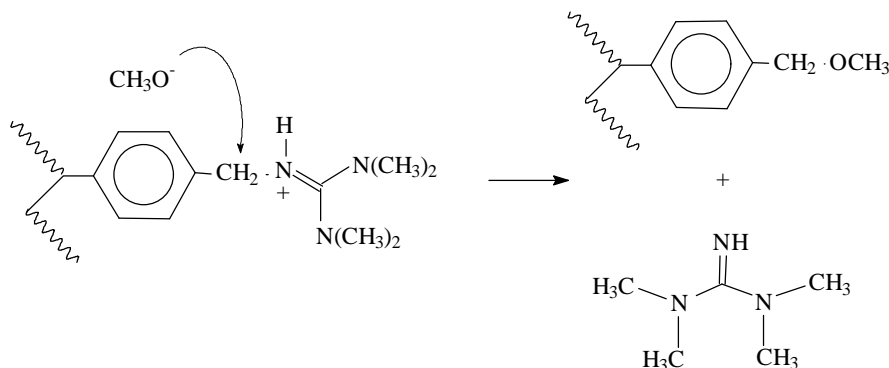
Scheme 13. Leaching of the guanidine moiety from the polymers.
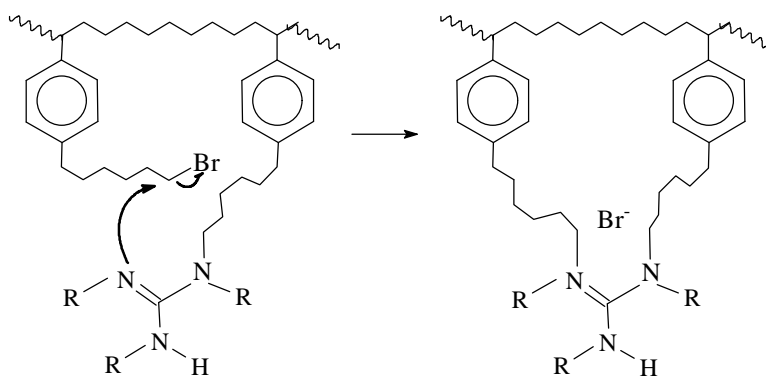
Scheme 14. Reaction of the heterogenized guanidines III-VI with unreacted 6-bromohexyl substituents.

alkanolamides
$RC(O)N(CH_2CH_2OH)_2$

isopropylic esters
$RCO(O)CH(CH_3)_2$

$HN(CH_2CH_2OH)_2$

$HOCH(CH_3)_2$

RCOOCH₃
fatty acid methyl esters

$H_2/CuCr_2O_4$

sucrose

RCH_2OH
fatty alcohols

sucrose polyesters

R = carbon chain of the fatty acid

biodiesel

Scheme 15. Some fatty acid methyl esters applications.

alkyl resins, tobacco, explosives, cellulose processing, etc[81].

Fatty Acid Alkyl Esters as Biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of the next century[33]. Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel[82]. Historically, it is believed that Rudolf Diesel himself[82] started research with respect to the use of vegetable oils as fuel for diesel engines. In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol[32, 83-87]. Different ways have been considered to reduce the high viscosity of vegetable oils:

- dilution of 25 parts of vegetable oil with 75 parts of diesel fuel[32];
- microemulsions with short chain alcohols (*e.g.* ethanol or methanol)[32];
- thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds[87];
- catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes[84], and
- transesterification with ethanol or methanol[88,89].

Among all these alternatives, the transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel[32] and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation[37,38,79,80,82].

Several types of vegetable oils, with a diversified composition in fatty acids, can be used for the preparation of biodiesel. Soybean[26,30,32,84], rapeseed[38,78,79], sunflower[28] and palm[29,37] oils are the most studied. However, there are no technical restrictions to the use of other types of vegetable oils. Considering the type of the alcohol, the use of methanol is advantageous as it allows the simultaneous separation of glycerol. The same reaction using ethanol is

more complicated as it requires a water-free alcohol, as well as an oil with a low water content, in order to obtain glycerol separation.

Normally, methanol is used as it is the cheapest alcohol in most countries. However, in Brazil it is advantageous to use anhydrous ethanol[90], which is already produced in large quantities to be mixed with gasoline. The guanidines described here have been shown to be efficient catalysts for the transesterification of vegetable oils with commercial anhydrous ethanol[69].

Fatty Acid Esters of Carbohydrates

The fatty acid esters of carbohydrates can be obtained by esterification of fatty acids, or by transesterification of their correspondent alkyl esters with carbohydrates (or other polyols) and constitute an important class of synthetic organic products. Their physico-chemical properties, which depend on the number and type of the esterified fatty acid, allow their application as non-ionic biodegradable surfactants[74], or as substitutes of vegetable oils for non-calorific diets[75-77]. The mixture of hexa-, hepta- and octaesters of sucrose, known as "olestra", has been studied for more than 20 years[75]. Their physical properties are very close to those of the triglycerides with similar esterified fatty acids, and the resistance to the pancreatic lipase (which avoids the absorption by the digestive tract) allows its application as non-calorific edible oil[75].

Typically, the sugar polyesters (SPE) are prepared through base-catalyzed transesterification of carbohydrates with fatty acid methyl esters, using sodium methoxide as catalyst[91-95]. However, some of these methods require very high temperatures (above 100 °C) and toxic low-volatile solvents (*e.g.* DMF and DMSO), compromising the final product for human consumption. Alternatively, Rizzi and Taylor[91], based on the studies of Feuge *et al.*[96], developed a two-stage solvent-free process, in which the SPE are synthesized by transesterification, using sodium hydride, Na-K alloy and soaps as catalyst. Despite the very good reaction yields (about 90%), this process still shows some inconveniences such as the need for high temperatures (150 °C), and the difficulty to purify the final product (the soaps are not easily eliminated).

Another solvent-free process was proposed by Akoh and Swanson[93], in which sorbitol and trealose octaoleate are produced in excellent yields (> 90%) through inter-esterification reactions of the correspondent acetates and methyl oleate, using Na as catalyst. The temperature (110 °C) and reaction time (2.5 h) are lower when compared to the previous work. However, the catalyst requires a water-free system in order to avoid its deactivation.

New milder solvent-free catalytic systems are being developed, and consist in the use of guanidine as catalyst, which furnished good preliminary results[97].

Conclusions and Perspectives

The industrial homogeneous catalysts will have to be substituted in the near future by heterogeneous catalysts due to environmental reasons. Good strong-base heterogeneous catalysts are still in development. One possibility would be the use of zeolites with strong basic sites[98]. Here the use of guanidines anchored on organic polymers was emphasized. To avoid leaching of the guanidine, however, it should be doubly anchored to the polymers. Another possibility would be the encapsulation of guanidines in an appropriate inorganic matrix. The Y zeolite is not appropriate for this purpose as the rather small diameter of its pore system slows down the diffusion of the fatty acid triglycerides.

Acknowledgments

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