Catalytic Processes in Biorefinery

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Abstract

The biorefinery is a system that uses as feedstocks biomasses and recover from these energy, fuel and chemicals. There are many processes considered in the biorefinery system, but in this thesis the biorefinery that uses as feedstock oil, in particular dedicated crops and waste vegetable oils were considered.

In the first part of this thesis the biodiesel production process was studied.

One possible route to produce biodiesel from waste oils (characterized by high concentrations of Free Fatty Acids, FFAs), is the use of a two steps process: an esterification reaction of FFAs with glycerol and a successive transesterification reaction with methanol of the whole mixture using a basic catalyst.

In this thesis the esterification step of FFAs with glycerol, in presence of a new acid heterogeneous catalyst based on sulfonated polymers with enhanced temperature resistance, was studied. The use of this type of catalyst has the advantage of using a relatively high temperature favouring the reaction by stripping of water formed during the esterification.

The use of an acid catalyst that is able to transesterify the glycerides and to esterify the FFAs is another way to obtained biodiesel from waste or non edible oils.

In this thesis the reactions of contemporany esterification of FFAs and tranesterification of glycerides were studied using new homogeneous or supported homogneous Zn(II) catalysts and a NbO$_2$/SiO$_2$ heterogeneous catalyst. The second part of this thesis was devoted to study of new catalysts for chlorination reaction of glycerol recovered from biodiesel production process. The behavior of three series of homologous catalysts, chloroacetic acid series (acetic acid, monochloroacetic, dichloroacetic and trichloroacetic acid), glycolic acid series (glycolic acid, di-glycolic acid and thio-glycolic acid) and amminoacid series (glutamic acid, aspartic acid and cysteine), were investigated for their activity and selectivity to produce dichlorohydrins, important intermediates for epichlorohydrin production. In the present study we explored also a completely new class of catalysts for glycerol chlorination, represented by acyl chlorides, never reported in the literature. The catalysts studied are acetyl chloride, propanoyl chloride, adypoyl chloride, butandioil di-chloride, propandioil di-chloride and phenylacetyl chloride and more precisely it is reported a comparison between the acyl chlorides respect to
corresponding carboxylic acid. The influence of some reaction parameters are studied as for example the effects of the pressure on activity and selectivity. Finally I use acyl chloride in stoichiometric amount in order to open new opportunities for chlorination process of glycerol with hydrochloric acid performed in situ.
List of Publications


List of other Publications


List of Patents


Conference contributions


x. R. Vitiello; A. Buonerba; R. Tesser; M. Di Serio; A. Grassi; E. Santacesaria. Use of Waste Materials for Biodiesel Production. DGMK Congress, October 8-10, 2012, Berlin, Germany.


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Chapter 1 – The biorefinery
1. Biorefinery

With the term “Biorefinery” we considered all the process that use bio-based feedstock to create biofuel (e.g. biodiesel and bioethanol), bio-energy (heat and power) and bio-based chemicals and materials (e.g. succinic acid and polylactic acid). The objective of a biorefinery is to optimize the use of resources and minimize wastes, together maximizing benefits and profitability. The processes that are included in the term biorefinery are many and include biological, chemical and thermal.

To produce bio-based products can be used various feedstock. However, at present there is no feedstock or process that would make these a clear alternative to fossil-based products. There are many options available, each with advantages and disadvantages. Two categories of feedstock dominate research: first and second generation. First-generation products are product from edible biomass such as starch-rich or oily plants. Second-generation products use biomass consisting of the residual non-food parts of current crops or other non-food sources, such as perennial grasses or algae. These are widely seen as possessing a significantly higher potential to replace fossil-based products.

The most common biomass feedstock are provided from different sectors as for example agriculture (dedicate crops and residues), industries (process residues and leftovers), households (municipal solid waste and wastewater), aquaculture (algae) and forestry. However the most common biomasses are the following:

- **Vegetable Oils**: this raw materials is mainly used for biodiesel production by transesterification. There are two categories of vegetable oils, namely, oils from dedicated crops and waste vegetable oils. For the first category the examples of dedicated crops are the palm, soybean, rapeseed and sunflowers seeds crops. The use of waste vegetable oils, as for example cooking oil or animal fat, is an effective method of recycling wastes.

- **Micro-algae**: this raw materials are a large and diverse group of unicellular photo- and hetero-trophic organisms. These organisms have attracted much attention in recent years due to their potential value as a renewable energy source. Focus has been on storage lipids in the form of triacylglycerols, which
can be used to synthesize biodiesel via transesterification. The remaining carbohydrate content can also be converted to bioethanol via fermentation. They are safe, biodegradable and need not compete with arable land.

- **Sugar**: for this feedstock the most common crops are sugar cane or sugar beet that have high amount of saccharose. This component can be easily extracted from raw materials and after this process it can be transformed in ethanol or bio-based chemicals. From those feedstock the sugar cane is the preferred both the economical point of view and both the environmental point of view.

- **Lignocellulosic Biomass**: this raw material comprising all the plant material composed of cellulose, hemicellulose and lignin. This type of raw material is difficult to convert into usable output because the protective shield of hemicelluloses and lignin that surrounds cellulose has to be broken down, which is a highly energy intensive process.

In the following figure is reported an outline of the changes that lead to the formation of bioproducts from biomass.

![Biomass flowchart](image.png)

**Figure 1.** Processes in biorefinery.
Biorefineries of the future will incorporate the production of fuels, energy and value-added chemicals, via the processing of biomass, into a single site.

In Figure 2 was reported the worldwide distribution of the biorefinery.

![Figure 2. Biorefinery distribution in the world [1].](image)

This figure includes first-generation and second-generation biorefineries and the percentage represents the amount of biorefineries in the world.

### 2. Biodiesel biorefinery

The energy demand and the biodiesel production increased in the past years and so did the amount of residues generated during its production [2]. Europe is still the biggest biodiesel producer, whereas Brazil had the highest increase in production rate in the last years when compared with United States and Europe, i.e. from 736 in 2005 to 2,400,000 m³ in 2010 [3].
Usually the feedstocks used for biodiesel production include agricultural crops and other plant material (as soybean oil, rapeseed/canola oil), recycled waste (used cooking oil) and animal by products (tallow).

As reported in the figure 4 biodiesel is produced from wide array of biomass resources, led by soybean oil, which accounted for more than 50% in 2013. Recycled waste, such as waste cooking oil, accounted for about 10% in 2013. Some of the most
environmentally friendly biodiesel feedstocks are used cooking oil and waste grease. According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, released in February 2010, biodiesel produced from waste grease results in an 86% reduction in greenhouse gases, compared to petro-diesel [5,6]. The biodiesel from refined vegetable oils is obtained by transesterification of triglycerides with a primary alcohol (usually methanol) catalyzed by basic homogeneous catalysts (KOH, NaOH, CH3OH), but these catalysts cannot be used with the waste or non refined oils that are characterized by a high concentration of Free Fatty Acids (FFA). In general the classical process can be performed at high yield with a raw material with less than 1% of FFA [7].

The problem could be solved using homogenous bronsted acid catalyst which can catalyze both esterification of FFA and transesterification of triglycerides [8], however the reaction rate of transesterification is low and great amount of spent catalyst have to be recovered and treated [9]. The reaction of biodiesel production is shown in the following figure (Fig. 5) where we can see that by transesterification reaction of fat or vegetable oils we obtain a fatty acid methyl ester (FAME), which is biodiesel and glycerol (10 wt %).

![Figure 5. Biodiesel production reaction.](image)

A more useful approach is the use of an heterogeneous acid catalyst however in general in this case high reaction temperatures are necessary and consequently also high pressures [10-13]. Solid materials capable of simultaneous FFA esterification and triglycerides transesterification under mild conditions still present a major challenge for catalytic scientists [13].

The problem of high FFA concentration can be resolved by refining the raw material.
FFA can be removed by caustic treatment or by distillation form the raw material, however for FFA concentration higher than 5% the loss in the final product and the cost of operation is too high [14, 15].

A very often used solution is to reduce FFA contained in the oil firstly by esterification with methanol to FAME by using an acid catalyst and then the transesterification of residual glycerides is performed, as usual, by using an alkaline catalyst [10,16].

\[
\text{CH}_3\text{OH} + \text{RCOOH} \rightleftharpoons \text{RCOOCH}_3 + \text{H}_2\text{O}
\]

**Figure 6.** Esterification reaction with methanol.

However this solution cannot be used for very high concentration of FFA (> 20%), as a matter of fact in this case the presence of chemical equilibrium gives high problem to achieve a FFA concentration less than 1 % [14].

In case of very high FFA concentration, it is possible use the glycerolysis. FFAs contained in the oil are firstly esterified with glycerol to glycerides at high temperature under vacuum: and then the transesterification of glycerides is performed, as usual, by using an alkaline catalyst [14, 16].

\[
\text{RCOOH} + \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \rightleftharpoons \text{RCOO} \begin{array}{c} \text{OH} \\ \text{OH} \end{array} + \text{H}_2\text{O}
\]

**Figure 7.** Esterification reaction with glycerol.

In general a modern biodiesel factory should have the possibility to treat any type of raw material and the integration of the previously described processes can give this result. A possible scheme of integration is reported in Fig. 1.
In this type of integrated biodiesel plant it is possible to treat all types of feedstock for biodiesel production without pretreatment.

The co-product formed by transesterification reaction is crude glycerol that is increasing concurrently with the biodiesel industry. For this reason the following paragraph is dedicated to glycerol that is contemporary the co-product of biodiesel production process and an important feedstock for biorefinery.

3. An important biorefinery feedstock from biodiesel production: the glycerol

The glycerol is an important feedstock for biorefineries, it is coproduced by transesterification reaction of triglycerides to produce biodiesel, in fact, for 10 Kg of biodiesel it is produced 1 Kg of glycerol. For this reason there is a great availability of
this product and the aim of most researchers is to find a new use of glycerol to produce chemicals with high value. The glycerol derived from biodiesel production could represent high purity glycerol and it is a very important industrial feedstock. Its applications are found in food, cosmetic, pharmaceutical and tobacco industries. However, crude glycerol derived from biodiesel production possesses very low economic value because of the impurities. Further refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility. Larger scale biodiesel producers refine their crude glycerol and sell it to markets in other industries. It is generally treated and refined through filtration, chemicals additions, and fractional vacuum distillation to yield various commercial grades. If it is used in food and cosmetic application, further purifications are needed such as bleaching, deodorizing, and ion exchange to remove impurities in traces. Purifying it to that stage, however, is costly and generally out of the range of economic feasibility for the small to medium size plants. Glycerol is material of outstanding utility in many application areas. The key of glycerol’s technical versatility is a unique combination of physical and chemical properties, compatibility with many other substances and easy handling. Glycerol is also virtually nontoxic to human health and to the environment. Physically, glycerol is a water-soluble, clear, almost colorless, odorless, viscous, hygroscopic liquid with a high boiling point. Chemically, glycerol is a trihydric alcohol, capable of being reacted as an alcohol yet stable under most conditions. With such an uncommon blend of properties, glycerol finds application among a broad variety of end uses. In some of these, glycerol is the material of choice because of its physical characteristics, while other uses rely on glycerol chemical properties.

Glycerol, when used in combination with other compounds yields other useful products [17-19]. The glycerol produced from biodiesel processes is important feedstock for biorefineries because it isn’t pure glycerol and the economic cost to purify it for pharmaceutical or cosmetic is high. Usually glycerol is used in many sectors. The following figure (Fig. 9) shows a summary of the possible uses of glycerol.
The opportunities for glycerol consumption are many, and following briefly describes the main reactions that use glycerol to produce chemicals:

- **Oxidation**: the glycerol can be oxidized within expensive oxidizing agents such as air, oxygen, hydrogen peroxide, or bleach. The reaction, in presence of heterogeneous or homogeneous catalysts, between inexpensive oxidizing agents and an inexpensive source of glycerol will allow the production of a number of new derivatives. A range of possible products can be formed by oxidizing glycerol, such as dihydroxyacetone, glyceraldehyde, glyceralic acid, glycolic acid, hydroxypruvic acid, mesoxalic acid, oxalic acid, and tartronic acid [18].

- **Reduction**: glycerol can be transformed, by reduction reactions, in two important chemicals intermediates, thus, 1,3-propanediol and 1,2- propanediol [18]. This reaction usually is catalyzed [18], but the type of catalysis can be different. The glycerol reduction can be catalyzed, for example, by chemical catalysts as Pt/WO$_3$/ZrO$_2$ [20], by a large number of microorganisms (Klebsiella pneumonia [*], Lactobacillus diolivorans[21], Clostridia and Enterobacteriaceae [22].
- **Dehydration**: this process transforms glycerol in acrolein, an important chemical intermediate for many synthesis as for example and it is possible to obtain this conversion in presence of many catalysts [23]. Some authors reported the acrolein synthesis in sub- and supercritical water condition, in this way they study the use of zinc sulfate as catalyst and they was investigate the influence of process parameters (temperature, pressure, residence time, zinc sulfate concentration). Another process that started from dehydration of glycerol is the production of the 3-hydroxypropionaldehyde that is synthetized by a one-step enzymatic catalysis that use usually the following genera of bacteria: Bacillus, Klebsiella (Aerobacter), Citrobacter, Enterobacter, Clostridium, and Lactobacillus .

- **Halogenation**: studies of glycerol halogenation have focused on production of $\alpha,\gamma$-DCH an intermediate in epichlorohydrin synthesis[24]. Epichlorohydrin is one among several new opportunities that have been recognized as a feasible use of large scale, low cost glycerol, and exemplifies a more general trend of an expanding use of natural polyols for the manufacture of commodity chemicals. Epichlorohydrin is an important raw material for the production of polymers such as epoxide resins, synthetic elastomers, and sizing agents for the papermaking industry.

- **Etherification**: the etherification reaction of glycerol is a important conversion to obtain a mixture of di- and tri-isobutyl ethers (GTBE) that is a good additive for diesel (both fossil and biodiesel) and also for gasoline as an octane booster. In diesel and biodiesel (7.5 wt %), it will lead to a reduction in the emissions of particulates, NOx, and unburned hydrocarbons. Moreover, blending diesel or biodiesel with GTBE also reduces the viscosity, cloud point, and pour point, but it reduces the calorific power somewhat [18].

- **Esterification**: another important use of glycerol is as feedstock for esterification reaction. From this process we can obtain monoglycerides, and polyglycerols which have numerous applications in foods, cosmetics and detergent industries. Glycerol monoesters (monoglycerides) can be obtained from glycerol esterification with fatty acids or from glycerol transesterification with fatty methyl esters in the presence of homogeneous catalysts. Such reactions give naturally a mixture of mono, di and triesters (40, 50,10%) and a
great amount of salts and by-products [25]. A molecular distillation as well as
various purification and decoloration steps are necessary to get high purity
products especially monoglycerides. From this reaction we can also obtain
diglycerides and triglycerides, important compounds due to their versatile
applications as biofuel additives. Those compounds are obtained in a selective
manner using heterogeneous catalysts [26].

- **Pyrolysis**: this process is conducted to produce value added products such as
hydrogen or syngas and medium heating value gas from waste glycerol using
pyrolysis and steam gasification processes. The thermal degradation of glycerol
can lead to a large number of substances, depending on the catalysts used for
the process. Some authors [27,28] tested the performance of bifunctional
catalysts MOₓ-Al₂O₃-PO₄ (containing different acid sites and different oxides of
transition metals (M)) in the degradation of glycerol. The higher the acidity, the
higher the selectivity for acrolein in the following order: W, Mo, Cu, V, Fe, Cr,
Ce. Moreover, catalysts containing Mn, Cr and Fe favor the formation of
oxidation products with breakage of the C-C bonds. The main reaction products
were acrolein and acetol (hydroxyacetone). In lower amounts were detected
acetaldehyde, propionaldehyde, allyl alcohol, acrylic acid, propionic acid,
acetone, carbon monoxide, carbon dioxide, phenol and other cyclic compounds
C6.
4. References

[26] Shanhui Zhu, Yulei Zhu, Xiaoqing Gao, Tao Mo, Yifeng Zhu, Yongwang Li; Production of bioadditives from glycerol esterification over zirconia supported heteropolyacids; Bioresource Technology 130 (2013) 45–51.
Part A – Biorefinery of oils
Chapter 2 - Biodiesel Production: General Aspects
1. Introduction

In this chapter the attention is focused on biodiesel (basically a mixture of fatty esters) as renewable fuel. Topics covered in this chapter are chemical composition and characteristics, properties and performance, complementary use as diesel fuel, main synthesis routes (e.g. transesterification and esterification), various catalysts used for manufacturing (e.g. homogeneous or solid acids) and industrial production processes. First of all the market potential for biodiesel is actually defined and limited by the market size of the petroleum diesel. In the last years, in Europe, the market of biodiesel is changed and in figure 1 is reported a distribution of this biofuel consumption in the Europe [1].

![Figure 1. European Biodiesel Consumption.](image)

This market is constantly changing, also if it is possible to note that in Italy there is more than 10% of European consumption. There are some differences in composition between petroleum diesel and biodiesel but the performances are similar and the most important are reported in the following table (Table 1) [1].

21
Table 1. Comparison between petroleum diesel and biodiesel [1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Petroleum Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Composition</td>
<td>C10-C21 (Hydrocarbons)</td>
<td>C12-C22 (Fatty acid methyl esters)</td>
</tr>
<tr>
<td>Kinetic Viscosity, mm2/s (at 40°C)</td>
<td>1.3-4.1</td>
<td>1.9-4.6</td>
</tr>
<tr>
<td>Specific gravity, Kg/L</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>188-343</td>
<td>182-338</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>60-80</td>
<td>100-170</td>
</tr>
<tr>
<td>Cloud point, °C</td>
<td>-15 to 5</td>
<td>-3 to 12</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>-35 to -15</td>
<td>-15 to 10</td>
</tr>
<tr>
<td>Cetane number (ignition quality)</td>
<td>40-55</td>
<td>48-65</td>
</tr>
</tbody>
</table>

From this comparison you can see that some characteristic properties are better in biodiesel than in petroleum diesel, for example the cetane number. Biodiesel not only has a higher cetane number than petroleum diesel, but also a higher flash point meaning better and safer performance [1].

2. Transesterification Reaction

The most common way to produce biodiesel is by transesterification of triglycerides of different types of oils (vegetable oils, animal fat or waste cooking-oils from the food industry) using alcohol, in presence of an acid or a basic catalyst. Vegetable oils are composed of triglycerides of fatty acids (a mixture of linear fatty acids, with an average
number of 18 carbon atoms, and containing in the chain mainly one, but also two or three or none double bonds). The alcohol used for transesterification reaction is usually methanol. The use of methanol is advantageous as it can quickly react with triglycerides (polar and shortest chain alcohol) and is a relatively inexpensive alcohol, while the same reaction using ethanol has as drawback that the produced ethyl esters are less stable and a carbon residue is observed after reaction. The general scheme of the transesterification reaction is reported in Figure 2, where R’, R’’ and R’’’ are various fatty acid chains.

![Figure 2. Transesterification reaction of oils.](image)

The trans-esterification reaction is actually more complex, proceeding with the formation of di-glycerides and mono-glycerides as intermediates [2] as reported in the following figure (figure 3).

- Triglycerides + CH₃OH  ⇌  Diglycerides + RCOOCH₃
- Diglycerides + CH₃OH  ⇌  Monoglycerides + RCOOCH₃
- Monoglycerides + CH₃OH  ⇌  Glycerol + RCOOCH₃

![Figure 3. Reaction Scheme of transesterification reaction.](image)
Glycerol is obtained as a by-product of the trans-esterification, typically about 10 %wt of the total amount of FAME. The reaction is catalyzed by basic or acid catalysts and the catalytic reaction can be in homogeneous or heterogeneous phase. The reaction time can be also reduced by increasing the liquid–liquid interfacial area by various process intensification techniques (e.g. static mixers, micro-channels reactors, microwaves assisted reactors, ultrasound assisted reactors, rotating/spinning tube reactors and centrifugal contactors). Finally, after the synthesis of fatty acid methyl esters they are necessary some other steps: the catalyst can be neutralized, the salts can be removed, the alcohol recovered and recycled, as well as glycerol and biodiesel can be purified [3].

3. Catalysts for biodiesel synthesis

3.1 Homogeneous catalysts

The traditional process is based on the use of a homogeneous basic catalyst, as for examples potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), and sodium ethoxide (NaOCH₂CH₃). The reaction temperature is very low, about 60 °C and the reaction is carried out at atmospheric pressure. The reaction can be promoted also by acid catalysts but with much lower activity. In basic catalyzed reaction a clear feedstock is required, in fact the free fatty acids concentration must be low. It should be under 0.5 wt %. If an oil is used that contains much free fatty acids such as oleic acid, saponification occurs.

The high activity of homogeneous basic catalyst is related to the much favorable reaction mechanism in which the carbonyl group of a triglyceride, diglyceride or monoglyceride is subjected to a nucleophilic attack from a catalytically active specie RO− [5]. CH₃O− is the catalytically active specie and after the attack to a carbonyl group a tetrahedral intermediate is formed that break down into a fatty ester molecule and a di, mono or glyceroxide anion [5]. At last, the proton transfer from CH₃OH to one of the glyceroxide anions restores the CH₃O− specie. In the literature are reported many papers on homogeneous catalysts alternative to the alkaline catalysts.
Also liquid amine-based catalysts were also studied for transesterification of oils [6]. Four what concerned the amines study are been considering the following compounds: diethylamine (DEA), dimethylethanol amine (DMAE), tetramethyldiaminoethane (TEMED), and tertramethylammonium hydroxide (TMAH) (as 25% in methanol). The highest conversion of 98% was achieved with TMAH as a catalyst at 65°C in 90 minutes. In these cases, a large amount (13%) of liquid amine catalysts is required for the transesterification.

The use of basic homogenous catalysts is limited from many disadvantages, the main is linked with the high sensitivity to FFAs and water. A solution could be the use of acid catalysts.

Metal complexes [6] of the type M(3-hydroxy-2-methyl-4-pyrone)2(H2O)2, where M = Sn, Zn, Pb, and Hg, have been used for soybean oil methanolysis under homogeneous conditions. Sn and Zn complexes showed great activities for this reaction, achieving yields of up to 90% and 40%, respectively, in 3 h, using a molar ratio of 400:100:1 (methanol: oil: catalyst), without emulsion formation.

Di Serio et al. have reported a work using acetates and stearates of Ca, Ba, Mg, Cd, Mn, Pb, Zn, Co and Ni as catalysts at 200 °C [7]. They observed that the activity of the different metals are related to the Lewis acid character of the metal and there is an optimal value of this acidity for promoting the transesterification reaction. The best catalyst was the stearates of Cd, Mn and Pb.

### 3.2 Heterogeneous catalysts

With the use of homogeneous catalysts we have a high reaction rate but this process has many disadvantages. The most important is that the product must be neutralized after the reaction, and from this process we have many salts.

For this reasons for what concerning the transesterification reaction there is a development of new heterogeneous catalysts, both of basic heterogeneous catalysts and acid heterogeneous catalysts.
In the literature have been reported different works and reviews about the heterogeneous basic catalysts. Some authors suggested a systematic approach for the classification of these [8-15]; this authors considered the following classification: single metal oxides, mixed metal oxides, zeolites, supported metal halides and hydrotalcites. For the single metal oxides, CaO [16-23] and MgO [10, 24–27] are the most used and many papers have been devoted to these catalysts. From the comparison of the different single oxides catalysts as: \( \text{La}_2\text{O}_3 \), MgO, ZnO and CeO$_2$, Bancquart et al. [24] concluded that the basic strength of the active sites on the surface are determinant in promoting the transesterification reaction, therefore, they observed that activities were in the order: \( \text{La}_2\text{O}_3 > \text{MgO} > \text{ZnO} \approx \text{CeO}_2 \). As a consequence, different attempts have been made to increase the surface basicity of the oxides by chemical treatment [22], or using mixed oxides and in some cases super basic solids have been obtained [25,28,29], characterized by high activity. The use of mixed oxides or supporting an oxide on another one has also the scope of preventing the leaching, thanks to the strong interaction between the two oxides, or to introduce a bi-functionality that increases the resistance to fatty acids and moisture [9,29]. The solubility of CaO in methanol, for example, has been evaluated by Granados et al. [18] corresponding to 0.035 wt%. Granados et al. have studied in detail the leaching aspects of CaO [30]. Albuquerque et al. [31] studied the behavior of CaO supported on, respectively, MCM-41 and SBA-15. CaO supported on SBA-15 has given good results for both activity and stability.

Other important class of catalysts reported in the literature are the mixed oxides. Good results have been reported good results with the use of \( \text{Al}_2\text{O}_3–\text{SnO}_2 \) [32], \( \text{Al}_2\text{O}_3–\text{ZnO} \) [32], MgO–\( \text{La}_2\text{O}_3 \) [33]. Other mixtures containing an alkaline earth oxide (mainly CaO) or rare earth metal (La) and a transition metal oxide (Ti, Mn, Fe, Zr, Ce) have been proposed [34]. In other cases CaO was simply supported on SiO$_2$, Al$_2$O$_3$, MgO or ZnO for increasing the mechanical strength of the catalyst and the resistance to leaching [35,37]. Some zeolites have been used as catalysts for biodiesel synthesis, despite the fact that triglycerides molecules cannot enter inside the zeolitic cavities. In particular zeolite X, ETS-10 have been tested after the exchange with K$^+$ and Cs$^+$ [38,39]. Other catalysts as: KF, KI, K$_2$CO$_3$ and KNO$_3$ on Al$_2$O$_3$ have shown good initial performances but are subjected more or less to deactivation and leaching [11,40–43]. A ferromagnetic catalyst KF/CaO–Fe$_3$O$_4$ has been tested by Hu et al. [44] showing
satisfactory activity and stability. Moreover, this catalyst can easily be recovered thanks to the magnetic properties. A high activity has been found for catalysts containing rare earth oxides and their mixtures, in particular La2O3 [45]. Many papers have been published on the use of Mg–Al hydrotalcites [10,46–53]. Hydrotalcites are very attractive catalysts, because, show high activities, are resistant to the presence of water and FFA [10,54] and give not place to leaching [10,50,54–56]. Recently, a commercial hydrotalcite has been used for a long time in a continuous reactor and has shown a slow deactivation due to fouling. This type of catalysts, therefore, is not suitable for unrefined oils and can advantageously substitutes the homogeneous alkaline catalysts KOH, NaOH and related alkoxides.

In conclusion often the results reported from different authors are different, especially for the reaction temperature that goes from 60 to 220 °C. This results suggest that heterogeneous basic catalysts are frequently subjected to leaching effect [14] and in many cases it is difficult to discriminate between the catalytic contribution of the homogeneous and heterogeneous reaction.

A list of basic heterogeneous catalysts, proposed in the literature, and reported in a review [4] is summarized in Table 2.

Other class of heterogeneous catalysts reported in the literature are the acid heterogeneous catalysts. The low activity of the acid catalysts with respect to the basic ones is due to the different reaction mechanism. In the case of the reaction promoted by basic catalysts, the first step of the mechanism is the nucleophilic attack of CH3O− on the carbonium atom of the carbonyl group [13], while, in the case of an acid catalyst, an electrophilic attack on the oxygen of the carbonyl is the first step followed by a second slower step of a nucleophilic attack of the alcohol on the carbon [13]. However, considering that Bronsted acid sites promote both esterification and transesterification many different heterogeneous acid catalysts have been studied in the literature.

Acid exchange resins cannot be used for promoting transesterification, because, are not stable at the required temperatures (about 200 °C). Therefore, many solid acid catalysts have been studied in the literature for promoting transesterification, in particular superacidic: tungstated and sulfated zirconia [57–63] have been tested.
Table 2. Basic heterogeneous catalysts reported in the literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (minutes)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/SBA-15</td>
<td>300</td>
<td>250</td>
<td>96</td>
<td>[64]</td>
</tr>
<tr>
<td>K$_2$CO$_3$/MgO</td>
<td>120</td>
<td>70</td>
<td>99</td>
<td>[65]</td>
</tr>
<tr>
<td>MgO–MgAl$_2$O$_4$</td>
<td>600</td>
<td>65</td>
<td>57</td>
<td>[66]</td>
</tr>
<tr>
<td>MgO–La$_2$O$_3$</td>
<td>140</td>
<td>25</td>
<td>100</td>
<td>[33]</td>
</tr>
<tr>
<td>MgO–ZrO$_2$</td>
<td>30</td>
<td>65</td>
<td>100</td>
<td>[67]</td>
</tr>
<tr>
<td>CaO</td>
<td>120</td>
<td>65</td>
<td>98</td>
<td>[17]</td>
</tr>
<tr>
<td>Ca(OCH$_3$)$_2$</td>
<td>180</td>
<td>65</td>
<td>98</td>
<td>[68]</td>
</tr>
<tr>
<td>CaO/SiO$_2$ (SBA-15)</td>
<td>300</td>
<td>60</td>
<td>95</td>
<td>[31]</td>
</tr>
<tr>
<td>Li/CaO</td>
<td>180</td>
<td>60</td>
<td>100</td>
<td>[21]</td>
</tr>
<tr>
<td>La$_2$O$_3$/CaO</td>
<td>60</td>
<td>60</td>
<td>94.3</td>
<td>[29]</td>
</tr>
<tr>
<td>CaO/ZnO</td>
<td>60</td>
<td>60</td>
<td>94.2</td>
<td>[69]</td>
</tr>
<tr>
<td>CaMg(CO$_3$)$_2$</td>
<td>180</td>
<td>60</td>
<td>99.9</td>
<td>[70]</td>
</tr>
<tr>
<td>MgO/CaO</td>
<td>-</td>
<td>60</td>
<td>92</td>
<td>[71]</td>
</tr>
<tr>
<td>CaZrO$_3$</td>
<td>360</td>
<td>60</td>
<td>88</td>
<td>[72]</td>
</tr>
<tr>
<td>CaO–CeO$_2$</td>
<td>120</td>
<td>85</td>
<td>97</td>
<td>[73]</td>
</tr>
<tr>
<td>SrO</td>
<td>30</td>
<td>65</td>
<td>95</td>
<td>[74]</td>
</tr>
<tr>
<td>Mg–Al HTA</td>
<td>240</td>
<td>65</td>
<td>90.5</td>
<td>[51, 64]</td>
</tr>
<tr>
<td>Li–Al HTA</td>
<td>60</td>
<td>65</td>
<td>83</td>
<td>[75]</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>-</td>
<td>200</td>
<td>97.5</td>
<td>[24]</td>
</tr>
<tr>
<td>Eu$_2$O$_3$/Al$_2$O$_3$</td>
<td>480</td>
<td>70</td>
<td>63.2</td>
<td>[28]</td>
</tr>
<tr>
<td>ETS-10 zeolite</td>
<td>1440</td>
<td>120</td>
<td>95</td>
<td>[38]</td>
</tr>
<tr>
<td>Anionic resins</td>
<td>60</td>
<td>50</td>
<td>80</td>
<td>[76]</td>
</tr>
<tr>
<td>KAISiO$_4$ doped with Li (2.3%)</td>
<td>2</td>
<td>120</td>
<td>100</td>
<td>[77]</td>
</tr>
</tbody>
</table>

Sulfated zirconia, for its strong Bronsted acidity resulted very active in promoting the esterification reaction and moderately active in promoting transesterification. Unfortunately, this catalyst gives place to a fast deactivation as a consequence of sulfur leaching. Tungstated zirconia is less active but more stable. Other catalysts reported in
the literature are: sulfated TiO$_2$ [78], sulfated SnO$_2$ [79,80], aluminum hydrogen sulfate [81]. Some of the mentioned catalyst are opportunely modified by adding other oxide like for example La$_2$O$_3$ or supporting them with the scope to increase activity and stability. Also different heteropoly acids (HPA) have been proposed as catalyst for both esterification and transesterification. At last, some Lewis acid catalysts in the form of metal oxides like Zr, Ti, Sn and Nb or mixtures have been proposed. In particular, TiO$_2$/SiO$_2$ obtained by grafting titanium alkoxide on the silica surface seems promising [82,83]. Using this catalyst, it has been shown that Lewis acid sites of medium strength are the main responsible of the transesterification activity [82,83]. However, Lewis acid catalysts seem more active than the Bronsted acid ones but are also more susceptible to poisoning for the presence of water and FFA. Many papers have recently been published describing the use of modified mesostructured supports as MCM-41 [84,86–89] and SBA-15 [85,90–93]. MCM-41 has been used for supporting both basic (CaO, K$_2$O) [87, 88] and acid catalysts as Nb$_2$O$_5$ [86], WO$_3$/ZrO$_2$ [84], sulfated zirconia [89]. SBA-15 has been employed for supporting: ZrO$_2$ [90], Al$_2$O$_3$ [91], heteropoly acids (HPA) [160], Ta$_2$O$_5$ [161], sulfonic acids [85]. Moreover, also acid catalysts are often subjected to leaching effect [14]. A list of acid heterogeneous catalysts, proposed in the literature, and reported in a review [4] is summarized in Table 3.
Table 3. Acid heterogeneous catalysts reported in the literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (minutes)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>60</td>
<td>200</td>
<td>64.5</td>
<td>[78]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/TiO$_2$</td>
<td>60</td>
<td>120</td>
<td>40</td>
<td>[80]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/SnO$_2$</td>
<td>180</td>
<td>180</td>
<td>65</td>
<td>[80]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/SnO$_2$ + Fe$_3$O$_4$</td>
<td>480</td>
<td>60</td>
<td>90</td>
<td>[94]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/SnO$_2$–SiO$_2$</td>
<td>180</td>
<td>180</td>
<td>80</td>
<td>[80]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/SnO$_2$–Al$_2$O$_3$</td>
<td>180</td>
<td>180</td>
<td>80</td>
<td>[80]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/ZrO$_2$–TiO$_2$/La$^{3+}$</td>
<td>300</td>
<td>60</td>
<td>95</td>
<td>[95]</td>
</tr>
<tr>
<td>ZrO$_2$/Al$_2$O$_3$</td>
<td>-</td>
<td>250</td>
<td>97</td>
<td>[96]</td>
</tr>
<tr>
<td>WO$_3$/ZrO$_2$</td>
<td>300</td>
<td>200</td>
<td>97</td>
<td>[97]</td>
</tr>
<tr>
<td>TiO$_2$/ZrO$_2$</td>
<td>-</td>
<td>250</td>
<td>95</td>
<td>[96]</td>
</tr>
<tr>
<td>ZnO/Al$_2$O$_3$</td>
<td>90</td>
<td>200</td>
<td>85</td>
<td>[98]</td>
</tr>
<tr>
<td>WO$_3$/ZrO$_2$/Al$_2$O$_3$</td>
<td>-</td>
<td>250</td>
<td>90</td>
<td>[96]</td>
</tr>
<tr>
<td>WO$_3$/ZrO$_2$/MCM-41</td>
<td>150</td>
<td>200</td>
<td>85</td>
<td>[81]</td>
</tr>
<tr>
<td>H$<em>3$PW$</em>{12}$O$_{40}$/ZrO$_2$</td>
<td>600</td>
<td>200</td>
<td>77</td>
<td>[99]</td>
</tr>
<tr>
<td>H$<em>3$PW$</em>{12}$O$_{40}$/Ta$_3$O$_5$</td>
<td>1440</td>
<td>65</td>
<td>60</td>
<td>[100]</td>
</tr>
<tr>
<td>Cs$<em>2$H$<em>8$PW$</em>{12}$O$</em>{40}$</td>
<td>60</td>
<td>65</td>
<td>96</td>
<td>[101]</td>
</tr>
<tr>
<td>MnO–TiO</td>
<td>20</td>
<td>260</td>
<td>87-92</td>
<td>[102]</td>
</tr>
<tr>
<td>VOPO$_4$</td>
<td>60</td>
<td>150</td>
<td>80</td>
<td>[103]</td>
</tr>
<tr>
<td>Sulfonic/SiO$_2$</td>
<td>300</td>
<td>150</td>
<td>60</td>
<td>[104]</td>
</tr>
<tr>
<td>Sulfonic acid/SBA-15</td>
<td>480</td>
<td>180</td>
<td>96</td>
<td>[85]</td>
</tr>
<tr>
<td>Fe–Zn double cyanide complexes</td>
<td>480</td>
<td>170</td>
<td>99</td>
<td>[105-107]</td>
</tr>
<tr>
<td>Nb$_2$O$_5$–MCM-41</td>
<td>240</td>
<td>200</td>
<td>95</td>
<td>[86]</td>
</tr>
</tbody>
</table>
4. **Esterification reaction**

Today the use of waste and non edible oils for biodiesel production is a reality. This raw materials have to be refined, the use of catalytic reactions is one of the preferred way to reduce the content of FFA. Two principal reactions can be used: the esterification with methanol or with glycerol.

In the following figure (Fig.4) were reported the free fatty acid composition of the common feedstocks for biodiesel production [108] that usually comprise five major fatty acid components: palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2) and linolenic (18:3).

![Free fatty acid composition](image)

**Figure 4.** Free fatty acid composition.

The esterification reaction can be catalyzed by both Bronsted and Lewis acids. Addition of a proton or a Lewis acid leads to a more reactive electrophilic group that favor the nucleophilic attack of the alcohol. The reaction is an equilibrium reaction and the presence of water reduces the yield of ester. The Bronsted acids are preferred in the esterification of FFA because they are more active and more resistant to water by deactivation [109].
4.1 Homogeneous Catalysis

The most used homogenous catalyst is the sulfuric acid (1-3% w/w) and the used temperature reaction condition are mild (40-95°C) [108]. This acid show high acid strength and can be found in high concentration without the addition of large amount of water because this acid it is used as concentrated acid. To favor the reaction an excesses of methanol is used. The molar ratio methanol/FFA is crucial for optimizing the ester yield [108]. For example, Chai et al showed that the optimal reaction conditions for a cooking oil containing 5% of FFA (methanol-to-FFA molar ratio of 40:1) are different from that for an acid oil containing 15-35% of FFA (methanol-to-FFA molar ratio of 20:1) [110]. This author showed that the optimal methanol-to-FFA molar ratio was 40:1.

To avoid the problem of water formation and of the necessity to use high methanol/FFA molar ratio Stacy et al. proposed the use of bubble column as reactor [111]. The reactor operate at 120°C and atmospheric pressure, in this situation methanol vaporizes and remove the formed water [112]. The proposed system have good performance also with pure FFA. For example, 95% of pure oleic acid is esterified in 60 minutes, using 0.1% w/w of sulfuric acid as catalyst and 4:1 methanol/FFA molar ratio [112].

However, the use of homogeneous acid catalyst involves many drawbacks: problem with plant corrosion, the necessity to neutralize the acid catalyst before the transesterification, increase the problem of product purification for reducing the traces of sulfur that can derive from the acid catalyst [113].

4.2 Heterogeneous Catalysis

The first heterogeneous process for FFA esterification with an heterogeneous catalyst was proposed by Jeromin et al. [114]. They proposed the use of solid ion (cation) exchange resins as catalyst. 94% of FFA of a not refined coconut oil (acid number 10%) was converted using Lewatit® SPC 118 BG ion exchange resin as catalyst in a packed bed reactor with a residence time of 1.2 h at 64°C and a volumetric ratio oil/methanol 5. From this starting point, mainly in last 10 year, the importance of pretreatment is increased together with the interest in the biodiesel production from waste and not
refined oil, a lot of different heterogeneous catalysts have been proposed in the literature [108,109,115,116].

We can recognize two class of catalyst: sulfonic acid-functionalized solids—both ion-exchange organic resins and inorganic supports—and inorganic metal-oxide based superacids [108,116]. However, until now only technologies based on the use of strong cation-exchange resin are commercialized [117, 118].

The reason for this situation is that the performances of strong cation-exchange resin are satisfactory for the industrial application (in terms of activity and stability) and their cost is much lower in respect to the other proposed catalyst.

Strong cation exchange resins are commonly obtained from styrene and various levels of the cross-linking agent divinyl benzene (DVB), which controls the porosity of the particles. They are supplied as beads that can have either a dense internal structure with no discrete pores (gel resins, also called microporous resins) or a porous, multichannelled structure (macroporous or macroreticular resins). After the polymerization the acid functionality are introduced by sulfonation [119].

The activity of the cation exchange resins depends on the sulfonation grade (H+ meq/g) but also from their structure. For this reason for example, different kinetic parameters in FFA esterification where determined for different resins that were characterized by similar acidity but different amount of DVB and consequently different chain cross-linking [120-123].

The gel (microporous) type resins have shown a greater activity than the macroporous ones [123].

Because their higher activity the gel type resins are the most used resins for FFA esterification in industrial plants [117,118].

This behaviour can be explained considering that the cation resin give place to a strong swelling in the presence of a polar solvent. The swelling phenomena increase the accessibility to acid sites inside the resin to the fatty acids, increasing in such way the conversion rate. In general the increase in DVB content in the resin reduces the swelling phenomena, reducing the accessibility of FFA to acid sites.

The activity depends strongly by the weight percent of used methanol [124]. For examples Jeřábek et al reported that in the case of microporous resin (DB20) the conversion increase with the concentration of methanol until the reaching of a plateau around 20% wt of methanol, while in the case of macroreticular resin the conversion
increase with the methanol concentration achieving a maximum around 10% of methanol [124].

In the case of gel resin the dry structure hasn’t pores and so it is inaccessible to reactants (for this reason at low methanol concentration we don’t observe conversion for methanol concentration below 5% wt, with the increase of the solvent concentration we have an increase of the swelling with a consequent increase in conversion rate, until a the achievement of an activity plateau for methanol concentration greater of 20% that is also the concentration at which the maximum of swelling is obtained.

The macro-reticular resins, on the contrary, have swelling-independent pores that are open also in the dry material. For this reason the activity of macro-reticular resins have activity also at low methanol concentration, however their activity is lower than that of gel type resin because not all mass of resin is swellable. In the case of macro-reticular resin for concentration of methanol higher than 10% a decrease in reaction rate is observed. This phenomena has been explained by Jefábek et al [124] considering that at low methanol concentration the concentration of sulfonic groups that don’t have reacted with methanol is lower than in the case of high methanol concentration.

The main poisons for the ion-exchange resin are the cations that can be dissolved in the waste oils [125, 126], even if the catalyst can be regenerated by treatment with mineral acid solutions. To solve this problem a pretreatment of raw material is necessary. The more diffuse solution in the industrial plants is the use of metals adsorption column before the esterification reactor [16].

### 4.3 Glycerolysis reaction

An alternative method, used to pre-treat the raw material with high FFA concentration, is to make the esterification with glycerol (glycerolysis or re-esterification reaction), at higher temperatures, continuously removing the produced water for shifting the equilibrium to the right [111,127,128]. In this way, higher conversions are obtained in a shorter time. In the second step, the neutral product can be submitted to transesterification, in the usual way, by using an alkaline catalyst.
4.3.1 Homogeneous catalysts

The reaction is carried out at high temperature (T>180°C) under vacuum of with stream of inert gas to remove the formed water. However the high temperature is necessary also to favor the mutual solubility of glycerol and FFA and increase the reaction rate.

In the case of not catalyzed reaction the reaction rate decrease strongly at low FFA concentration. This behavior is justified by the fact that the acid groups of FFA act as Bronsted catalyst in the reaction. To reduce the reaction time a catalyst can be used.

The use of sulfuric acid is avoid because it produces the formation of great amount of byproduct, also acrylalsdehyde derived by the dehydration of glycerol has been found in the distilled water [129]. More useful are the Lewis acids that, in this case, because the low content of water in the reaction environment (it is continually removed during the reaction) aren’t deactivated by water.

Starting from the pioneering work of Feuge et al [130] that studied the behavior of several salts and oxides that found that the best catalysts were ZnCl₂, SnCl₂ and SnCl₄, nowadays the most used catalysts resulted salts of Sn or Zn [131]. Also Titanium and Tin alkoxides have been proposed as catalyst for FFA glycerolysis reaction [130].

The effect of the catalyst is the strong reduction of reaction time even with low concentration, for example the acidity of an soap-stock containing 50% wt of FFA after 50 minutes of reaction at 220°C is reduced to 35 mg/KOH in absence of catalyst while in the same reaction arrive to 4.6 mg KOH/g by using 0.2% wt of Zn (zinc acetate) [132]. Also metal Zn can be used and its performances are similar to that of Zn salts [132].

These results can be explained considering that FFA can react with metallic Zn with the consequent formation of carboxylic Zn salts. So also in the case of metallic Zn we are using an homogenous catalysis.

4.3.2 Heterogeneous catalysts

On the contrary in the case of heterogeneous catalysts only Bronsted acid catalysts have been proposed [110-115]. It is clear that by using heterogeneous catalysts there is not the necessity to neutralize the catalyst between the first and second step and the catalyst can be reused without any problem and moreover it is easier to develop a continuous process.
At this purpose, the authors described the use of dodecamolybdophosphoric acid encaged in USY zeolite, as catalyst for the esterification of glycerol with acetic acid to obtain monoacetin, diacetin and triacetin. In the literature is reported the esterification of carboxylic acids with alcohols in a batch reactor using acid zeolites as catalyst. Bossaert et al. [111] and Diaz et al. [112] have studied the esterification reaction of glycerol with fatty acid using siliceous mesoporous materials (silica gel, MCM-41, HMS) functionalized with Bronsted propylsulfonic acid groups. Takagaki et al. [113] used carbon material prepared from D-glucose as a precursor of a solid acid catalyst. Sulfonation of incompletely carbonized D-glucose results in amorphous carbon consisting of small polycyclic aromatic carbon sheets with high density of SO$_3$H groups. The carbon material exhibits remarkable catalytic performance for the esterification of higher fatty acids. This can be attributed to high density of SO$_3$H groups with strong acidity in the material.
5. References


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Chapter 3 - Use of Waste Materials for Biodiesel Production
1. Introduction

The esterification reaction with methanol of oils or fats containing free fatty acids (FFA) can be performed for a direct biodiesel production. This is a pre-treatment step, requiring an acid catalyst, in the framework of a conventional transesterification process, this last promoted by an alkaline homogeneous catalyst (NaOH, KOH or related methoxides). The esterification of FFAs with methanol is currently carried out in the presence of strong Brønsted acid catalysts such as sulfuric acid or p-toluenesulfonic acid [1-4]. When the acid catalyst is homogeneous, before starting the second transesterification step we need to neutralize the acid catalyst.

Moreover, it is not easy to remove totally from the final product the sulphur derived from the used catalyst. Therefore, such homogeneous acids are not environmentally benign and their use is a costly operation. For this reason heterogeneous catalysts like sulfonic resin or acid oxides seem more attractive [5,6]. However, in order to have a satisfactory rate of reaction we need to adopt temperatures in the range 100-200°C but because the boiling point of methanol is 65°C the consequence is the necessity to operate at relatively high pressures [7]. Moreover, water formed during the reaction cannot be eliminated and the final conversion is limited because an unfavourable equilibrium is reached. An alternative method, suggested in recently published patents [8], is to make the esterification with glycerol, at higher temperatures, continuously removing the produced water for shifting the equilibrium to the right. In this way, higher conversions are obtained in a shorter time. In the second step, the neutral product can be submitted to transesterification, in the usual way, by using an alkaline catalyst. In the mentioned patents, some examples are reported in which only homogeneous catalysts are used. However, for the same esterification reaction, other authors reported the use of heterogeneous catalysts [9-15].

The carbon material exhibits remarkable catalytic performance for the esterification of higher fatty acids. This can be attributed to high density of SO$_3$H groups with strong acidity in the material. Wang et al [14] described the esterification of free fatty acids (FFAs) of waste cooking oil (WCO) with crude glycerol in the presence of the solid superacid SO$_4^{2-}$/ZrO$_2$–Al$_2$O$_3$. This reaction lowers the acidity of WCO before biodiesel production. Waldinger et al [15] reported the use of Lipases, that display high
regioselectivities and broad substrate tolerance, as catalysts for the efficient esterification of glycerol under the conditions of irreversible acyl transfer. A variety of unsaturated fatty acids, such as oleic, linoleic, erucic, ricinoleic, hydroxystearic and coriolic acid, were used for this purpose.

In this thesis, we have studied the performances of some different heterogeneous catalysts in promoting the esterification of oleic acid with glycerol. In particular, we have tested the behaviour of respectively: Amberlyst-15, Nafion, and new type of temperature resistant acid resins (200-220°). The temperature resistant acid resins are Sulfonated Multiblock Copolymers Syndiotactic Polystyrene-co-1,4-cis-Polybutadiene.

These acid resins have shown very interesting performances in the described reaction, in comparison with both the other heterogeneous catalysts and sulphuric acid. Moreover, they can be used at temperatures much higher than the conventional commercially available sulphonic resins. This has a beneficial effect on the reaction rate and on the possibility of shifting the equilibrium by continuously removing produced water from the reaction environment. Therefore, we have further deepened the behaviour of these thermal resistant resins also considering the reusability of the catalyst.

2. Experimental Section

Two heterogeneous commercially available catalysts (Amberlist-15 and Nafion R50 (Aldrich)) and two non-commercial catalysts (Sulfonated Multiblock Copolymers Syndiotactic Polystyrene-co-1,4-cis-Polybutadiene (sPSB-SA)) have been studied. sPSB-SA1 catalyst is a not reticulated co-polymer, while sPSB-SA2 is the same polymer reticulated.

2.1 General procedure and Materials.

The manipulation of air and moisture sensitive compounds was performed under nitrogen atmosphere using standard Schlenk techniques and a MBraun glovebox. Toluene (Carlo Erba, 99.5%) was used as received or dried over calcium chloride, refluxed over sodium for 48 h and distilled under nitrogen atmosphere before use in moisture and oxygen sensitive reactions. Multiblock copolymers syndiotactic polystyrene-co-1,4-cis-polybutadiene (sPSB) were synthesized according to literature
procedure [16]. Thiolacetic acid (TAA; 96%, Sigma-Aldrich), benzophenone (BZP; ≥99%, Sigma-Aldrich), formic acid (98%, Carlo Erba), hydrogen peroxide (35 wt% in water, Carlo Erba), potassium bromide (Sigma-Aldrich), dimethylsulfoxide-d6 (DMSO-d6; Euriso-top), and 1,1,2,2-tetrachloethane-d2 (TCDE; Euriso-top) were used as received.

2.2 Measurements and Characterizations.

NMR spectra were recorded on AVANCE Bruker spectrometers: the chemical shifts are referred to TMS, as external reference, using the residual protio signal of the deuterated solvents. Elemental analysis was carried out on a CHNS Thermo Scientific Flash EA 1112 equipped with a thermal conductivity detector. FTIR spectra were recorded on a Bruker Vertex 70 spectrometer equipped with deuterated triglycine sulfate detector and a Ge/KBr beam splitter. The FTIR spectra were performed in solution or on film by casting. DSC analysis was carried out on a TA Instrument DSC 2920 calorimeter (heating rate = 10 °C/min) and the thermogravimetric FTIR analysis (TGA–IR) on a Netzsch TG 209 F1 (heating rate = 10 °C/min) coupled to a Bruker Vertex 70 FTIR spectrometer by means of a PTFE transfer line and a FTIR gas cell thermostated at 200°C. The acquisition run consists of 30 scans in 28 s, with a resolution of 2 cm⁻¹ and a delay of 2 seconds between the runs. Wide angle powder x-ray diffraction (WAXD) spectra were obtained, in reflection, with an automatic Bruker D8 powder diffractometer using the nickel-filtered Cu Kα radiation. The polymer samples were irradiated at 365 nm and power of 100 W in a Ultraviolet incubator Bio-Link BLX (Vilber Lourmat).

2.3 Protocol for sulfonation of sPSB copolymers.

1.20 g (0.47g, 8.65·10⁻³ mol) of a multiblock copolymer sPSB₅₅ (55 mol% of butadiene), were treated with 200 mL of toluene (6.0 g of sPSB/L of Toluene) in a two-neck 500mL round bottom flask under vigorous stirring at room temperature for 72 hours. The resulting slurry was then heated at 80 °C for 1 hour where a polymer gel was formed. The flask was allowed to cool at 50 °C, and benzophenone (0.013g, 7.21·10⁻⁵ mol; molₜ / molₜ = 1:120) and thiolacetic acid (0.70mL, 8.65·10⁻³ mol; molₜ / molₜ = 1:1) were added in the order. The flask was irradiated at 365 nm and power of 100 W in an
UV incubator for 4h. The reaction was monitored by coagulation of 5 mL of the polymer slurry in a plenty of methanol. The polymer was recovered by filtration, dried in vacuum and analyzed by $^1$H-NMR to check the degree of functionalization. Formic acid (8.2mL; 0.216 mol; mol$_B$/mol$_{\text{HCOOH}}$ = 1:25) was added to the polymer slurry resulting from the thioacetylation step at 70 °C. Hydrogen peroxide (3.75 mL, 4.33·10$^{-2}$ mol; 35 wt% in water; mol$_B$/mol$_{\text{H}_2\text{O}_2}$ = 1:5) was slowly added to the polymer solution in 1 h. The flask was then allowed to cool at room temperature and 300 mL of acetonitrile were added followed by solvent distillation by a rotary evaporator at 35 °C, avoiding the complete drying of the polymer. Additional 200mL of acetonitrile were added and the solvent was distilled off until the formation of a reddish-brown polymer gel. Further addition of a plenty of acetonitrile affords the precipitation of the polymer permitting an easily recovery by filtration. The recovered polymer was placed on a PTFE sheet and dried in vacuum at room temperature for 48 hours. The almost complete drying was accomplished by heating the polymer on a hot plate in air at 120°C of 3h. Reticulated sPSB-SA were obtained reducing the thioacetylation degree by lowering the molar ratio thiolacetic acid/alkene to 0.95, in order to preserve alkene units in polymer backbone, that were directly crosslinked in the second reaction step.

The main characteristics of all the tested resins catalysts are reported in Tab. 1.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Acidity (eq/g)</th>
<th>Max Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberslyst 15</td>
<td>4.5</td>
<td>120</td>
</tr>
<tr>
<td>Nafion R50</td>
<td>0.8</td>
<td>190</td>
</tr>
<tr>
<td>sPSB-SA1</td>
<td>5.4</td>
<td>200</td>
</tr>
<tr>
<td>sPSB-SA2</td>
<td>4.3</td>
<td>200</td>
</tr>
</tbody>
</table>

Tab. 1. Properties of used resins
2.4 Catalytic Tests

Some experiments were carried out without catalyst to evaluate the contribution of the un-catalyzed reaction. Moreover, also experiments using sulphuric acid as catalyst were performed in order to compare the activity of the heterogeneous catalysts with the one of a conventional homogeneous esterification catalyst.

The reagents used for catalytic tests were glycerol (Fluka, 99%) and oleic acid (Aldrich, 90%). The esterification experiments were carried out using a glass reactor with a volume of 150 mL equipped with a magnetically driven stirrer heated in an oil bath under atmospheric pressure. A nitrogen steady flow was passed over the reaction mixture through one flask opening for stripping the water formed during the esterification. Removed water was collected in a graduated glass vessel, and the volume of water collected along the time was used to monitor the esterification progress. The reaction temperature was controlled by using a thermometer immersed in the reactant mixture. The system was initially charged with the desired amount of oleic acid or of a mixture of neutral oil and oleic acid and heated until a pre-fixed temperature, then, glycerol and catalyst were added. This time instant corresponds to the initial time of the reaction. The reaction was conducted for times between 3 and 24 hours. The reaction temperature range explored was 120°C-180°C. During each run, small samples of liquid phase were withdrawn; in this way, the evolution with time of the mixture acidity was monitored for different reaction times. A molar ratio oleic acid/glycerol of 1.3/1 mols/mols was used and the amount of loaded catalyst was between 0.25 and 1 wt%.

The withdrawn samples of the reaction mixture were analyzed by a standard acid–base titration procedure for the evaluation of the free residual acidity [ASTM D4662-98 standard]. The final compositions of the obtained products were determined by gas-chromatographic analysis [UNI 10946:2001].

3. Results and discussion

The sPSB copolymers are stereo and regio regular polymers with a multiblock microstructure, where segments of syndiotactic polystyrene (sPS) are alternating to segments of prevalently 1,4-cis-polybutadiene (molar ratio 1,4-cis-PB/1,2-PB ≈ 0.85). sPSB with a styrene molar fraction greater than about 0.4 are semi-crystalline and the
segments of sPS (Tg = 105°C, Tm = 250°C) provide to the copolymer high thermal, mechanical and chemical resistance. The sPSB copolymers present the same complex crystalline morphologies of the sPS homopolymer, for which were described 5 crystalline forms, two of which (δ and ε) are nanoporous and highly permeable to low molecular weight molecules[17]. Moreover these copolymers present a phase separated morphologies were domains of the two kinds of polymers are mutually segregated, whose dimensions are depending on the composition[16]. These properties suggested that sPSB copolymers could be good candidate as substrate for the synthesis of sulfonated polymers by selective functionalization of the butadiene segments, preserving the properties of the syndiotactic polystyrene. Actually a multiblock sulfonated copolymer comprising hydrophobic (semi-crystalline and permeable) and hydrophilic segments could show interesting properties in chemical and morphological terms, with possible applications as surfactant, in membrane science and catalysis.

The process for the sulfonation of the sPSB copolymers comprises two steps depicted in Figure 1.

---

Figure 1. Synthetic strategy for sulfonation of sPSB copolymers.
In the first reaction the butadiene units were saturated by radical addition of thiolacetic acid, promoted by benzophenone and UV irradiation. In the same reactor, the thioacetyl groups were consecutively oxidized by in situ generated peracid by addition of formic acid and hydrogen peroxide. Formally, the overall process consists of an addition of an hydrogen atom and a sulfonic acid group to the alkene functionality of the butadiene units, leaving unaffected the styrene units.

The characterization of the sPSB-SA copolymers was accomplished by nuclear magnetic spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and wide angle x-ray diffraction (WAXD). In the 1H NMR spectrum (Figure 2a) of a sPSB–SA copolymer (44 mol% sulfonic acid functionalized) the signals of the methine and the methylene bearing the sulfonic acid moiety, respectively generated by the sulfonation of the 1,4 and of the 1,2 butadiene units, were found respectively at 2.38 and 2.62 ppm, in agreement with literature reported value for alkyl-sulfonated polymers[18]. The FTIR analysis also confirmed the polymer functionalization, revealing the typical vibrations of the sulfonic acid groups (Figure 2b)[19]. In spite of the low styrene content of this copolymer, it was found in the δ-toluene clatrate crystalline form of the sPS [17] (see WAXD pattern in Figure 2c), confirming that the developed process preserves the sPS crystallinity.

The scanning calorimetry (DSC) and thermogravimetric analysis coupled with infrared spectroscopy (TGA-IR) (Figure 3). This trio of techniques reveals that the sPSB–SA shows a bimodal thermal desulfonation, likely due to the double nature of the sulfonic acid group (Figure 3b). The first desulfonation peak at 176°C was attributed to the decomposition of the primary sulfonic acid group located onto the 1,2 vinyl unit, whereas the main peak at 235°C was ascribed to the desulfonation of the predominant sulfonated 1,4 butadiene units.
Figure 2. Characterization of sPSB–SA (entry 1, Table 1): a) 1H NMR spectrum (TCDE/DMSO, v/v = 3:1); b) FTIR spectrum; c) WAXD pattern.
Figure 3. Thermal behaviour of sPSB–SA (entry 1, Table 1): a) DSC (black curve) and TGA (red dashed curve) traces; b) SO$_2$ gas evolution profile during thermal decomposition, detected by TGA-IR analysis.

The results of a first set of experimental runs carried out at 120°C (which is maximum possible operative temperature for Amberlyst-15) are reported in Fig. 4. Only the sulphuric acid and the sPSB-SA1 resin showed quite the same high conversion (>90%) at 120°C, the other tested catalysts giving the same FFA conversion of the blank run.

The low activity of Nafion R50 could be justified with the low content of acid group, while the strong difference in the activity between sPSB-SA1 and Amberlyst 15, being the acidity of the resins quite similar, point out that also strong difference in resin microstructure should be present. This aspect will be the object of a future paper. Moreover, the specific activity of the sPSB-SA resins (referred to the acid equivalent) is higher than that of sulphuric acid: the conversions of FFA obtained at 120°C after 3 h, using the same equivalent of acid groups (1.157*10^-3 eq), with H2SO4 as catalysts was 14% while with sPcP-1 was 25%.
Figure 4. Conversion of FFA after 4h of reaction time for the different studied catalysts (1% w/w) at 120°C

Figure 5. FFA conversion v/s reaction time at 180°C and 120°C using 0.25% w/w sPSB-SA1 as catalyst.
**Figure 6.** FFA Conversion v/s reaction time obtained at 180°C. Catalyst: 1% w/w of fresh and used sPSB-SA2

Because the high thermal stability of sPSB-SA resins sPSB-SA2 has been used also at 180°C obtaining a high increase in the reaction rate. In fig. 5 the evolution of the conversion of FFA along the time for two runs performed using 0.25% of sPSB-SA1 as catalyst at 180°C and 120°C, respectively is reported.

The introduction of crosslinks in the resin reduces the overall acidity of the resin (see Tab.1) and consequently its activity. After 1 h of reaction, at 180°C, using 1% of catalyst sPSB-SA1 a conversion of 95% was obtained, while, with sPSB-SA2, in the same condition, a conversion of 80% was achieved. However, as sPSB-SA2 has more stable shape and can easily be separated from the products, it has been used to test the resistance to the deactivation.

The sPSB-SA2 was used three times for 4 h at 180°C. After each reaction, the catalyst was separated from the reaction mixture by filtration. It was then washed with ethanol and dried at 60°C. Recovered catalyst was then mixed with a fresh batch of oleic acid and glycerol for the next run. A slight reduction of the activity can be seen, this effect could be attributed to the decomposition of the primary sulfonic acid group located onto the 1,2 vinyl unit or to a loss of the catalyst. However, the results are very encouraging but
to have more realistic data on the life of the catalyst, a minipilot plant is being designed to perform continuous runs.

4. Conclusion

A new acid resin, stable at high temperature, has been synthesized. This Syndiotactic Polystyrene-co-1,4-cis-Polybutadiene resin has shown high activity in esterification reaction and a good resistance to the deactivation. The aspect of the final product, in comparison with the homogeneous catalyst (H$_2$SO$_4$) was reported in the following figure (figure 7). The obtained results are very promising and further study will be done to define its microstructure and to test the performance of the resin in a continuous reactor.

![Figure 7. Final product using homogeneous (left) and heterogeneous (right) catalyst.](image)
5. References


Chapter 4 - Niobia supported on silica as a catalyst for Biodiesel production from waste oil
1. Introduction

One of the most reliable ways to treat raw materials containing high concentration of FFA is the use of an acid catalyst which can promote both the esterification of FFA and transesterification of triglycerides [1].

In this sense, homogenous Brönsted acid catalysts (such as sulphuric, sulfonics, phosphoric and hydrochloric acids) [2] and Lewis acid catalysts [1,3,4] have been proposed to catalyze both the esterification and transesterification reactions in biodiesel production, but their use foresees high costs of the process due to the plant maintenance and/or product purification and/or waste catalyst disposal. Heterogeneous acid catalysts represents a great challenge that could allows to overcome the above mentioned drawbacks [5,6]. It must be pointed out that Brönsted acid catalysts are mainly active in promoting esterification reaction, while Lewis acid catalysts are more active in transesterification [7]. Therefore, both acid sites of suitable strength should be present on the surface of an ideal heterogeneous catalyst [7].

Moreover, it must be taken into account a possible deactivation of catalysts, which could be due to (i) the leaching of active phase (ii) the fouling of the surface or (iii) the poisoning of the active sites. Consequently, the development of suitable regeneration methods is a key point in the search of very active solid acid catalysts to be used in a new technology for biodiesel production [8].

Several heterogeneous acid catalysts have been proposed in the recent literature for biodiesel production: mixed metal oxides, sulphonated resins, sulphated metal oxides, heteropolyacids, vanadyl phosphate and many others [7,9].

In particular, niobium-based materials, previously employed as useful acid catalysts for many catalytic reactions [10,11], have also yielded promising results in biodiesel production. Thus, Portilho et al., for example, claimed the use of niobic acid treated with a phosphoric acid solution and niobium oxide supported on alumina as efficient catalysts for the transesterification of canola oil with methanol or ethanol [12]. García-Sancho et al showed that biodiesel can be produced via methanolysis of sunflower oil in the presence of a MCM-41 silica containing niobium oxide [13]. This mesoporous niobosilicate can be used even in the presence of oleic acid (2.2 wt%) and water (0.4 wt%) without losing activity [13]. On the other hand, niobic acid (hydrated niobium oxide, Nb₂O₅·nH₂O) has already been proposed as catalyst for the esterification of FFA.
with methanol or ethanol [14,15]. Niobia supported on silica [16] and on silica-alumina [17] has been used as catalysts for the esterification of acetic acid with alcohols. Niobium–silicon mixed oxide nanocomposites, prepared by a sol–gel method, showed the presence of active sites for transesterification of triglycerides and esterification of FFA [18]. In the present chapter the performance of niobia supported by impregnation on silica in biodiesel production from soybean oil containing a high FFA concentration (a waste oil model) has been deeply investigated. The catalytic behavior has also been determined in a continuous tubular reactor in order to evaluate the suitability of this catalyst for the development of an industrial process.

2. Experimental

2.1 Catalysts synthesis

The supported Nb$_2$O$_5$ catalysts with different loading (3-12% Nb$_2$O$_5$) were prepared by dry impregnation of niobium oxalate [19], obtained from niobium pentoxide [20], on a commercial silica (Engelhard). The commercial silica sample is of spherical shape (mean diameter= 3-5 mm). The catalysts have been prepared by impregnation of both the pellets and of the powder obtained by grinding in a mortar the commercial silica (powder diameter <100 µm). After impregnation, the catalysts were dried at 60°C for 10 h and calcined at 900°C for 6 h. The denominations of all the catalysts used in the catalytic tests with their compositions are reported in Table 1.
### Table 1: Niobia content and surface area of the catalysts and the support
(xNbSi, powder; 12NbSi(I), pellets)

<table>
<thead>
<tr>
<th>Support/Catalyst</th>
<th>wt % Nb2O5</th>
<th>Surf. Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>291</td>
</tr>
<tr>
<td>SiO₂ (calcined at 900°C)</td>
<td>-</td>
<td>285</td>
</tr>
<tr>
<td>3NbSi</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>5NbSi</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>12NbSi</td>
<td>12</td>
<td>266</td>
</tr>
<tr>
<td>12NbSi(I)</td>
<td>12</td>
<td>250</td>
</tr>
</tbody>
</table>

#### 2.2 Catalysts characterization

Textural analyses were carried out by using a Thermoquest Sorptomatic 1990 Instrument (Fisons Instrument) by determining the nitrogen adsorption-desorption isotherms at 77 K. The samples were thermally pre-treated under vacuum overnight up to 473 K (heating rate = 1 K/min). Specific surface area (S\text{BET}) were determined by using the BET method.

Powder X-ray diffraction (XRD) patterns were obtained using a Philips powder diffractometer. The scans were collected in the range 5–80° (2θ) using Cu K\text{α} radiation with a rate of 0.01° (2θ/s). The X-ray tube operated at 40 kV and 25 mA.

X-ray photoelectron (XPS) studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyzer (model 80-365B) and a Mg K\text{α} (1253.6 eV) X-ray source. High resolution spectra were recorded at 45° take-off-angle in the constant pass energy mode at 29.35 eV. Charge referencing was done against adventitious carbon (C1s at 284.8 eV). The pressure in the analysis chamber was kept lower than 5 x 10⁻⁶ Pa. A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. All recorded spectra were always fitted using Gaussian-Lorentzian curves to more accurately determine the binding energy of the different element core levels.
Confocal Raman microscope (Jasco, NRS-3100) was used to obtain Raman spectra. The 647–nm line of an water cooled Kr+ laser (Coherent), 800 mW, was injected into an integrated Olympus microscope and focused to a spot size of approximately 2 µm by a 100x objective. A holographic notch filter was used to reject the excitation laser line. Raman scattering was collected by a peltier-cooled 1024·128 pixel CCD photon detector (Andor DU401BVI). For most systems, it takes 60 s to collect a complete data set.

The surface acidity of the 12NbSi catalyst was evaluated by Temperature Programmed Desorption of NH$_3$ (NH$_3$-TPD), which has been conducted using the Thermo Finnigan TPD/R/O 1100. Before the NH$_3$-TPD measurement, the powdered catalyst (0.1–0.2 g) was outgassed in a flow of pure helium (20 cm$^3$/min), at different treatment temperature (600, 300 and 50 °C) for 30 min. Then, the sample was cooled at 40°C and saturated with a stream of 10% NH$_3$ in He (20 cm$^3$/min) for about 30 min. Afterward, the catalyst was purged in a helium flow until a constant baseline was attained. The ammonia desorption was determined in the temperature range of 40–500 °C with a linear heating rate of 10 °C min$^{-1}$ in a flow of He (10 cm$^3$/min). Desorbed NH$_3$ was detected by a Thermal Conductivity Detector (TCD). The eventual presence of water in the evolving gases was removed by a trap containing anhydrous magnesium perchlorate, located between the detector and the reactor.

The measurement of acid strength of the 12NbSi catalyst was also done by the Hammett indicators (Neutral red, pK$_{a}$ = 6.8; Butter yellow, pK$_{a}$ = 3.3; Benzeneazodiphenylamine, pK$_{a}$ = 1.5; Dicinnamalacetone, pK$_{a}$ = -3; Benzalacetophenone, pK$_{a}$ = -5.6). The measurements were done on samples freshly dried at 300°C before carrying out the indicator tests, and handled in a dry box. Moreover, the tests were also performed on the sample after contacting with the air for 72 h, with the aim to verify the effect of the humidity adsorption on the surface acidity.

The acidity of the 12NbSi catalyst was also investigated by using pyridine adsorption coupled to FTIR spectroscopy. The spectra were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR8300). Self supported wafers were placed in a vacuum cell greaseless stopcocks and CaF$_2$ windows.

Before pyridine adsorption, the 12NbSi sample was thermally treated at 300°C in air for 2 h, followed by evacuation at 10$^{-2}$ Pa for 2h at the same temperature. Following this pretreatment, the wafer was cooled to room temperature and a spectrum was recorded as
reference. In a second set of experiments, the pretreatment was excluded to verify the effect of the dehydration on the surface acidity.

2.3 Catalytic tests

The screening of the catalysts was performed using a series of 5–6 small stainless steel vial reactors reported in the following figure (figure 1).

![Vial reactors and oven.](image)

The reactants, soybean oil or acid soybean oil (FFA =10%, w/w) (2 g) and methanol (0.88 g), and a defined amount of the catalyst (0.1 g) were introduced in each reactor. The reactors were introduced in a ventilated oven which initial temperature was fixed at 50°C for 14 min, and then increased at a rate of 20°C/min until it reached the reaction temperature, 180°C, which was kept for 1 h. At the end, the reactors were quenched in a cold bath. Blank runs (without catalyst) were also done to evaluate any contribution of the non-catalytic reaction.

The most active catalyst was also tested under the same experimental conditions used by García-Sancho et al. [13] with a MCM-41 silica containing niobium oxide (methanol/sunflower oil molar ratio= 12, Cat= 5 wt%, T=200°C, t= 4 h).

One of the most interesting aspects concerning the use of heterogeneous catalysts is the absence of soluble homogeneous species in the reaction medium [21]. After catalyst filtration, the concentration of niobium in solution was determined by using the UV-visible standard procedure [22] with the purpose to measure the eventual leaching.

On the other hand, to achieve information on the catalyst life in the industrial reaction conditions, some runs have been performed at 220 °C in a laboratory continuous
micropilot plant using the best catalytic system reported in the following figure (figure 2).

The reaction system consisted of a stainless steel packed bed reactor of 30 cm of length and d=1/2 inch. A weighted amount of the 12NbSi catalyst, as pellets (12NbSi(I), 30 g), was charged in the reactor. The measured void fraction was of 0.66. The reaction was carried out at constant pressure of 60 bars by using a back-pressure regulator.

Two different runs were performed: using silica pellets (reference test, run 0) and with 12NbSi (I) catalyst pellets (run 1).

The soybean oil or the acid soybean oil (FFA = 10%) flow rate was fixed at 2.6 ml/min while for methanol 5.3 ml/min was used. Samples of the outlet reaction mixture were withdrawn at different times on stream. The FAME (fatty acid methyl esters) yields were determined by using the HNMR technique (Bruker 200 MHz) measuring the area of the $H^1_{\text{NMR}}$ signal related to methoxylic and methylenic groups using the following equation [23]:

$$Y_{\text{FAME}} = 100 \frac{A_{1/3}}{A_{2/3}}$$

where ($A_1$) and ($A_2$) are the area of H-NMR signal related to methoxylic and methylenic groups, respectively.
FFA concentration is determined by measuring the residual FFA concentration by titration (w_{FFA}) [24].
The free fatty acid (FFA) conversion (\lambda_{FFA}) was calculated using the following equation:

\[ \lambda_{FFA} = \frac{w_{FFA}^0 - w_{FFA}}{w_{FFA}^0} \times 100 \]

The conversion of glyceride groups (\lambda_{Gly}) (due to the transesterification reaction) can be calculated using the following equation [1]:

\[ \lambda_{Gly} = Y_{FAME} \left( 1 + \frac{PM_{oil}}{3PM_{OA}} \frac{w_{FFA}^0}{100 - w_{FFA}^0} \right) - \lambda_{FFA} \frac{PM_{oil}}{3PM_{OA}} \frac{w_{FFA}^0}{100 - w_{FFA}^0} \]

Were:

\[ PM_{oil} = \text{molecular weight of soybean oil, [g/mol]} \]
\[ PM_{OA} = \text{molecular weight of oleic acid, [g/mol]} \]
\[ w_{FFA}^0 = \text{initial FFA concentration, \% w/w} \]

The stability of the catalyst was verified by determining, after 100 h on stream, the content of niobium on the discharged catalyst was determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

3. Results and Discussion

3.1 Preliminary Catalytic Screening

First of all, since at high temperatures the stainless steel internal surface of the vials could catalyze the transesterification and esterification reactions, different runs without catalyst were performed at 180 °C using acid oil as reagent, obtaining FAME yields in the range 7-10% and a FFA conversion of 15-20%.
The influence of the amount of niobia on the catalytic activity has been studied and the obtained results are reported in Figure 3.
As it can be seen, by increasing the amount of supported niobia a significant increment of the FFA conversion was obtained. Calcined silica exhibits a very low activity (the obtained conversion is in the range of the blank runs). However, the activity improves significantly (35% of FFA conversion) in the case of 3NbSi which possesses the lowest Nb$_2$O$_5$ loading (3%). A further increase of the amount of supported niobium oxide does not lead to an important amelioration of the catalytic activity, with FFA conversions of 42% and 48% for 5NbSi (5% Nb$_2$O$_5$) and 12NbSi (12% Nb2O5), respectively.

On the other hand, the transesterification activity (glyceride group conversion) is relatively low and it is barely affected by the niobia loading, under these experimental conditions.

The leaching tests were carried out for each catalyst, confirming the stability of this family of supported niobia catalysts, since the presence of Nb in the filtered solution was not evidenced by UV-Vis analysis. The best catalyst (12NbSi) was also tested in the same condition used by García-Sancho et al. with a MCM-41 silica containing niobia.
(methanol/sunflower oil molar ratio= 12, Cat= 5 wt%, T=200°C, t= 4h) [13]. The obtained result (70% FAME yield) was lower than that obtained with a niobia supported on a MCM-41 silica catalyst with a 8% Nb_2O_5 (87% FAME yield). However, the cost of the MCM-41 silica synthesis is higher than that of a commercial silica and, for an industrial application, the use of the latter type of silica as support is favored (if the catalyst stability is proven also for a long reaction time). Moreover, the catalytic results pointed out that the 12NbSi catalyst has good activity also in transesterification reaction when the temperature is increased until 200°C. This is in agreement with data reported by García-Sancho et al. [13], who found an important amelioration of the transesterification activity, by using the MCM-41 silica containing niobia, increasing the temperature from 175°C to 200°C.

3.2 Catalyst Characterizations

The textural characteristics of the most active catalyst (12NbSi) were determined from the N_2 adsorption-desorption isotherms at -196°C. The adsorption of niobia on silica has little effect on the specific surface area (see Tab. 1) and no crystalline phases could be determined by XRD, even for the catalyst with the highest niobia loading, 12NbSi (see Fig.4), in agreement with the literature data [25,26].

![Powder XRD pattern of the 12NbSi catalyst.](image)

**Figure 4:** Powder XRD pattern of the 12NbSi catalyst.
This fact reveals that niobium is well dispersed on the silica surface. X-ray photoelectron spectroscopy has been used to get insights into the surface nature of catalysts. The XPS data are summarized in Table 2. The Si 2p signal is symmetrical and appears at binding energy (BE) values of 103.2–103.8 eV, typical of Si in silica. The O 1s region only shows a single and almost symmetric peak at BE: 532.6–533.5 eV, close to the value observed for a silica (533.1 eV), whereas bulk Nb_2O_5 displays this peak at lower BE (530.2 eV), thus corroborating the absence of segregated Nb_2O_5 particles on the external surface of the siliceous support, as can be also deduced from the highest surface Si/Nb molar ratio in comparison with the corresponding bulk values (Table 2). On the other hand, the two components of the Nb 3d doublet appear at 206.3–206.9 eV (3d_{5/2}) and 208.8–209.6 eV (3d_{3/2}) when commercial silica is used as support, whereas this doublet is observed at higher BE in the case of MCM-41-based materials. However, in both cases, these BE values have been reported for Nb(V) in an oxidic environment. The surface Si/Nb atomic ratio values are higher than the corresponding bulk ones (Table 2), which is a consequence of the presence of niobia into the pores, thus difficult to detect by this XPS technique. After reaction, these ratio increases due to the covering of the active sites by organic species, as can be inferred from the surface carbon analysis, which yields values as high as 43 and 61% for the spent 12NbSi and MCM-8Nb, respectively.

The surface acidity of the 12NbSi catalyst has been evaluated by temperature programmed desorption of adsorbed NH_3 (see Fig. 5). Before NH_3 adsorption, the catalyst was pretreated at 600°C. Surprisingly, the 12NbSi catalyst didn’t show any desorption peak. These data are in contrast with the highest esterification activity found with this 12NbSi catalyst. For this reason, the TPD analysis was repeated after pre-treating at lower temperature (300°C and 50°C) (see Fig. 5), and acid sites were now detected, decreasing with the increase of the pretreatment temperature.
### Table 2. XPS data (binding energies and Si/Nb atomic ratios) of catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si 2p (eV)</th>
<th>O 1s (eV)</th>
<th>Nb 3d (eV)</th>
<th>Surface Si/Nb atomic ratio</th>
<th>Bulk Si/Nb atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5NbSi_rt</td>
<td>103.8</td>
<td>533.2</td>
<td>206.4 (3d_{5/2})</td>
<td>271</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>209.0 (3d_{3/2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12NbSi_rt</td>
<td>103.8</td>
<td>533.2</td>
<td>206.3</td>
<td>48.9</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>208.8</td>
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<td></td>
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<tr>
<td>12NbSi_300</td>
<td>104.1</td>
<td>533.5</td>
<td>206.4</td>
<td>183.5</td>
<td>16.3</td>
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<td></td>
<td></td>
<td>209.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12NbSi_300_spent</td>
<td>103.3</td>
<td>532.7</td>
<td>206.9</td>
<td>267</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>209.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-Nb8_rt</td>
<td>103.6</td>
<td>533.0</td>
<td>208.0</td>
<td>51.2</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>210.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-Nb8_spent</td>
<td>103.2</td>
<td>532.7</td>
<td>207.7</td>
<td>73.4</td>
<td>22.7</td>
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<td></td>
<td></td>
<td></td>
<td>210.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5:** NH$_3$-TPD profiles for the 12NbSi catalyst pretreated at 600°C, 300°C and 50°C.
Shirai et al. found for a niobia/silica catalyst that, after pretreatment at high temperature, the Brönsted acid sites disappeared, while the Lewis acid sites are independent from the pretreatment temperature [16].

This fact has been confirmed by FTIR analysis of adsorbed pyridine (Fig. 6). The 12NbSi catalyst, pretreated at 300°C overnight under vacuum, only showed at 25°C the vibration modes associated to pyridine adsorbed on Lewis acid sites at 1445 cm\(^{-1}\) and 1600–1610 cm\(^{-1}\) [16,25,27]. However, the acid sites are very weak, since these bands were not observed after evacuation at 150°C.

![FTIR spectrum of adsorbed pyridine of the 12NbSi catalyst (pretreated at 300°C overnight under vacuum) at 25°C.](image)

**Figure 6:** FTIR spectrum of adsorbed pyridine of the 12NbSi catalyst (pretreated at 300°C overnight under vacuum) at 25°C.

However, the formation of stronger acid sites after exposure to the air moisture has been confirmed by the use of Hammett indicators. The 12NbSi catalyst, previously dried at 300°C and handled in a dry box, didn't show any acidity. When the catalyst was put at ambient condition, after 2 h, the acid strength was determined with Hammett indicator (-5.6 < pK\(_a\) < -3).

In order to elucidate the structure-activity relationships, Raman spectroscopy has been used to characterize the 12NbSi catalyst, and the spectra were collected at ambient condition and wet (sample was wet and then the spectrum was registered without dehydration), and were compared with that of Nb\(_2\)O\(_5\) as reference (Fig. 7).
Figure 7. Raman spectra of the 12NbSi catalyst, at ambient condition and wet(12NbSi), Nb$_2$O$_5$ and SiO$_2$.

It has been reported that regular tetrahedral NbO$_4$ structures are associated to Raman frequencies appearing in the 790–830 cm$^{-1}$ region, distorted NbO$_6$ octahedra in the 500–700 cm$^{-1}$ region and highly distorted octahedral NbO$_6$ structures give rise to bands in the 850–1000 cm$^{-1}$ region [28]. A Raman feature at 995 cm$^{-1}$ and 938-934 cm$^{-1}$, observed in the spectra of 12NbSi and wet 12NbSi, can be related to the symmetric stretching vibration modes associated to terminal mono-oxo Nb=O bonds of NbO$_6$ octahedra belonging to the H-Nb$_2$O$_5$ structure [29-32]. By comparison with the Nb$_2$O$_5$, the signal at 995 cm$^{-1}$ should correspond to the bulk Nb$_2$O$_5$ species [33]. On the other hand, the vibration bands around 630 cm$^{-1}$ can be associated with polymerized surface metal oxide species (M-O-M and O-M-O vibrations) [33]. Ultimately, the Raman technique
confirms the presence of small Nb$_2$O$_5$ particles, not detected by XRD, on samples with high niobium content on silica [34]. Although the Raman spectra of 12NbSi and wet 12NbSi are similar, they aren't identical as evidence the different relative intensities of the Raman signals at 995 cm$^{-1}$ and 730 cm$^{-1}$.

The characteristic bands at 995 cm$^{-1}$ and 940 cm$^{-1}$ of Nb=0 species that are associated to Lewis acid sites [34] are still present on the wet 12NbSi catalyst; however, the formation of more Nb-OH groups cannot be excluded because the change of spectra in the region of distorted octahedral NbO$_6$ structures (500-700 cm$^{-1}$).

The previous data confirm the well established observation that the molecular structure of niobia supported on silica is influenced by the hydration degree [32,34].

On the other hand, when the niobia/silica catalyst is immersed in aqueous solution, Brönsted acid sites are predominantly generated by coordination of the water molecules to Lewis acid sites [25].

### 3.3 Effect of pretreatment on catalytic activity

As it has been previously mentioned, pretreatment conditions affect greatly on the catalyst acidity. In order to evaluate its influence on the catalytic activity, different runs have been done with the catalyst dried at 300$^\circ$C and handled in a dry box, and the catalyst remained in contact with atmosphere for 2 h (Fig.8).

The dry 12NbSi catalyst exhibits a high activity in the transesterification reaction ($\lambda_{GLY}$= 48 %) and a low activity in the esterification reaction ($\lambda_{FFA}$= 20 %), whereas the behavior of the wet sample is inverse: the activity in the esterification process ($\lambda_{FFA}$= 50 %) is higher than that of the transesterification reaction ($\lambda_{GLY}$= 5 %), and they are similar to that reported in Fig. 1 for the 12NbSi catalyst.

These results agree well with those derived from the characterization and data previously reported on the relative activity of Lewis and Brönsted acid sites [7,35,36]: the Lewis acid sites present on dried catalysts favor the transesterification reaction while the esterification process is more favored by Brönsted acid sites, formed after exposure to the atmosphere.
Figure 8: The conversion of glyceride groups ($\lambda_{\text{Gly}}$) and of FFA ($\lambda_{\text{FFA}}$) of acid soybean oil (FFA = 10% w/w) obtained with the 12NbSi catalyst. 12NbSi dry = dried at 300°C; 12NbSi (2 h) = exposed to atmosphere for 2 h; (Reaction time = 1 h, reaction temperature = 180°C, catalyst = 0.1 g, acid soybean oil = 2 g, methanol = 0.88 g)

3.4 Continuous runs

Using the silica pellets (30 g) as catalyst (run 0) (Methanol 5.6 cm$^3$/min; acid oil 2.6 cm$^3$/min (FFA = 9.5% w/w), T=220°C), a conversion of 20-30% of FFA was obtained with a total FAME yield of 25-30%.

The results obtained with pellets of the 12NbSi catalyst, under similar experimental conditions (run 1), are reported in Fig.9.

The results were very interesting since this 12NbSi catalyst was very active in both esterification (FFA conversion = 95-90%) and transesterification reactions (FAME yield = 80-90%), and the activity remained constant for more than 100 h on stream.
Figure 9- FFA conversion and FAME yield obtained in continuous run 1. Methanol 5.3 cm$^3$/min; acid oil 2.6 cm$^3$/min (FFA = 10 % w/w); T=220°C; Cat. 12NbSi.

However, in order to verify the stability of the catalyst, the niobium content on discharged catalyst was determined by ICP-MS. Unfortunately, a leaching phenomena was discovered, because the niobia content in the spent catalyst was 3%-5% instead of 12%.

Nevertheless, this niobia content in the catalyst is enough active (see data reported in Fig. 1) and, from the conversion data in the continuous run, the leaching cannot be inferred (probably the conversions are near the equilibrium values).

The obtained results confirms that the leaching is one of the most strong problem in heterogeneous catalysis for biodiesel production [21].
4. Conclusions

The distribution of strength and nature of acid sites on niobia supported on silica is strongly dependent on the environment in contact with the catalyst. When the catalyst is dried, Lewis acid sites are mainly present, whereas the contact with atmosphere favors the reaction with the humidity and the formation of Brönsted acid sites of moderate strength (-5.6 < $pK_a \leq -3$).

Niobia supported on silica is active in both esterification of FFA and transesterification of triglycerides, with no loss of activity in the continuous run for 100 h. However, the characterization of the used catalyst revealed the slow leaching of niobia, which reduces its potential of industrial application in biodiesel production, if this problem will be not solved.
5. References


Chapter 5 -
Homogeneous/Heterogenized zinc catalysts for biodiesel production
1. Introduction

For synthesis of Biodiesel from waste oils containing high concentration of FFAs, the attention has been recently focused on Lewis acid catalysts, i.e. metal salts which are able to promote simultaneously esterification and trans-esterification [1–14]. Extensive studies [15] carried out on homogeneous Zn, Co, Pb, Mn, Ca, and Mg catalysts have clearly demonstrated that the intrinsic acidity of the metal center plays a crucial effect on its activity. In this case, the main drawback ensues from the corrosive action of the Lewis acids. A solution can be the heterogenization of the metal complexes, which also favors their separation and recycling. Given this premise, our laboratory has recently [16-18] designed effective homogeneous Zn(II) catalysts containing modular nitrogen ligands I in Fig. 1.

![Figure 1. General formula of type I complexes (X= Cl, MeCO₂, CF₃CO₂, CF₃SO₃).](image)

The catalysts were successfully used in the trans-esterification of soybean oil in homogeneous conditions, and the presence of the functional group R on the pyridine portion allowed to identify the stereoelectronic features which enhance the performance of the catalysts. The additional hydroxyl was instead introduced as a potential anchoring function, in order to make the catalysts suitable for a successive heterogenization. Aiming to demonstrate the feasibility of this strategy, in chapter we report two successful approaches for immobilizing catalysts of type I, their use in FAMEs'
production starting from both neutral and acid oils, and the attempts to separate and re-
cycle the active species.

Two immobilized catalytic systems were designed:
a) soluble catalysts based on polymers (i.e. dendrimers [19]), that are separable by using
ultrafiltration techniques.
b) a catalyst supported on a solidmatrix (i.e. silica), which can be easily
recovered by filtration of the reaction mixture.

2. Experimental section

2.1 General considerations

All reagents were purchased from Sigma-Aldrich and used without further purification.
The silica AEROLIST (surface area, 150 m2/g) was activated by heating in oven at 300
°C for 5 h. Complex II was described elsewhere [16]. The complexes were characterized
by NMR spectroscopy, using Varian VXR 200 and Varian Gemini 200 spectrometers.
1H NMR data were reported in ppm and the shifts were referenced to the resonance of
the residual protons of the solvent (CD3)2SO (2.55 ppm). Abbreviations used in NMR
data: s, singlet; d, doublet; t, triplet; m, multiplet; and br, broad. The Zn content in the
supported catalyst was determined by ICP (inductively coupled plasma) analysis on an
Aurora M90 Bruker spectrometer.

2.2 Synthesis of dendrimeric complexes [Zn(OAc)2Gx], x = 0–3

PAMAM-G0-3 (polyamineamides) were used for the construction of the grafted catalysts
(Scheme 1 shows PAMAM-G2). This choice was motivated by the following
considerations:
1) the presence of appropriate terminal functions (-NH2) useful for the synthesis of
imino ligands.
2) molecular weights compatible with the ultrafiltration step.
3) the high solubility in methanol, which consents its use as both solvent and reactant in
the trans-esterification reaction, thus avoiding mixtures of solvents.
The synthesis of the complexes was conducted in a single step, by mixing in methanol stoichiometric amounts of 2-pyridinecarboxaldehyde and the appropriate PAMAM, in the presence of zinc acetate (the functionalized PAMAM ligands are indicated with the label Gx, as in Scheme 3 for [Zn(AcO)$_2$G$_2$]).

2-Pyridinecarboxaldehyde (0.107 g, 1.00 mmol) and solid Zn(OAc)$_2$ (0.182 g, 1.00 mmol) were added to a solution of PAMAM-GX (1.00/n mmol; n = \[\text{NH}_2\] groups) in 3 mL of methanol. The solution was stirred for 1 h at room temperature. The yellow product was precipitated by adding diethyl ether, filtered off and dried under a vacuum.

The characterization was carried out by NMR spectroscopy. The presence of a singlet at $\delta$8.5 testifies the formation of the imino CH=N bonds, and the integration of suitable peaks demonstrated that all the -NH$_2$ groups were functionalized and involved in coordination. The thermal stability of the dendrimeric complexes was tested by TGA–TDA analysis under nitrogen atmosphere. All the samples showed the same behavior and only a low weight reduction in the temperature range 30–180 °C (5%) was observed. The weight loss can be attributed to the loss of adsorbed water.
Scheme 1. Synthesis of $[\text{Zn}(\text{AcO})_2\text{G}_2]$.
2.3 Catalysis with the dendrimeric complexes

The activity of the complexes was investigated in the transesterification of neutral soybean oil. A mixture of methanol, oil and catalyst was stirred in a batch glass reactor in the same experimental conditions described in a work [16]. Soybean oil (4.00 g), methanol (1.76 g) and [Zn(OAc)2Gx] (0.12 mmol based on Zn) were introduced in a batch glass reactor. The temperature of the oil bath was initially fixed at 50 °C and then increased at a rate of 10 °C/min until it reached 150 °C. After 1 h there action was quenched, cooling rapidly the reactor. The reaction mixture was place in an Amicon® stirred cell and methanol was added. Ultra filtration was carried out for 30 min at a pressure of 3 bar. The catalyst was separated and re-used for other catalytic cycles. The reaction mixture was analyzed by NMR spectroscopy [17].

The results for the corresponding homogeneous catalysts are reported in (Table 1).

The dimension of the PAMAM support plays a modest effect on the catalytic activity: at the same temperature FAMEs yields deviated a few percentage units from G0 through G3. This can be explained by assuming that all the zinc centers are available for the substrate, due to their superficial exposure.

The mechanism hypothesized for the reaction is likely similar to that established in the case of the corresponding mononuclear homogeneous systems, which is described in detail elsewhere [2].

The highest activity was found for [Zn(OAc)2G2], which promoted a 90.1% conversion at 150 °C (TOF=98 h⁻¹). As expected, the temperature had a marked influence: a decrease of only 40 °C lowered the yield of about 80%. However, it should be emphasized that the performance at 150 °C is quite satisfactory when compared with that of the corresponding homogeneous acetate complexes of type I, which in the same condition showed TOFs up to 57 h⁻¹ [16]. In all cases, except for [Zn(OAc)2G0], the formation of a solid dark residue was observed, due to partial decomposition of the complex. Nevertheless, reuse of catalysts [Zn(OAc)2G2] and [Zn(OAc)2G0] was attempted, because the former showed the highest activity, and the latter did not apparently decompose during the reaction. The catalysts were ultrafiltered by using a membrane with a cut-off of 1000 Da. After ultrafiltration, the permeate containing the
reaction mixture was analyzed to evaluate the catalytic activity, while the recovered catalyst was used for a new cycle. The results are shown in Table 2. In both cases a decrease in activity was observed, which was more pronounced for \([\text{Zn(OAc)}_2\text{G}_2]\).

Table 1. Transesterification\(^a\) of soybean oil with dendrimeric complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>MW</th>
<th>T (°C)</th>
<th>FAME yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Zn(OAc)}_2\text{G}_0])</td>
<td>1608.93</td>
<td>150</td>
<td>86.6</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Zn(OAc)}_2\text{G}_0])</td>
<td>130</td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>([\text{Zn(OAc)}_2\text{G}_0])</td>
<td>110</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>([\text{Zn(OAc)}_2\text{G}_1])</td>
<td>3610.35</td>
<td>150</td>
<td>88.2</td>
</tr>
<tr>
<td>5</td>
<td>([\text{Zn(OAc)}_2\text{G}_1])</td>
<td>130</td>
<td>45.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>([\text{Zn(OAc)}_2\text{G}_1])</td>
<td>110</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>([\text{Zn(OAc)}_2\text{G}_2])</td>
<td>7617.18</td>
<td>150</td>
<td>90.1</td>
</tr>
<tr>
<td>8</td>
<td>([\text{Zn(OAc)}_2\text{G}_2])</td>
<td>130</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>([\text{Zn(OAc)}_2\text{G}_2])</td>
<td>110</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>([\text{Zn(OAc)}_2\text{G}_3])</td>
<td>15616.82</td>
<td>150</td>
<td>85.4</td>
</tr>
<tr>
<td>11</td>
<td>([\text{Zn(OAc)}_2\text{G}_3])</td>
<td>130</td>
<td>42.6</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>([\text{Zn(OAc)}_2\text{G}_3])</td>
<td>110</td>
<td>5.4</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: soybean oil, 4g; methanol, 1.76g; catalyst, 0.12 mmol (based on Zn); reaction time, 1h.

Table 2. Recycles in transesterification\(^a\) of soybean oil with dendrimeric complexes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1(^{st}) run (^b)</th>
<th>2(^{nd}) run (^b)</th>
<th>3(^{rd}) run (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Zn(OAc)}_2\text{G}_0])</td>
<td>86.6 %</td>
<td>76.9 %</td>
<td>50.0 %</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Zn(OAc)}_2\text{G}_2])</td>
<td>90.1 %</td>
<td>57.5 %</td>
<td>6.2 %</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: soybean oil, 4g; methanol, 1.76g; catalyst, 0.12 mmol (based on Zn); reaction time, 1h.

\(^{b}\) Conversion.
As a general comment, it should be noted that the results reported in Table 2 represent the average of multiple tests. In all cases it was observed that the formation of the dark precipitate, although the yield was not reproducible. This aspect, combined with the fact that its collection is difficult, allowed only to verify the presence of zinc, through a qualitative assay for its recognition. In the case of [Zn(OAc)$_2$G$_6$], the non-observation of a macroscopic precipitate cannot exclude a similar formation of metal clusters, which removes metal from the catalyst.

2.4 Catalyst supported on silica

The strategy for homogeneously involves linkage of complex II to silica (the synthesis is described elsewhere [16]), by reacting the superficial -OH groups with the -Si(OEt)$_3$ groups of the pendant reported in the following figure (Fig.2)

![Figure 2. General formula of type II complex.](image)

For the synthesis, to a solution of complex II (0.37 g) in 70 mL of dry toluene SiO (1.05 g) was added. The mixture was stirred for 20 h under reflux. The solid was then separated, washed with dichloromethane for 16 h in a Soxhlet apparatus and dried under a vacuum. The ICP analysis revealed the presence of 2.3% in weight of Zn.
**Scheme 2.** Strategy for the heterogenization of catalyst II.

As expected, the easy separation of the resulting powder sup-II from the reaction medium allowed its re-use in several catalytic runs. The system was tested in the transesterification of soybean oil, both neutral (FFA < 1%) and suitably acidified by addition of oleic acid (5.08% and 9.07% w/w). These substrates were prepared by weighing, and the percentages were also verified by titration with KOH. Soybean oil (11.2 g), methanol (5.00 g) and supported catalyst(0.56 g) were stirred (rate 500 rpm) in a Parr Instrument® steel reactor. The temperature in the reactor was increased from room temperature to 150 °C in 35 min. After 2 h the reactor was cooled and the reaction mixture was separated from the catalyst and analyzed. Soybean oil and methanol were added to the residual catalyst for successive runs. The FAME yields were determined by NMR spectroscopy [17] and the residual FFA concentration by titration [18].

After each catalytic run, the reactor was rapidly cooled and, after the removal of the reaction mixture, fresh methanol and oil were again added to the residual catalyst. Reaction conditions, conversion and residual acidity are given in Table 3.
Table 3. Recycles in transesterification\textsuperscript{a} of soybean oil with sup-II

<table>
<thead>
<tr>
<th>Entry</th>
<th>Run</th>
<th>Initial acidity (%)</th>
<th>FAME yield (%)</th>
<th>Residual acidity (%)</th>
</tr>
</thead>
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<td>1</td>
<td>1\textsuperscript{st}</td>
<td>&lt;0.1</td>
<td>31.1</td>
<td>-</td>
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<tr>
<td>2</td>
<td>2\textsuperscript{nd}</td>
<td>&lt;0.1</td>
<td>33.8</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>3\textsuperscript{rd}</td>
<td>&lt;0.1</td>
<td>28.0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>4\textsuperscript{th}</td>
<td>&lt;0.1</td>
<td>17.7</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>5\textsuperscript{th}</td>
<td>&lt;0.1</td>
<td>13.2</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1\textsuperscript{st}</td>
<td>5.08</td>
<td>39.7</td>
<td>1.8</td>
</tr>
<tr>
<td>7</td>
<td>2\textsuperscript{nd}</td>
<td>5.08</td>
<td>36.9</td>
<td>2.0</td>
</tr>
<tr>
<td>8</td>
<td>3\textsuperscript{rd}</td>
<td>5.08</td>
<td>27.0</td>
<td>2.6</td>
</tr>
<tr>
<td>9</td>
<td>4\textsuperscript{th}</td>
<td>5.08</td>
<td>25.7</td>
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<tr>
<td>10</td>
<td>5\textsuperscript{th}</td>
<td>5.08</td>
<td>24.8</td>
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</tr>
<tr>
<td>11</td>
<td>1\textsuperscript{st}</td>
<td>9.07</td>
<td>43.3</td>
<td>2.1</td>
</tr>
<tr>
<td>12</td>
<td>2\textsuperscript{nd}</td>
<td>9.07</td>
<td>41.7</td>
<td>3.3</td>
</tr>
<tr>
<td>13</td>
<td>3\textsuperscript{rd}</td>
<td>9.07</td>
<td>35.2</td>
<td>3.6</td>
</tr>
<tr>
<td>14</td>
<td>4\textsuperscript{th}</td>
<td>9.07</td>
<td>30.3</td>
<td>4.3</td>
</tr>
<tr>
<td>15</td>
<td>5\textsuperscript{th}</td>
<td>9.07</td>
<td>28.2</td>
<td>4.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}. Reaction conditions: soybean oil, 11.2g; methanol, 5.0g; catalyst, 0.20 mmol (based on Zn); reaction time, 2h.

The activity observed for the neutral oil (entry 1, TOF = 28 h\textsuperscript{-1}) is higher than that for the corresponding homogeneous counterpart II (TOF = 15 h\textsuperscript{-1} \textsuperscript{[16]}), and can be considered as satisfactory, given the heterogeneous nature of the catalyst. Notably, the activity remained almost constant for the first three catalytic cycles and then decreased. It should be noted that this effect cannot be attributed to leaching of zinc, as the metal content after the fifth run was found to be identical to the initial value (ICP analysis = 23 mg Zn/g of solid).

The introduction of FFA aimed to verify the stability and the activity of the catalyst under conditions more similar to those of waste oils. Conversions were even higher than in the case of the neutral oil. However, a non-negligible contribution due to the acidic nature of the substrate must be also taken into account. In fact, the conversions without
catalyst were 6% and 17%, respectively for 5.08% and 9.07% w/w acidic contents. If this contribution is simply subtracted from the overall yields, the activity of the catalyst toward the different substrates can be assumed to be similar.

Also in the case of the acid oils, conversion remained constant within the first catalytic cycles, and then decreased. A reduction in the acidity of the substrate was also observed, which gradually was less evident in subsequent catalytic runs. This testifies that the supported catalyst displays a significant activity even in the esterification of FFA.

3. Conclusion

In this chapter have been described two efficient strategies for immobilizing catalysts based on Zn(II). Both the homogeneous catalysts supported on silica and the dendrimeric species have proven the capability of promoting the trans-esterification of neutral and acid soybean oil. Further studies will be dedicated to improving the robustness of the catalysts for enhancing their activity and durability.
4. **References**

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217.


92.


481.


95.


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Part B – Alogenation Reaction of Glycerol in Gas-Liquid Semibatch Reactor
Chapter 6—Chlorination reaction of glycerol. State of the art.
1. Introduction

Biodiesel production has strongly increased in the last years as one of the possible substitutes of diesel from petroleum. As known, crude glycerol is an important by-product of biodiesel synthesis corresponding to about 10% wt of the produced biodiesel [1-10]. Clearly, by increasing the biodiesel production also the availability of glycerol increases and its price consequently goes down more and more.

For these reasons strong effort are doing for finding new application of glycerol (see chapter 1). In this chapter, we focused our attention to the glycerol hydrochlorination process for producing chlorohydrins. The strong industrial interest for this production route is confirmed by the fact that recently some big companies have announced plans to commercialize their technology to manufacture epichlorohydrin starting from glycerol [11-22]. Studies of glycerol hydrochlorination have focused mainly on the production of 1,3-di-chloro-2-propanol (1,3-DCH) an intermediate in epichlorohydrin synthesis. The production of epichlorohydrin occurs through the following reaction steps:

\[
\text{HO}_2\text{C(OH)CH(OH)OH} + 2\text{HCl} \xrightarrow{\text{Catalyst}} \text{ClC(OH)CH(OH)OH} + 2\text{H}_2\text{O} \tag{1}
\]

\[
\text{ClC(OH)CH(OH)Cl} + \text{NaOH} \xrightarrow{} \text{OCl}_3 + \text{NaCl} \tag{2}
\]

Instead of NaOH also Ca(OH)$_2$ can be used.

Epichlorohydrin is an important raw material for the production of some polymers such as epoxide resins, synthetic elastomers, and sizing agents for the papermaking industry. Starting from glycerol the reaction proceeds through a first hydrochlorination reaction, primarily forming 1-chloro-2,3-propanediol (1-MCH) and water along with small amounts of the isomer 2-chloro-1,3-propanediol (2-MCH) (mono-chlorohydrins). This is followed by a second hydrochlorination step from which 1,3-DCH is obtained as main product together with modest amounts of 1,2-chloro-3-propanol (1,2-DCH). Different carboxylic acids can be used as catalysts. The hydrochlorination of glycerol is very selective in giving 1,3-DCH. On the contrary, starting from propene and following the
traditional technology, a mixture of 1,3-DCH and 1,2-DCH (30:70%) is obtained. This is an important advantage of the process via glycerol, because, 1,3-DCH is much more reactive than 1,2-DCH and consequently the plants for obtaining epichlorohydrin, in this case, are much smaller in size and hence less expensive.

In this chapter, the activity and selectivity shown by different carboxylic acids used as catalysts in promoting the reaction and the effect of the catalyst concentration have been examined and compared; then, the reaction mechanisms suggested in the literature and the importance of using gaseous hydrochloric acid and the role of both the HCl pressure and the temperature on the reaction rate have been examined and discussed. Comparison of the new process via glycerol for producing epichlorohydrin with the traditional process via propene.

The process for the synthesis of epichlorohydrin is a rather old process. The classical process starts from propene and through a first step, consisting in a high temperature chlorination, allyl chloride is obtained [23]; subsequently, allyl chloride with hypochlorous acid gives place to glycerol dichlorohydrins isomers and finally the reaction of the glycerol dichlorohydrins with sodium hydroxide or calcium hydroxide, leads to epichlorohydrin. The main reactions involved in the epichlorohydrin synthesis [23] are shown in Figure 1. As it can be seen, from the second step of this process a mixture of dichlohydrides is obtained, more precisely the reaction product is a mixture composed of 70% of 1,2-DCH and 30% of 1,3-DCH. As already mentioned, the reactivity of 1,2-DCH, the most abundant component, is much lower. This gives place to the following disadvantages: an increase of the reactor size (reactive distillation column) to obtain a satisfactory conversion of the less reactive reactant and the formation of undesired by-product as a consequence of the long residence time [24,25]. This process has also the disadvantages of an abundant use of chlorine. The availability of great amounts, at low cost, of glycerol stimulated the development of alternative processes based on the use of this substance as raw material instead of propene. It must be recognized that the process based on glycerol hydrochlorination, to obtain chlorohydrins, was known from a long time [26-33]. The old process involved the reaction of glycerol with aqueous hydrochloric acid at high concentration, using acetic acid as catalyst. The reaction was performed at 80-100°C. The process based on the use of aqueous HCl is
affected by many drawbacks, such as: (i) The reaction is slow because of the abundant water present in the system coming from both the aqueous hydrochloric acid and the water produced by the reaction. (ii) The difficult separation of the dichlorohydrins from the reaction mixture. (iii) Acetic acid, used as catalyst, can be lost from the reaction mixture by evaporation, since its relatively low boiling point (117 °C). The disadvantages listed above discouraged the possibility of further studies in this direction. On the contrary, new studies have been directed towards processes using gaseous hydrochloric acid instead of aqueous solutions and new catalysts, less volatile than acetic acid, such as carboxylic acids of higher molecular weight. In this way, it is possible to keep constant the concentration of the catalyst inside the reactor during the reaction [10-12].

Figure 1 – Reaction scheme for the traditional process via propene.

The use of organic acids less volatile than acetic acid allows to operate at higher temperatures thus increasing significantly the reaction rate. The use of gaseous HCl
allows also an easier recover of the produced dichlorohydrins from the reaction mixture, because, 1,3-DCH and 1,2-DCH are both more volatile than the unreacted glycerol and the intermediates monochlorohydrins 1-MCH and 2-MCH. Gaseous HCl can be fed to the reaction system either pure or diluted with an inert gas [10-12]. The process for producing dichlorohydrins, according to this method, is performed starting from pure or crude glycerol, as a byproduct of biodiesel production, treated with gaseous hydrochloric acid, in the presence of a carboxylic acid.

The pressure of HCl has a positive effect on both reaction rate and selectivity toward 1,3 DCH, and usually is kept in the range 1-10 bars. The complete conversions of glycerol, however, involves a reaction time that is dependent on the pressure of HCl, the adopted temperature and the catalyst concentration. This time varies from 2 to 24 hours according to the adopted operative conditions. However, different patents [34-41] and publications [10-12,42-49] appeared in the literature on this subject in the recent years starting from 2005. In particular, Santacesaria et al. [10-12], on the basis of experimental observations, suggested the reaction scheme reported in Figure 2. As it can be seen, glycerol reacts with HCl in two steps giving place in the first step to monochlorohydrins and then to dichlorohydrins in the second one. It is interesting to point out that very few amounts of 2-DCH and 1,2-DCH are obtained and if the reaction time is long enough 1,3-DCH is obtained with very high yields (85-95%).

![Figure 2](image_url) – Overall reaction scheme from glycerol to epichlorohydrin proposed by Santacesaria et al. [10-12,24,25]
At last, both 1,2 and 1,3 di-chlorohydrins gives place to epichlorohydrins. This last reaction is promoted by a basic environment, that is, by contacting di-chlorohydrins with an aqueous solution of Ca(OH)$_2$ or NaOH.

Some patents have also been published in the literature in which an inert organic solvent is used, non-miscible with water and in which dichlorohydrins are soluble. In this type of process the reaction is performed at temperatures below the boiling point of the mixture, usually less than 110 °C [28].

2. Catalysts proposed.

As already seen in the scheme reported in the previous chapter (Fig. 2), the reaction between glycerol and gaseous HCl gives place in a first step to monochlohydrins (mainly 1-MCH and small amounts of 2-MCH). Subsequently, hydrochlorination proceeds and the dichlorohydrins (mainly 1,3-DCH and small amounts of 1,2-DCH) are produced. In Table 1, some physico-chemical properties of the chlorinated derivatives of glycerol and of glycerol itself are reported. In the same Table are also reported some properties of acetic acid that is the most commonly employed catalyst.

As mentioned before, glycerol hydrochlorination is catalysed by carboxylic acids, in particular by acetic acid. But this catalyst has the main disadvantage of a relatively low boiling point (117°C) which is near to the temperature normally adopted for this reaction.

<table>
<thead>
<tr>
<th>Glycerol derivates</th>
<th>Molecular mass (g/mol)</th>
<th>Density (g/ m³)</th>
<th>Refractive index</th>
<th>Solubility in water at 25°C</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>92.09</td>
<td>1.261</td>
<td>1.475</td>
<td>Soluble</td>
<td>290</td>
</tr>
<tr>
<td>α-MCH</td>
<td>110.54</td>
<td>1.320</td>
<td>1.480</td>
<td>Soluble</td>
<td>213</td>
</tr>
<tr>
<td>β-MCH</td>
<td>110.54</td>
<td>1.322</td>
<td>-</td>
<td>High</td>
<td>-</td>
</tr>
<tr>
<td>α,γ-DCH</td>
<td>128.99</td>
<td>1.364</td>
<td>1.483</td>
<td>15.6</td>
<td>174</td>
</tr>
<tr>
<td>α,β-DCH</td>
<td>128.99</td>
<td>1.360</td>
<td>-</td>
<td>12.7</td>
<td>182</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>60.05</td>
<td>1,050</td>
<td>-</td>
<td>Soluble</td>
<td>117°C</td>
</tr>
</tbody>
</table>

Table 1-Properties of the components involved in the glycerol hydrochlorination reaction [8].
As a consequence a loss of catalyst by evaporation from the reaction environment can occur. The catalytic performances of acetic acid are reported by different authors sometimes also in comparison with other carboxylic acids. Tesser et al. [12], for example, have used acetic acid as a catalyst with a concentration of 8 mol%, by operating in a hastelloy semibatch stirred reactor at 5.5 bar and 100°C. In these conditions, acetic acid gives place to a good performance, more precisely, after 4 hours of reaction, glycerol was completely converted mainly to 1,3-DCH (89.37% mol). Also B.M. Bell et al. [42] used acetic acid as catalyst. They have studied the reaction at 7.6 bars and 110°C with 5 mol% of acetic acid obtaining a total conversion of glycerol after less than 4h of reaction. The mixture of the reaction products contained about 93 mol% of dichlorohydrins, and 6 mol% of monochlorohydrins. In this case, at the end of the reaction, 2-MCH had a concentration higher than 1-MCH, this because, 2-MCH is much less reactive to further chlorination than 1-MCH, therefore, the amount of 2-MCH (5-6%) formed in the initial phase of the reaction does not further change along the time. Also W.J. Kruper et al. [39] have studied the hydrochlorination reaction of glycerol with gaseous hydrochloric acid in the presence of acetic acid as catalyst. The test was conducted at 5.6 bars and 93°C for 90 minutes. After this time, the obtained reaction products were: 1,3-DCH (92.6 mole%) and 1,2-DCH (1.7 mole%); also both monochlorohydrins were observed (4.4 mole%) and unreacted glycerol (1.0 mole%). These results were obtained by using a purified commercial glycerol. W.J. Kruper et al. [39] have also studied the possibility to conduct the chlorination reaction, with gaseous HCl, in the presence of acetic acid as catalyst, but using crude glycerol as the one coming directly from biodiesel plants. The test was conducted at 8.3 bar and 120°C for 90 minutes. The reaction products, discharged from the reactor, was a liquid with a suspension of a white solid. After filtration the filtrate was analyzed by GC, and the products where 1,3-DCH (95.3 wt%), 1,2-DCH (2.6 wt% ), 2-acetoxy-1,3-dichloropropane (0.7 wt%), 1-acetoxy-2,3-dichloropropane (0.1 wt%) and acetoxychloropropanols (0.87 wt%). Luo et al. [57] have studied the formation of dichlorohydrins from glycerol and HCl, in the presence of acetic acid as catalyst, but using an aqueous solution of hydrochloric acid. They conducted the reaction in a well stirred batch reactor of 500 cm³ reactor. The authors evaluated the trend with time of reagent and products concentrations and observed that glycerol decreased reaching a
minimum after about 100 minutes, while, 1-MCH increased reaching a maximum at the same time and then reacted by forming mainly 1,3 DCH and therefore decreased. After 100 minutes the concentration of glycerol remained low but constant. In all the described cases, the observed behavior, characterized by a maximum of mono-chlorohydrins concentration, clearly means that mono-chlorohydrins are intermediates of the di-chlorohydrins formation, confirming the reaction scheme of Fig. 2.

A recent patent [37] proposed for the hydrochlorination the use of a reactor column consisting in a vertical cylinder with an external recirculation of the liquid reaction mixture. The column was filled with glycerol (97.5%), water (0.5%) and acetic acid as catalyst (2%); such mixture was re-circulated with a flow rate of 5.0 Kg/h. Gaseous HCl was fed from the bottom of the reactor column with a flow rate of 4.6 Kg/h. In the external recirculation line a vacuum rectification column had been inserted, downstream to the reactor, from which a stream composed by a mixture of di-chlorohydrins, water formed during the reaction, and unreacted hydrochloric acid were separated with a flow rate of 9.3 kg/h. The distillation residue is then recycled to the reactor. Finally, a purge of the residue of the distillation products, containing unwanted by-products, was collected in a tank for waste disposal. Krafft et al. have reported, in another recent patent [34], the use of glacial acetic acid as catalyst. The authors used glycerol and acetic acid (10 mole%) with gaseous hydrochloric acid at 110°C. They used, for 2h, a HCl flow rate of 5.2 mol/h, then for additional 100 minutes a flow rate of 3.8 mol/h and finally for 317 minutes a flow rate 1.3 mol/h. They obtained, in this way, a glycerol conversion of 99.1% and 1,3 DCH resulted, also in this case, the main product. (> 75 mole %). Also Siano et al. [36] reported in their patent the use of acetic acid as catalyst. The test was carried out at 100°C by flowing, at atmospheric pressure, gaseous HCl in the reaction environment. A second addition of catalyst during the reaction, has been made to compensate for the loss of catalyst caused by the stripping effect of HCl during the reaction. The duration of the reaction was 5 hours but already in the first hour it was observed a high rate of 1,3-DCH formation. After two hours of reaction the conversion of glycerol was almost complete, but the amount of 1,3-DCH formed was 20 mole%, while, after five hours of reaction the amount of formed 1,3-DCH was about 70 mole%.

The advantage of operating in a flowing stream of gaseous HCl is related to the high volatility of 1.3 DCH in that conditions that allows to recover this product by condensation from the flowing stream. However, as mentioned before, acetic acid is
subjected to some drawbacks such as the catalyst loss by evaporation during the reaction, limiting the reaction temperature to less than 100-110°C. In order to overcome these problems many researchers have investigated the possibility to find new catalysts to substitute acetic acid. Siano et al. [36], for example, studied the use of malonic acid as a possible catalyst and compared its performance with the one of acetic acid. This catalyst was studied under different operating conditions (flowing stream of HCl and total reflux) and at different temperatures. More precisely, the tests were conducted at temperatures ranging from 80°C to 110°C and from the results it was observed that the yield in 1,3-DCH, after three hours of reaction, increased by increasing the temperature, reaching at 110 °C a maximum of about 57 wt%. The same authors [36] have also tested levulinic acid, operating at 100°C under total reflux, with 8 mole % of catalyst and a flowing stream of HCl of 50NL/h. In these conditions, after 3 hours of reaction, the conversion of glycerol was almost complete, but the yield in 1,3-DCH was slightly above 30 mole % being 1-MCH the main product (60 mole %). Also citric acid was found to be a good catalyst of glycerol chlorination [36]. It was used again at a concentration of 8 mole %, temperature of 100°C and a flowing stream of HCl of 50NL/h, for 3 hours. After 3 hours of reaction the residual glycerol was slightly above 5 mole %, and the yield in 1-MCH was greater than 70 mole %. This shows that this catalyst is more selective toward 1-MCH, being the second step of chlorination very slow. The same authors, used also succinic acid and propionic acid, as possible catalysts. The operative conditions were the same of the previous tests. Using succinic acid it has been observed almost complete conversion of glycerol in 150 minutes of reaction and the collected 1,3-DCH was more than 30 mole %. Propionic acid, has shown an activity comparable with acetic acid and after 3 hours of reaction, a complete conversion of glycerol and a yield in 1,3-DCH of 41 mole%. The same results have been reported in more details by Tesser et al. [10-12]. Schreck et al. [35] in their patent have tested a lot of catalysts. Among these the most active, showing a glycerol conversion greater than 90 mole % in 4 hours, resulted: hexanoic acid, 4-trimethylammoniumbutyric acid, 4-dimethylbutyric acid, 4-amino- butyric acid, glycine, glycolic acid, lactic acid, 4-aminophenylacetic acid, 4-hydroxyphenylacetic acid, 4-methylvaleric acid, heptanoic acid, epsilon-caprolactone and gamma-Butyrolactone. Therefore, all these catalysts have activities comparable to the activity of acetic acid, but not all are so selective to 1,3-DCH.
Some carboxylic acids, characterized by high boiling point, such as adipic and caprylic acid have been proposed as catalysts by Krafft et al. [34]. In this case, it was observed, working at 120°C, with HCl in solution, a conversion of glycerol above 95% using caprylic acid as catalyst with a selectivity to 1-MCH of 57.2 % and to 1,3-DCH of 39.7 %. Working at 130 °C, with azeotropic HCl in solution, a conversion of glycerol above 95% was obtained, using caprylic acid (96.7 %) and adipic acid (99.4 %), but a very high selectivity to 1,3-DCH was obtained in the presence of adipic acid (82.3 %) greater than caprilyc acid (60.3 %).

Tesser et al. [12] tested different carboxylic acids, too. All catalysts were tested at 100°C, in conditions of total reflux except for HCl, with a stream of HCl of 24g/min and with a catalyst concentration of 8 mole%, as reported in Table 2. Among the catalysts tested the most active resulted: acetic, malonic, propionic, succinic, citric and levulinic acid. In conclusion, it has been shown by several authors that there are many different catalysts having high boiling that can advantageously replace acetic acid. It is interesting to point out that some carboxylic acids are very selective towards mono-chlorohydrins, in particular 1-MCH, as explained in a recent patent by Di Serio et al. [41]. These authors reported the use of dicarboxylic or hydroxycarboxylic acids as catalysts. All tests were carried out also in this case under reflux using a vertical condenser. The reaction was carried out for 3 hours, at 100°C, using a catalyst concentration of 8 mols %. From the obtained results it can be seen that maleic and fumaric acids show a similar catalytic behavior, with a conversion of glycerol slightly above 90 mols % with an almost total selectivity to 1-MCH.

Also tartaric and oxalic acids, after 3 hours at 100°C, using a catalyst concentration of 8 mole %, have shown a selectivity near to 100 % towards 1-MCH, although the conversion of glycerol was not total (about 70 mol%).

As before mentioned some catalysts promote selectively the first hydrochlorination step, mainly toward the formation of 1-MCH, while dichlorohydrins start to be formed only after the complete conversion of glycerol. Clearly, the hydrochlorination mechanism for these type of catalysts would be different as it will be discussed later. For concluding, an attempt could be made to classify the efficiency of the different catalysts tested by considering the influence of: (i) the length and branching of the alkyl chain of the monocarboxylic acids; (ii) the presence near to the carboxylic group of different functional groups; (iii) the presence in the molecules of more than one carboxylic group.
(di-, tri-carboxylic). These aspects will be considered and discussed in more detail in a next chapter devoted to the reaction mechanism. However, we can summarize here the most important experimental observations: (i) some catalysts are active in glycerol hydrochlorination but promoting only the first step to mono-chlorohydrins, while, others promote both the successive hydrochlorination steps to respectively mono and di-chlorohydrins; (ii) some dicarboxylic acids like adipic acid are more active than monocarboxylic ones provided that the alkyl chain between the two carboxylic acid is not too short to give place to steric hindrance effect or too long to decrease its solubility in glycerol.

At last, we have seen that in some cases catalysts different from carboxylic acids have been used with satisfactory results. However, the used compounds are probably reactive substances that gives place in situ to the true catalyst and normally are all organic substances. On the contrary, Lee et al. [44] investigated, for the same reaction, some inorganic compounds as catalyst. They studied, first of all, the behavior of a commercial polyoxometalate catalyst $\text{H}_3\text{PW}_{12}\text{O}_{40}$. This catalyst was used after a thermal pre-treatment at 300 °C for 2h. The reaction between glycerol and HCl solution was carried out, at 100 °C, for times between 5 and 30 hours. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ showed a total conversion of glycerol in all the experimental runs and the main products formed were di-chlorohydrins. However, small amounts of acrolein, dichloropropane, propanediol, and dichloroethane were obtained as by-products. The authors [44] attributed the total conversion of glycerol and the high selectivity to DCH to the fact that the Brönsted acid sites of the catalyst are particularly active in promoting the glycerol chlorination reaction. The same authors [45] have studied the reaction using many other commercial heteropolyacids catalysts such as: $\text{H}_3\text{PMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X = 0–12$), $\text{H}_4\text{SiMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X = 0–12$), $\text{H}_{3+X}\text{PW}_{12-X}\text{V}_X\text{O}_{40}$ ($X = 0–3$), and $\text{H}_{3+X}\text{PMo}_{12-X}\text{V}_X\text{O}_{40}$ ($X = 0–3$). All catalysts, were tested after a thermal treatment at 300 °C for 2h. $\text{H}_3\text{PMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X = 0–12$) and $\text{H}_4\text{SiMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X = 0–12$) showed 100% conversion of glycerol. Even in these cases, mono-chlorohydrins are intermediate products formed in a great amount but, again small amounts of acrolein, dichloropropane, propanediol, and dichloroethane were obtained as byproducts.

Considering that the tungsten-containing HPA are more acidic than the molybdenum-containing HPA catalysts [46-50], it can be inferred that the acid property of HPA catalysts plays a very important role in determining the selectivity to DCH.
example, H₃PMo₁₂₋ₓWXO₄₀ (X = 0–12) showed a higher selectivity to DCH than H₃SiMo₁₂₋ₓWXO₄₀ (X = 0–12), this can be explained by the fact that the catalyst containing phosphorus as heteroatom is even more acidic than the corresponding HPA with silicon. H₃₊ₓPW₁₂₋ₓVₓO₄₀ (X = 0–3), and H₃₊ₓPMo₁₂₋ₓVₓO₄₀ (X = 0–3) showed both 100% conversion of glycerol in the reaction. The reactions was carried out in a liquid-phase batch reactor (200 ml), 12.6 g of glycerol (reactant), 78.9 g of aqueous HCl solution (37 wt%, chlorination agent), 20 g of H₂O (reaction medium), and 15 g of HPA catalyst were charged into a batch reactor. After the homogeneous solution was heated to 110°C with vigorous stirring (450 rpm), nitrogen was fed into the reactor to keep the reaction pressure at 10 bar. The catalytic reaction was carried out at 110°C for 20 h with vigorous stirring [45]. In both HPA catalysts, containing vanadium, the selectivity to DCH decreases as the amount of vanadium is increased. However, H₃₊ₓPW₁₂₋ₓVₓO₄₀ (x = 0–3) catalysts showed a selectivity for DCH higher than H₃₊ₓPMo₁₂₋ₓVₓO₄₀ (x = 0–3) at the same level of vanadium substitution. The above results can be attributed to the acidic property of HPA substituted catalysts decreasing in the order: tungsten-containing HPA>molybdenum containing HPA>vanadium-containing HPA. The above results strongly support the observation that the acid property of HPA catalysts plays a key role in determining the selectivity for DCH. The more acidic is the HPA catalyst the more active is the catalyst toward the formation of DCH from glycerol. Song et al. [51] have studied the effect of the operating conditions on the production of DCH. They studied, for example, the influence of the stirring rate on the formation of DCH in the presence of H₃PW₁₂O₄₀ as catalyst. The obtained results showed that stirring rate is very important for an efficient formation of DCH in this solvent-free gas (hydrochloric acid)-liquid (glycerol/chlorohydrins) system. However, the selectivity to DCH was almost constant at the highest stirring rates (≥600 RPM), suggesting that mass transfer between glycerol and hydrochloric acid gas could become a key factors in this reaction system. For this reason, the authors have made all the reaction experiments at 900 RPM in order to avoid any mass transfer limitation. Another important aspect is the reaction temperature. The authors [51] studied the effect of the reaction temperature on the formation of DCH from glycerol and gaseous hydrochloric acid. In all the experimental runs, performed at different temperatures, conversion of glycerol was 100% but selectivity to DCH gradually increased by increasing the reaction temperature until reaching a constant value of about 98%, above 150°C, while, selectivity to MCH gradually decreased by
increasing the reaction temperature. It is interesting to note that trichlorohydrins (TCH), a chlorination product of DCH, was formed in a very small amount only at very high reaction temperature. The dependence of product selectivity on the reaction pressure showed the same trend as those of the reaction temperature. In other words, selectivity to DCH increased by increasing both pressure and temperature. The same authors reported also that adding a substance that absorbs water, such as silica gel, the reaction favorably moves toward the formation of DCH [51,52]. This means that water has a negative effect on glycerol chlorination. At last, the same authors [51], using H$_3$PW$_{12}$O$_{40}$ as a catalyst model controlled the effect of the amount of catalyst on the formation DCH and noted that the selectivity to DCH was continuously increased by increasing the catalyst amount. In conclusion, the strong Brönsted acid sites of H$_3$PW$_{12}$O$_{40}$ catalyst favorably contribute to glycerol chlorination to obtain 1,3-DCH.

3. Reaction scheme, reaction mechanism and kinetics

3.1 Hydrochlorination reaction mechanism

The glycerol hydrochlorination is a reaction investigated from a long time but only recently some different mechanisms have been proposed. As the reaction takes place in the presence of a carboxylic acid as catalyst, Santacesaria et al. [10-12] have hypothesized, in agreement with the previous literature [53-54], that in the presence of a strong acid environment, due to HCl, the reaction occurs through an initial esterification. The reaction mechanism proposed by Tesser et al. [10] is represented schematically in Figure 3.
The first step of the scheme of Figure 3 is a nucleophilic addition in which one glycerol hydroxyl attacks the protonated carbonyl group. The first step is then followed by the formation of an oxonium group and subsequently by the addition of a chloride ion that leads to the formation of a monochlorohydrin. The last step is a nucleophilic substitution $S_N2$ and occurs mainly in the alpha position that is much more favored with respect to the beta position. According to the proposed mechanism the product obtained in a larger amount is always 1-MCH. In conclusion, according to the authors the overall reaction is in practice a nucleophilic substitution of a carboxylic group with a chloride ion. It is well known that carboxylic groups are leaving groups better than the hydroxyl groups. For
this reason, carboxylic acids are good catalysts for this reaction, because, in acid environment, easily form esters and can then be substituted by chlorine more easily than the hydroxyl groups. But the acidity of the carboxylic acids cannot be too strong to avoid that the corresponding esters are too stable for completing the reaction. As a matter of fact, by comparing the results reported in the last four example reported at the bottom of Table 2, it is possible to observe that acetic acid is much more active and selective than monochloroacetic acid and the activities and selectivities decrease more and more for respectively di-chloro and tri-chloro acetic acids. A useful parameter to be considered in the mentioned cases is the pKa. As it can be seen, pKa gradually decreases by introducing more chlorine in the acetic acid molecule, that is, mono, di and tri-chloroacetic have a gradually increased acidity with respect to acetic acid and this is detrimental for the hydrochlorination reaction. Probably, this is due to the increased stability of the corresponding ester.

The reaction mechanism described above is in agreement with the experimental evidence that the amount of 1-MCH that is formed is always greater than the amount of 2-MCH. Moreover, 2-MCH does not further reacts to give 1,2-DCH. The absence of two vicinal OH groups, in the case of 2-MCH, probably prevents the formation of the intermediate oxonium so hindering the second chlorination reaction. On the contrary, the 1-MCH can undergo a further chlorination with a mechanism similar to that shown above forming mainly 1,3-DCH accompanied by small quantities of 1,2-DCH. The reaction scheme suggested by Tesser et al. [10] on the basis of the experimental observation is:

![Figure 4- Scheme of the hydrochlorination reactions (see Santacesaria et al. [10-12])](image)

The first step of the reaction, that is, the formation of an ester between glycerol and the carboxylic acid used as catalyst is surely an equilibrium reaction more or less shifted to
the right. The successive hydrochlorination requires again the formation of an ester between a monochlorohydrin and the carboxylic acid and obviously also this reaction is an equilibrium reaction. Tesser et al. [10-12] have suggested that when the constant of the first equilibrium step of esterification is much greater than the second one only the first reaction can occur, while, the second one is prevented, because, all the loaded catalyst is involved in the most favorable equilibrium until the concentration of the main reactant glycerol becomes very low. In conclusion, the reaction mechanism remains the same of Fig. 3 or 4 but the following esterification reactions can have different equilibrium constants:

\[
glycerol + \text{catalyst} \xrightleftharpoons{K_{eq1}} \text{ester}_1 + \text{water} \quad (3)
\]

\[
1-MCH + \text{catalyst} \xrightleftharpoons{K_{eq2}} \text{ester}_2 + \text{water} \quad (4)
\]

If \( K_{eq1} \approx K_{eq2} \) the formation of mono and dichlorohydrins follows a reaction-in-series mechanism according to that proposed. On the contrary, if \( K_{eq1} \gg K_{eq2} \) the catalyst gives mainly monochlorohydrin because the catalyst gives mainly the ester\(_1\) as intermediate. However, also a strong difference in the two direct kinetic constants or a significant influence of the HCl mass transfer limitation, in the initial period of the reaction, can contribute in determining the selectivity to MCH shown by some catalysts. However, it is then interesting to observe that catalysts having \( pKa \geq 4 \) are normally selective to dichlorohydrin, while, the catalysts with \( pKa \) in the range 1.2-3 are more selective to monochlorohydrins. At last, the selectivity to monochlorohydrins shown by different catalysts [41] open a perspective to the industrial production of 1-MCH and consequently also to the production of glycidol that both could become building blocks for other interesting synthesis.

Other two different alternative mechanisms have been proposed in the literature [42,55-59]. Bell et al. [42] suggested a mechanism, derived from an old paper [55], in which esterification is again the first step but, after the ester formation they suggest the formation of a tautomeric cyclic molecule that in the acid environment is converted to an acetoxonium cationic ring which is destabilized by a chloride ion and gives place to
monochlorohydrins after the hydrolysis of the corresponding ester, as it can be seen in the scheme of Figure 5.

\[
\text{HOOCR} + \text{HOCH}_2\text{CH(OH)}\text{CH(OH)}\text{OH} \rightleftharpoons \text{HOCH}_2\text{CH(OH)}\text{CH(OH)}\text{O} + \text{H}_2\text{O}
\]

\[
\text{HOCH}_2\text{CH(OH)}\text{CH(OH)}\text{O} \rightleftharpoons \text{HOCH}_2\text{CH(OH)}\text{CH(OH)}\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{HOCH}_2\text{CH(OH)}\text{Cl} + \text{OHOCR}
\]

**Figure 5.** Mechanism of glycerol hydrochlorination catalyzed by carboxylic acids, according to Bell et al. [42,55].

The further chlorination step would occur with the same mechanism and gives place mainly to 1,3-DCH. This mechanism is intriguing but, as it has been seen, requires a final hydrolysis for closing the catalytic cycle, that is, according to this mechanism, the presence of water would be important for favoring the last indispensable reaction step. On the contrary, it has been demonstrated that aqueous HCl is less active than gaseous anhydrous HCl and that the presence of water negatively affects both the reaction rate and the yields [56].
Luo et al. [57, 58] and Lim et al. [59] both studied the kinetics of glycerol hydrochlorination using aqueous HCl (37% b. w.) and assumed a mechanism similar to the one proposed by Tesser et al. [10] but not considering any possible intermediate specie with the exclusion of the esters, that is, they considered only the double sequence esterification-chlorination applying a second order kinetic law to all the occurring reactions and a pseudo-steady state condition to the esters compounds. This mechanism can be considered a direct bimolecular nucleophilic substitution $S_{N2}$ in which Cl$^{-}$ anion substitute in one step RCOO$^{-}$ in the ester molecule (Figure 6):

Moreover, the chlorination reactions of Fig. 4 (reaction 1 and 3) were considered irreversible. From their kinetic runs it can be observed that the presence of water has a detrimental effect on the reaction rate as recently confirmed by Dmitriev et al. [56].

Xiuquan Ling et al. [60] proposed a reaction scheme slightly different from the one proposed by Tesser et al. [10] reported in Fig. 4. Assuming as reversible only the reaction 3. They studied the kinetics of glycerol chlorination in the presence of different catalysts such as: acetic, propionic, malonic, succinic and adipic and studied in particular the behavior of adipic acid. The authors collected the experimental data by using the GC-MS analysis method. Although these authors announced in the work the proposal of a new mechanism they interpreted all their experimental data with pseudo-first order kinetic laws and the reaction scheme has been presented as reaction mechanism.

More recently, Salmi et al. [61] reinterpreted data from Tesser et al. [10] and their own experimental results with a more general and detailed mechanism in which all the possible intermediate species are considered. Intermediates species considered are: $E_1$ (first ester between glycerol and catalyst, $E_2$ second ester between MCH and catalyst, $I_1^+$ first ionic intermediate (protonated E1), $I_2^+$ second ionic intermediate (protonated E2). The proposed mechanism is the same of Fig. 2 but the kinetic approach is based on the
quasi-steady state hypothesis applied to the four mentioned intermediate species. The authors applied their model to the runs performed by Tesser et al. [10] in the presence of malonic acid and to their runs made in the presence of acetic acid.

4. Reactors and Processes

Until now three companies (DOW Chemicals, Solvay EPICEROL Technology and CONSER SpA ECH-EF=Eco Friendly) have developed their own process for producing di-chlorohydrins from glycerol and HCl, using different catalysts (different carboxylic acids or mixture of them) [23] and some plants have recently been constructed or are still under construction in China (Solvay, DOW Chemicals, CONSER SpA), Thailand (Solvay) and Korea (Dow Chemicals). All these plants need as unit operations: (i) a well mixed gas-liquid reactor, in which glycerol, containing the catalyst in an opportune concentration, is contacted with gaseous HCl (under moderate pressure 1-10 bars) at the reaction temperature (100-120°C); (ii) a heat exchanger to remove the reaction heat being the reaction moderately exothermic. The heat exchanger can also be located inside the reactor; (iii) a stripping unit, to separate the unreacted HCl and eventually also the water produced as a consequence of the occurred hydrochlorination reactions; (iv) the separation units having the scope of recovering pure di-chlorohydrins as feedstock for the successive step of epichlorohydrin synthesis. Di-chlorohydrins are much more volatile than mono-chlorohydrins and glycerol and a distillation column is probably enough for this separation. The residue of the column will contain monochlorohydrins, small amounts of glycerol and the catalyst (a carboxylic acid) if its boiling point is high, otherwise, catalyst must be separated before, for example in the stripping unit. The residue can be recycled at the gas-liquid reactor. Some undesired by products can be formed and a purge is probably necessary. On the basis of the list of the previously described unit operations a simplified scheme (Figure 7) of general validity can be sketched. The operation units of this scheme are all conventional systems not requiring particular mention with the exclusion of the reactor unit requiring: (i) a system providing a large gas-liquid interface area to avoid HCl mass transfer limitation; (ii) a good heat exchange to eliminate the reaction heat maintaining the desired temperature; (iii) a good mixing system to warrant a good dispersion of the gas in the liquid phase and a uniform
composition. There are some different solutions that can be adopted to satisfy the mentioned requisites. A large gas-liquid interface area can be realized by using for example: a falling film reactor with gaseous HCl flowing in countercurrent, a spray tower loop reactor, a Venturi loop reactor, a bubble tray column, a perforated plate column.

**Figure 7.** A simplified scheme of glycerol hydrochlorination

The simplest and economical solution would be a bubble column. Clearly, the optimal choice is related to the reaction conditions, that is, temperature, pressure and catalyst concentration, determining the reaction rate and therefore the HCl consumption. However, the choice is complicated by the corrosiveness of HCl in the presence of water that is formed as by product of the reaction. It is well known, that few materials are compatible whit HCl in the presence of moisture (for example: Glass, Hastelloy, Teflon, enameled steel), therefore, some of the mentioned possibility could be realized with difficulty. The problem of the compatibility of the materials with moisturized HCl is important also for the stripping unit and very probably a neutralization is necessary after this unit to eliminate any trace of this reagent before the separation by distillation of the di-chlorohydrins. Finally, it is important to point out that the process via glycerol has an important advantage with respect to the process via propene, because, the hydrochlorination reaction is highly selective toward the formation of 1,3-DCH. To better emphasize the mentioned advantage a simulation has been made by Santacesaria et al. [11] for comparing the yields of the two processes. A reactive distillation column
has been simulated with a commercial process simulation package (Chemcad 5.2) for two different feeding streams: the first stream was a mixture with the traditional composition (1,3-/1,2-, 30/70%) coming from a via propene process, while, the second one was constituted by pure 1,3-dichlorohydrin. The simulation of the epichlorohydrin reactive column has been performed by introducing the kinetic expression and parameters taken from Carra` et al. [24] by using the model published by Carrà et al. [25]. In both cases the reactive column has been simulated by assuming: total pressure, 1 bar; reboiler heat duty, 17000 kcal/h; 15 theoretical plates; liquid holdup, 0.02 L/stage. The comparison between the two different feeds to the column, is reported in Figure 8, where, epichlorohydrin yields are plotted as a function of the reflux ratio adopted in the reactive column. The yield is the ratio between the distilled epichlorohydrin and the fed dichlorohydrins. As it can be seen, a higher epichlorohydrin yield is always obtained also at low reflux ratios with a feed that is constituted by pure 1,3-dichlorohydrin. Moreover, in order to obtain a satisfactory yield in epichlorohydrin by feeding a 30/70% mixture a very high reflux ratio must be used with obvious greater consumption of energy.

![Figure 9](image_url). Comparison between the epichlorohydrin yields of two different feeds plotted as a function of the reflux ratio adopted in the reactive column [25].
5. References


Theriault, C. N.; Wolfe, C. P.; Glycerin as a Renewable Feedstock for Epichlorohydrin Production. The GTE Process, Clean 2008, 36, 657 – 661


Chapter 7-Homologous chlorinated set of catalysts
1. Introduction

In this chapter it is considered the possible conversion of glycerol into useful products by halogenation reaction: (1,3-chloro-2-propanol (α,γ-DCH), 1,2-chloro-3-propanol (α,β-DCH), 1-chloro-2,3-propanediol (α-MCH), and 2-chloro-1,3-propanediol (β-MCH) using different classes of catalysts: (1) alogenate carboxylic acid; (2) glycolic acids and aminoacids; (3) acyl chloride.

Also the influence of some experimental variables on the activity and selectivity of the glycerol chlorination reaction have been studied, such as the amount of the catalysts and the influence of HCl pressure.

2. Experimental part

The experiments of chlorination have been carried out in a 300 cm$^3$ hastelloy steel reactor equipped with a magnetically driven stirrer that has been supplied by Parr Instrument and allows to work at a maximum of 25 bars. Glycerol and catalyst are initially loaded into the reactor. Then, the reactor is closed and heated to the desired temperature. When the desired temperature was reached, HCl is sent to the reactor keeping constant the overall pressure and reading the volumetric-flow rate that compensate the hydrochloric acid consumption by the reaction. During each experimental run, samples are periodically withdrawn, in order to have the evolution of the reaction products during the time. After 4 h of reaction the hydrochloric acid in excess is flushed by N$_2$ through traps containing NaOH solutions, the stirring is stopped, and the system is brought back to room temperature. A scheme of the fed-batch reactor is reported in Figure 1.

2.1 Chemical and Catalysts

2.1.1 First homologous series: monochloro-, dichloro- and trichloroacetic acids.

In this first part of this work, it is studied in detail the activity and selectivity of some class of catalysts, and more precisely in the first time three series of omologous
carboxylic acid have been studied. At this purpose, we have investigated the behavior of a homologous chlorinated series of catalysts, such as: acetic, monochloroacetic, dichloroacetic and trichloroacetic acid, focusing in particular the attention on both activity and selectivity shown by each catalyst.

![Figure 1](image.png)

**Figure 1.** Gas-liquid reactor using in chlorination reactions. 1- Jacketed reactor made di Hastelloy, approximated capacity 300 ml; 2- cylinder of hydrochloric acid; 3- valve for samples withdrawal of the reaction mix; 4- magnetic stirrer; 5- Reader temperature; 6- manometer; 7- system for suppressing the excess HCl (two Drechsel bottles, arranged in series, which contain a solution of sodium hydroxide).

A kinetic model, based on a reliable mechanism, developed in a previous work [1] but implemented for the HCl gas-liquid partition has been used for interpreting all the kinetic runs. Then, the obtained kinetic constants have been elaborated by using the Taft equation in the attempt to correlate chemical structure of the catalyst and the activity. All the properties of the used catalysts, set for the experimental runs are listed in Table 1. For what concerns the comparison of the studied catalysts, a summary of the catalytic tests performed is reported in Table 2.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Molar mass (gmol⁻¹)</th>
<th>Boiling Point (°C)</th>
<th>Acidity (pKa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid (AA)</td>
<td>60.05</td>
<td>118-119</td>
<td>4.79</td>
</tr>
<tr>
<td>Monochloroacetic Acid (MCA)</td>
<td>94.50</td>
<td>189</td>
<td>2.86</td>
</tr>
<tr>
<td>Dichloroacetic Acid (DCA)</td>
<td>128.94</td>
<td>194</td>
<td>1.25</td>
</tr>
<tr>
<td>Trichloroacetic Acid (TCA)</td>
<td>163.39</td>
<td>197</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Table 1. Used Catalysts: Properties

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Catalyst content (% mol)</th>
<th>Glycerol (g)</th>
<th>Stirring (rpm)</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>MCA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>5.5</td>
</tr>
<tr>
<td>3</td>
<td>DCA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>5.5</td>
</tr>
<tr>
<td>4</td>
<td>TCA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>MCA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>MCA</td>
<td>8.0</td>
<td>150</td>
<td>1200</td>
<td>100</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 2. Experimental Runs: operative conditions
The results, expressed in terms of products distribution after 4 hours of reaction time are reported in Table 3 for the runs performed at constant pressure of 5.5 bars (see Table 2).

**Table 3 - Experimental Run: Products distribution after 4 hours of reaction (mol %)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>α-MCH</th>
<th>β-MCH</th>
<th>α,γ-DCH</th>
<th>α,β-DCH</th>
<th>glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>0.70</td>
<td>7.66</td>
<td>89.37</td>
<td>2.85</td>
<td>0</td>
</tr>
<tr>
<td>MCA</td>
<td>69.98</td>
<td>6.37</td>
<td>10.09</td>
<td>0.33</td>
<td>13.46</td>
</tr>
<tr>
<td>DCA</td>
<td>41.94</td>
<td>4.71</td>
<td>1.99</td>
<td>0</td>
<td>51.98</td>
</tr>
<tr>
<td>TCA</td>
<td>26.64</td>
<td>3.08</td>
<td>1.47</td>
<td>0</td>
<td>69.43</td>
</tr>
</tbody>
</table>

As it is possible to observe, pKa of the catalysts seems to have a strong influence on the reaction rate. We have for the activity that AA>MCA>DCA>TCA, while, the corresponding pKa are: 4.75>2.85>1.48>0.7. In conclusion glycerol conversion decreases by increasing the chlorine atoms numbers in the catalyst. This fact can be better observed by considering the experimental data trends reported in Figure 2, where the cumulative consumption of HCl monitored during the experimental runs is reported.
**Figure 2** - Cumulative consumption of hydrochloric acid for the experimental runs performed with different homogeneous catalysts at the same total pressure of 5.5 bars.

The experimental data trends confirm that acetic acid is much more active than MCA, DCA and TCA.

For what concerns, the influence of the pressure on activity and the selectivity we have focused our attention on MCA, being this catalyst more active then DCA and TCA and having a lower volatility with respect to AA. At this purpose, some runs have been performed, working at different pressures, by using MCA as catalyst and monitoring both the glycerol conversion and the selectivity to mono- and di-chlorhydrins. In Figures 3 it can be seen that an increase in the HCl pressure leads to a markedly increase in glycerol conversion.

![Glycerol conversion as a function of time for runs 2, 5 and 6 of Table 2 for MCA catalyst.](image)

**Figure 3** – Glycerol conversion as a function of time for runs 2, 5 and 6 of Table 2 for MCA catalyst.
In Fig. 4, it can be seen that the selectivity to monochlorohydrins decreases with pressure, while, on the contrary selectivity to dichlorhydrins increases as it can be seen in Fig. 5.

**Figure 4** - Selectivity to monochlorohydrins as a function of time for runs 2, 5 and 6 of Table 2 for MCA catalyst.
Figure 5 - Selectivity to dichlorohydrins as a function of time for runs 2, 5 and 6 of Table 2 for MCA catalyst.

Moreover, Figure 2, shows that in the first part of the reaction the hydrochloric acid consumption is higher, because there are present two separated effects that are: (i) the HCl migration from the gaseous to the liquid phase, (ii) the reaction rate effect. Then the consumption slowly declines for MCA, DCA and TCA with a smaller slope and a smooth decrease of the HCl consumption proceeds through the rest of the experimental run. The high rate of HCl consumption observed in the initial part of the runs suggest that in some cases gas-liquid mass transfer could be operative. For describing mass transfer rates HCl solubility data in the reaction environment are necessary. These data are necessary also because HCl concentration appears in the kinetic laws. Solubility data of this type are not available in the literature and experimental data have been collected by us.
2.2 Mass transfer and HCl solubility

First of all, the solubility tests have been experimentally performed by imposing a HCl pressure on the mixture of the chosen composition recording, from time to time, the HCl flow-rate. The experimental results are reported in Figure 6 in terms of cumulative consumption, while, in Tab. 4 are reported all the experimental conditions for the mentioned runs.

Table 4 – Solubility tests: experimental conditions. \( X_i \) is the molar fraction referred to the component \( i \).

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure (bar)</th>
<th>( X_{\text{Gly}} ) mol</th>
<th>( X_{\text{H2O}} ) mol</th>
<th>( X_{\alpha} ) mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>2.0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S-2</td>
<td>5.5</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S-3</td>
<td>5.5</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Then HCl solubility at 100 °C was estimated by calculation adopting the PSRK state equation and using CHEMCAD v.6.3. From these calculations it is possible to obtain estimated values for the HCl equilibria concentrations in the liquid phase. These values are reported in Table 5, for the different pure compounds present in the reaction media.

Table 5 - HCl solubility concentration in the different compounds present in the reaction media.

<table>
<thead>
<tr>
<th>Value [mol/cm(^3)]</th>
<th>0.01127</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{HCl}^W} )</td>
<td></td>
</tr>
<tr>
<td>( K_{\text{HCl}^{\text{Gly}}} )</td>
<td>0.01291</td>
</tr>
<tr>
<td>( K_{\text{HCl}^{\alpha\beta}} )</td>
<td>0.00671</td>
</tr>
<tr>
<td>( K_{\text{HCl}^{\alpha}} )</td>
<td>0.01008</td>
</tr>
<tr>
<td>( K_{\text{HCl}^{\alpha\gamma}} )</td>
<td>0.00676</td>
</tr>
</tbody>
</table>
The solubility in a multicomponent reaction mixture can be calculated as the sum between the product of the molar fraction of the $i$ component for the related solubility contributions.

$$\text{Solubility} = \sum x_i \cdot K_{H^\text{Cl}}^i$$

(1)

In this way, the Henry’s constant can be calculated as it follows:

$$H_{H^\text{Cl}} = \frac{\text{Solubility}}{p}$$

(2)

With P the reactor’s pressure.

The values obtained with this predictive approach resulted always higher than the experimental ones. Therefore, the solubility function reported in (1) has been multiplied by a factor $\gamma$, that have been regressed on the experimental data for each solubility run. This factor correct the discrepancy between experimental solubility and PSRK prediction. The simulations of the experimental runs after the introduction of the corrective $\gamma$ factor are reported in Figure 6, while the values of $\gamma$ obtained by regression analysis are reported in Table 6.
Figure 6 – Solubility tests: dots represent the experimental data, lines the simulations curves.

Table 6 – Solubility tests: regressed parameters.

<table>
<thead>
<tr>
<th>Run</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.266</td>
</tr>
<tr>
<td>2</td>
<td>0.201</td>
</tr>
<tr>
<td>3</td>
<td>0.308</td>
</tr>
</tbody>
</table>

A further confirmation of the validity of this approach has been made on different systems available in the literature [2] considering the solubilities of HCl in respectively methanol, ethanol and water.

In Table 7 are compared the experimental solubility data and the values estimated with the PSRK equation. As it can be seen, also in those cases solubilities from PSRK equation are always overestimated and this justify the introduction of the corrective factor $\gamma$.  

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Table 7– Calculated and experimental solubilities (*) of some known substances.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Temperature (°C)</th>
<th>Experimental [17]</th>
<th>Calculated with PSRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0</td>
<td>838</td>
<td>1165</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>756</td>
<td>926</td>
</tr>
<tr>
<td>Methanol</td>
<td>0</td>
<td>1092</td>
<td>2647</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>877</td>
<td>1578</td>
</tr>
<tr>
<td>H2O</td>
<td>0</td>
<td>829</td>
<td>1554</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>724</td>
<td>1259</td>
</tr>
</tbody>
</table>

(*) Solubilities expressed in g of HCl/1000 g of solvent

For what concerns the mass-transfer rate expression, we have adopted the double-film theory developed by Whitman assuming, as a first approximation, that no resistance to mass transfer is given by the gas-side film. In this way, it is possible to write a mass-transfer rate expression for HCl in the liquid film as it follows:

\[
J_{\text{HCl}} = k_t \cdot a \cdot ([\text{HCl}]^* - [\text{HCl}]) = \beta \cdot ([\text{HCl}]^* - [\text{HCl}])\text{[=]} \text{mol/(cm}^3 \cdot \text{min]}(3)
\]

Where, \([\text{HCl}]^*\) represent the equilibrium concentration at the gas-liquid interphase evaluated as:

\[
[\text{HCl}]^* = H_{\text{HCl}} \cdot P \tag{4}
\]

2.3 Property-structure study

In order to correlate the activity of the used catalysts with the related chemical structure, a first attempt has been made by considering the dependence of the kinetic constants, obtained by mathematical regression analysis on the fed-batch experimental runs, reported in Table 8, with the pKa values [3]. In this way, a rough linear dependence as it can be seen in Figure 7.
**Table 8** – List of the parameters obtained by mathematical regression analysis on the experimental data.

<table>
<thead>
<tr>
<th>Run</th>
<th>$k_1^*$</th>
<th>$k_2^*$</th>
<th>$k_3^*$</th>
<th>$k_4^*$</th>
<th>$k_{1^*}$</th>
<th>$k_{3^*}$</th>
<th>$\beta^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17022</td>
<td>1793.67</td>
<td>20332.70</td>
<td>645.14</td>
<td>1.76E-06</td>
<td>5.74E-07</td>
<td>3.00</td>
</tr>
<tr>
<td>2</td>
<td>2896.72</td>
<td>223.40</td>
<td>422.87</td>
<td>12.99</td>
<td>1.82E-07</td>
<td>5.55E-07</td>
<td>2.99</td>
</tr>
<tr>
<td>3</td>
<td>986.59</td>
<td>102.79</td>
<td>143.08</td>
<td>1.93E-05</td>
<td>1.40E-06</td>
<td>5.75E-07</td>
<td>3.25</td>
</tr>
<tr>
<td>4</td>
<td>509.43</td>
<td>57.95</td>
<td>129.61</td>
<td>1.13E-04</td>
<td>1.14E-07</td>
<td>5.72E-07</td>
<td>2.38</td>
</tr>
<tr>
<td>5</td>
<td>2896.72</td>
<td>223.40</td>
<td>422.87</td>
<td>12.99</td>
<td>1.82E-07</td>
<td>5.55E-07</td>
<td>0.025</td>
</tr>
</tbody>
</table>

*Expressed in $[\text{cm}^3/\text{mol}^2 \text{min}^{-1}]$

** Expressed in $[\text{min}^{-1}]$

**Figure 7** – Plot of the kinetic constant against the pKa of each catalyst.

Following on this analysis, we have tried to deepen the calculations by using the generalized Taft equation [2,4-7] provided by the following relation:

$$\log \left( \frac{k_i}{k_0} \right) = \rho^* \cdot \sigma^* + \delta \cdot E_s$$  \hspace{1cm} (5)
The original approach of Taft equation, considers a property-structure study on the reagents of a chemical reaction. In our work, this equation has been applied to the investigated catalysts, considering that the catalyst is very probably involved in the reactions forming esters with glycerol and monochlorohydrin. The carboxilic group is a better leaving group than hydroxil and this is probably the intimate mechanism of this reaction. The Taft equation allows to calculate two contributes relative to the reactivity of the adopted catalyst, that are respectively $\rho^*$ and $\delta$. These two contributes represent the sensitivity to both the electronic nature of the substituents ($\rho^*$), and the steric effect ($\delta$). To apply this approach, it is necessary to know both the $\sigma^*$ and $E_s$ values of the various substituents introduced in the acetic acid, this last assumed as a reference molecule. These values can be taken from the literature [7]. These two contributions represent respectively the polar and the steric substituent constants. It is now possible to apply the Taft equation (5), by determining through a simultaneous fitting on the kinetic constants reported in Table 8, the values of $\delta$ and $\rho^*$. The obtained values are reported in Table 9.

**Table 9- Taft values $\delta$ and $\rho^*$**

<table>
<thead>
<tr>
<th></th>
<th>$\delta$</th>
<th>$\rho^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>-0.21786</td>
<td>-0.76789</td>
</tr>
<tr>
<td>$k_2$</td>
<td>-0.44228</td>
<td>-0.93646</td>
</tr>
<tr>
<td>$k_3$</td>
<td>-1.08825</td>
<td>-1.78066</td>
</tr>
</tbody>
</table>

In Fig. 9 and 10 it is possible to appreciate the linear trends obtained for both the steric and polar contribution of the Taft equation. These plots clearly show that both polar and steric effect are important in all the hydrochlorination occurring reactions. This represents an improvement in respect to consider pKa as unique factor influencing activity and selectivity in the mentioned reactions.
Figure 9 – Taft’s equation steric contribution diagram for the different used catalysts.

Figure 10 – Taft’s equation polar contribution diagram for the different used catalysts.
3. Kinetic interpretation of the experimental runs

The collected experimental data have been interpreted with a gas-liquid kinetic model that is able to describe all the physical and chemical phenomena that occur during the reaction. In particular, a gas-liquid fed-batch reactor scheme has been considered, by taking into account both the HCl mass transfer from the gas to the liquid phase and the reaction rates of the reaction network.

We have considered the following reaction scheme:

1] Gly + HCl $\leftrightarrow$ $\alpha$
2] Gly + HCl $\rightarrow$ $\beta$
3] $\alpha$ + HCl $\leftrightarrow$ $\alpha,\gamma$
4] $\alpha$ + HCl $\rightarrow$ $\alpha,\beta$

For this reaction set it is possible to write the following kinetic rate laws, all expressed in mol/(cm$^3$·min).

\[ r_1 = k_1 \cdot [\text{Cat}] \cdot [\text{Gly}] \cdot [\text{HCl}] - k_{-1} \cdot [\text{Cat}] \cdot [\text{H}_2\text{O}] \cdot [\alpha] \]  \hspace{1cm} (6)

\[ r_2 = k_2 \cdot [\text{Cat}] \cdot [\text{Gly}] \cdot [\text{HCl}] \hspace{1cm} (7) \]

\[ r_3 = k_3 \cdot [\text{Cat}] \cdot [\text{Gly}] \cdot [\alpha] - k_{-3} \cdot [\text{Cat}] \cdot [\text{H}_2\text{O}] \cdot [\alpha,\gamma] \]  \hspace{1cm} (8)

\[ r_4 = k_4 \cdot [\text{Cat}] \cdot [\text{Gly}] \cdot [\alpha] \hspace{1cm} (9) \]

In order to describe the evolution with the time of each chemical compound, it is then possible to write the mass balance as it follows:

\[
\text{moles accumulated} = \text{moles (reacted + transferred – sampled)} [= \text{mol} \cdot \text{min}^{-1}]
\]

Starting from this balance equation, it is possible to write the following differential equations for respectively the liquid and the gas phase.

**Liquid phase**

\[
\frac{d[n_{\text{ Gly}}]}{dt} = -r_1 \cdot V_R - F_{Gly}
\]  \hspace{1cm} (11)
\[
\frac{dn_\alpha}{dt} = (+r_1 + r_2 + r_3) \cdot V_R - F_\alpha
\] (12)

\[
\frac{dn_{\alpha \beta}}{dt} = +r_3 \cdot V_R - F_{\alpha \beta}
\] (13)

\[
\frac{dn_\beta}{dt} = +r_2 \cdot V_R - F_\beta
\] (14)

\[
\frac{dn_{\alpha \beta}}{dt} = +r_4 \cdot V_R - F_{\alpha \beta}
\] (15)

\[
\frac{dn_{H_2O}}{dt} = (+r_1 + r_2 + r_3 + r_4) \cdot V_R - F_{H_2O}
\] (16)

\[
\frac{dn_{HCl}}{dt} = (-r_1 - r_2 - r_3 - r_4) \cdot V_R + J_{HCl} \cdot V_R - F_{HCl}
\] (17)

**Gas phase**

\[
\frac{dn_{HCl}^{gas}}{dt} = F_{HCl}^{IN} - J_{HCl} \cdot V_R
\] (18)

Where \( F_i \) represents the molar flow-rate related to the component \( i \), necessary to consider the sampling amount (each run is characterized by 2 samples of respectively 20 cm\(^3\)).

While \( F_{HCl}^{IN} \) represents the inlet gaseous HCl molar flow-rate calculated as it follows:

\[
F_{HCl}^{IN} = K_p \cdot (P_{SET} - P_{TOT})
\] (19)

Where \( P_{SET} \) represents the set point pressure experimentally imposed, while \( P_{TOT} \) is total pressure of the system calculated considering the atmosphere in the reactor as an ideal gas constituted by pure HCl, whose value can be calculated as it follows:

\[
P_{TOT} = \frac{n_{HCl}^{gas} \cdot R \cdot T}{V_{GAS}}
\] (20)

Here, \( V_{GAS} \) is the volume of the gas head space expressed in cm\(^3\).

The experimental runs have been submitted to mathematical regression analysis, determining, on the experimental data, both the kinetic and mass transfer constants, for all the involved reactions.

The model is able to describe properly all the collected experimental data. The first four runs are characterized by a relatively high \( \beta \) value, this fact represents an indication that the gas-liquid mass transfer has not a limiting effect for these runs.
differs from the others for the $\beta$ value, because, very probably this is the only experimental run performed at 2.0 bar. Furthermore, as it is possible to observe in Table 8, the reverse kinetic constants of reactions 1 and 3 can be considered negligible. For this reason, all the reactions occurring in the reaction network can be considered irreversible. A further interesting effect that can be pointed out by observing the kinetic constants, is related to the selectivity of each catalyst to give mono- and di- chlorohydrin. In fact by comparing the $k_1/k_2$ ratios for all the catalytic systems MCA resulted much more selective to $\alpha$-mono-chlorohydrin with respect to the other catalysts. Moreover, $k_3/k_4$ ratios show that all catalysts are selective to give 1,3-di-chlorohydrin instead of 1,2-di-chlorohydrin.

4. Conclusions

In this chapter, starting from acetic acid catalyst as reference molecule, the effect of introducing one, two or three chlorine atoms in the molecule on the activity and selectivity in glycerol hydrochlorination reaction has been investigated. In particular, we observed that pKa of the catalyst has an important role in defining activity and selectivity. For a good activity and selectivity to 1,3-di-chlorohydrin a pKa in the range between 4-5 seems the optimal choice. Acetic acid has this characteristic but is not the ideal catalyst because has a high volatility in the reaction conditions. It is important therefore to find less volatile catalysts maintaining high both activity and selectivity. According to our experience on many different catalysts, the criterium of the choice based only on the pKa value is not sufficient for predicting the catalyst behavior. An improvement is represented by the Taft equation approach. It has been shown by applying the Taft equation to the homologous series: acetic, mono chloroacetic, dichloro acetic, trichloro acetic acids that both the polar and steric effect are important in determining the catalyst behavior in terms of activity and selectivity. For what concernig this study has also been evaluated the HCl solubilities in the reaction environment by adopting an experimental plus predictive mixed approach.

It has been verified that PSRK equation gives always overestimated values of HCl solubility and a corrective factor has been determined. At last, a mathematical model has been developed and successfully applied to the fed-batch runs, describing with a
good approximation all the experimental data. By using this gas-liquid kinetic model, it was possible to determinate the kinetic parameters, usefully employed to perform the property-structure study based on the use of the Taft equation.
5. Reference


Chapter 8-Glycolic Acids and Aminoacids Sets
1. Introduction

In chapter 8 the work carried out by employing, in the glycerol chlorination reaction, two sets of homologous catalysts, (in particular a series of aminoacids and a series of glycolic acids) is described. The main scope of the work was to compare their activity in chlorination and to acquire a scientific insight about the effect of the presence of different functional groups in the catalyst molecule on its activity and on products distribution, more precisely the selectivity to monochlorohydrins (MCHs) and to dichlorohydrins (DCHs).

For this purpose, the tests have been performed under the same conditions of temperature, pressure and stirring speed, i.e. T= 100°C, P= 4.5 barg, catalyst concentration = 8mol % with respect to glycerol, reaction time = 4h, stirring rate=1000 rpm.

For each run, liquid phase samples have been withdrawn, respectively at 1, 3 and 4 h, in order to evaluate concentration-time profiles. These samples, previously neutralized with an excess of sodium bicarbonate, were analyzed at the gas chromatograph, obtaining in such a way the glycerol conversion and the chlorinated products distribution.

At the end of the run, after 4h of the reaction, HCl in excess is eliminated from the system by bubbling in traps containing NaOH. Stirring is then stopped and the system is cooled to room temperature.

2. Chemical and Catalysts

2.1 Experimental Runs

The catalysts tested in the series of glycolic acids are, respectively: glycolic acid (GA), thioglycolic acid (TGA) and diglycolic acid (DGA); in the series of amino acids, the following catalyst have been selected for testing in the target reaction: cysteine (CYS), aspartic acid (ASPA) and glutamic acid (GLUA).

All the reagents used for the experimental runs have been purchased from Sigma Aldrich at the highest level of purity available (glycerol anhydrous >99.0% and catalyst >99.0%)
and were used as received without further purification. Gaseous hydrochloric acid has been purchased from Air Liquide Italy (99.8% vol).

In Tab. 1, an overview of all the performed experiments is reported, together with the experimental conditions and the amounts of reactants loaded in the reactor.

**Table 1.** Experimental conditions for all runs.

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>$W_{\text{cat}}$ (g)</th>
<th>$W_{\text{Gly}}$ (g)</th>
<th>$T$ (°C)</th>
<th>$P$ (barg)</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASPA</td>
<td>17.30</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>3.90</td>
</tr>
<tr>
<td>2</td>
<td>GLUA</td>
<td>19.13</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>4.07</td>
</tr>
<tr>
<td>3</td>
<td>CYS</td>
<td>15.75</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>8.37</td>
</tr>
<tr>
<td>4</td>
<td>GA</td>
<td>9.89</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>3.83</td>
</tr>
<tr>
<td>5</td>
<td>DGA</td>
<td>17.43</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>2.90</td>
</tr>
<tr>
<td>6</td>
<td>TGA</td>
<td>11.98</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>3.73</td>
</tr>
<tr>
<td>7</td>
<td>GLUA</td>
<td>4.80</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>4.07</td>
</tr>
<tr>
<td>8</td>
<td>GLUA</td>
<td>9.60</td>
<td>150</td>
<td>100</td>
<td>4.5</td>
<td>4.07</td>
</tr>
<tr>
<td>9</td>
<td>GLUA</td>
<td>19.13</td>
<td>150</td>
<td>100</td>
<td>1.0</td>
<td>4.07</td>
</tr>
<tr>
<td>10</td>
<td>GLUA</td>
<td>19.13</td>
<td>150</td>
<td>100</td>
<td>8.0</td>
<td>4.07</td>
</tr>
<tr>
<td>11</td>
<td>AA</td>
<td>7.8</td>
<td>150</td>
<td>100</td>
<td>8.0</td>
<td>4.79</td>
</tr>
</tbody>
</table>

A first comparison between all the catalysts can be made in terms of products distribution after 4 h of reaction time, as reported in Tab. 2 for the experimental runs performed at constant pressure of 4.5 barg and temperature of 100 °C.

From the data reported in Tab. 2 and Fig. 1 related to the first set of catalysts (amino acids), it can be observed that a total conversion of glycerol is reached, in the adopted conditions, only by using glutamic acid. The results of glycolic acids as catalysts are reported in Tab. 2 and fig. 2.
Table 2. Experimental Runs: product distribution after 4 h of reaction (mol %), T=100°C, catalyst 8% mol – amino acids series and glycolic acids series

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat</th>
<th>α-MCH</th>
<th>β-MCH</th>
<th>α,γ-DCH</th>
<th>α,β-DCH</th>
<th>Gly</th>
<th>MCHs selectivity</th>
<th>DCHs Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASPA</td>
<td>69.1</td>
<td>6.6</td>
<td>13.4</td>
<td>0.4</td>
<td>10.5</td>
<td>84.6</td>
<td>15.4</td>
</tr>
<tr>
<td>2</td>
<td>GLUA</td>
<td>22.2</td>
<td>4.3</td>
<td>72.3</td>
<td>1.2</td>
<td>0</td>
<td>26.5</td>
<td>73.5</td>
</tr>
<tr>
<td>3</td>
<td>CYS</td>
<td>50.1</td>
<td>5.3</td>
<td>3.4</td>
<td>0.2</td>
<td>41.0</td>
<td>93.9</td>
<td>6.1</td>
</tr>
<tr>
<td>4</td>
<td>GA</td>
<td>48.4</td>
<td>5.2</td>
<td>45.4</td>
<td>1.0</td>
<td>0</td>
<td>53.6</td>
<td>46.4</td>
</tr>
<tr>
<td>5</td>
<td>DGA</td>
<td>57.4</td>
<td>0.7</td>
<td>40.8</td>
<td>1.1</td>
<td>0</td>
<td>58.1</td>
<td>41.9</td>
</tr>
<tr>
<td>6</td>
<td>TGA</td>
<td>32.4</td>
<td>5.6</td>
<td>60.6</td>
<td>1.4</td>
<td>0</td>
<td>38.0</td>
<td>62.0</td>
</tr>
<tr>
<td>11</td>
<td>AA</td>
<td>0.6</td>
<td>7.5</td>
<td>89.3</td>
<td>2.6</td>
<td>0</td>
<td>8.4</td>
<td>91.6</td>
</tr>
</tbody>
</table>
Figure 1. Products distribution and glycerol consumption for catalysts GLUA, ASPA and CYS (P=4.5 barg, T=100°C, cat. conc. 8% mol)
Figure 2. Products distribution and glycerol consumption for catalysts GA, DGA and TGA (P=4.5 barg, T=100°C, cat. conc. 8% mol
This catalyst has also shown a relatively high selectivity to $\alpha,\gamma$-DCH, resulting in performances quite similar to acetic acid, but with the advantage of a very low volatility (melting point 199°C, soluble in the reaction mixture). It is also possible to observe that ASPA and GLUA, characterized by only two carboxylic groups and by similar pKa value, have shown higher activity than CYS. For what concerns selectivity, ASPA and CYS are more selective to monochlorohydrins production, while dichlorohydrins are the main products when GLUA is used as catalyst.

It is possible to appreciate that all the catalysts in this set have shown a complete conversion of glycerol. In every case, a mixture of mainly $\alpha$-MCH and $\alpha,\gamma$-DCH has been obtained, but thioglycolic acid produces much more dichlorohydrins than monochlorohydrins.

From this first catalysts screening, it can be concluded that glutamic acid has shown the best performances, both in terms of activity and selectivity to the desired products, which are dichlorohydrins. For this reason, this catalyst has been deeply studied by performing other tests with the aim to investigate the effect of hydrochloric acid pressure (runs 9-10 in Tab.1) and catalyst concentration (runs 7-8 in Tab.1).

The results obtained from the mentioned tests are reported in the Tab.3 and Fig. 3 and 4

**Table 3.** Experimental Runs: product distribution after 4 h of reaction (mol %) – Glutamic acid at different pressures and at different concentrations of catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>$\alpha$-MCH</th>
<th>$\beta$-MCH</th>
<th>$\alpha,\gamma$-DCH</th>
<th>$\alpha,\beta$-DCH</th>
<th>Gly</th>
<th>MCHs selectivity</th>
<th>DCHs selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>64,2</td>
<td>6,4</td>
<td>28,7</td>
<td>0,7</td>
<td>0</td>
<td>70,6</td>
<td>29,4</td>
</tr>
<tr>
<td>8</td>
<td>51,3</td>
<td>7,0</td>
<td>40,7</td>
<td>1,0</td>
<td>0</td>
<td>58,3</td>
<td>41,7</td>
</tr>
<tr>
<td>2</td>
<td>22,2</td>
<td>4,3</td>
<td>72,3</td>
<td>1,2</td>
<td>0</td>
<td>26,5</td>
<td>73,5</td>
</tr>
<tr>
<td>9</td>
<td>74,2</td>
<td>6,2</td>
<td>12,7</td>
<td>0,4</td>
<td>6,5</td>
<td>86,0</td>
<td>14,0</td>
</tr>
<tr>
<td>10</td>
<td>7,9</td>
<td>8,1</td>
<td>81,6</td>
<td>2,4</td>
<td>0</td>
<td>16,0</td>
<td>84,0</td>
</tr>
</tbody>
</table>

The tests reported in Tab.3 have been carried out respectively at different pressures and different amounts of Glutamic acid. More precisely tests 2, 7, 8 have been performed at
constant pressure, by using respectively 2, 4 and 8 mol% of catalyst, while the tests 2, 9, 10 at constant catalyst concentration (8% mol) respectively at 4.5, 1.0 and 8.0 barg of HCl pressure.

As it can be seen in Fig. 3, the increase of HCl pressure has a positive effect on both the activity and the selectivity of the reaction. In fact, at 1 barg a complete conversion of glycerol was not reached, even after 4 hours of reaction, while at 4.5 barg the glycerol is completely converted and the selectivity to dichlorohydrins is rather high. A further increase of pressure to 8 barg, results in a further increase of selectivity, reaching 84 mol% of $\alpha,\gamma$-DCH. The observed behavior can be explained by considering that an increase of pressure leads to an increase in HCl solubility.

![Figure 3. Products distribution (mol %) after 4 h of reaction using GLUA (8% mol), T=100°C, at different pressures.](image)

The effect of catalyst concentration has been also studied by adopting a medium-level pressure of 4.5 barg and 100 °C, while the amount of catalyst (GLUA) has been varied as reported in Tab. 1 (runs 2-7-8). The corresponding obtained results are shown in Fig. 3.
In this case we can observe that by passing from 2 to 8 mol.% of catalyst, the selectivity has been gradually shifted from monochlorohydrins to dichlorohydrins as can be expected from the reaction sequence. In all the tests of this group, unlike the tests carried out at different pressures, it can be noted that there is never a glycerol residue; in every case, monochlorohydrins and dichlorohydrins are the only detected compounds, indeed.

2.2 Kinetics and modelling

All the collected experimental data have been simulated by means of a gas-liquid kinetic model that has been already reported elsewhere in details [1]. Even if all the involved reactions can be assumed as reversible, previous investigation have demonstrated that only the formation of $\alpha$-monochlorohydrin and $\alpha,\gamma$-dichlorohydrin have a weak equilibrium behavior [2-6]. Notwithstanding this aspect, the kinetic constants of the reverse reactions are quite low (see Table 4) and, very likely, are negligible.
The constants for β-monochlorohydrin and α,β-dichlorohydrin production are lower of some order of magnitude, so completely excluded from the present model. In conclusion, the model has been developed by assuming that the formation of β-monochlorohydrin and α,β-dichlorohydrin are considered irreversible reactions, while the other chlorination steps have been considered reversible. In this way, it is possible to write the following simplified reaction scheme with related reaction rate expressions, all expressed in \([\text{mol}/(\text{L} \cdot \text{min})]\).

\[
\begin{align*}
\text{Gly} + \text{HCl} & \overset{\tau_1}{\underset{\tau_2}{\rightleftharpoons}} \alpha\text{-MCH} + \text{H}_2\text{O} \\
\tau_1 &= [\text{CAT}] \cdot (k_1 \cdot [\text{Gly}] \cdot [\text{HCl}] - k_{-1} \cdot [\text{H}_2\text{O}] \cdot [\alpha\text{-MCH}]) \\
\text{Gly} + \text{HCl} \quad \rightarrow \quad \beta\text{-MCH} + \text{H}_2\text{O} \\
\tau_2 &= [\text{CAT}] \cdot (k_2 \cdot [\text{Gly}] \cdot [\text{HCl}]) \\
\alpha\text{-MCH} + \text{HCl} & \overset{\tau_3}{\underset{\tau_4}{\rightleftharpoons}} \alpha,\gamma\text{-DCH} + \text{H}_2\text{O} \\
\tau_3 &= [\text{CAT}] \cdot (k_3 \cdot [\alpha\text{-MCH}] \cdot [\text{HCl}] - k_{-1} \cdot [\text{H}_2\text{O}] \cdot [\alpha,\gamma\text{-DCH}]) \\
\alpha\text{-MCH} + \text{HCl} \quad \rightarrow \quad \alpha,\beta\text{-DCH} + \text{H}_2\text{O}
\end{align*}
\]

**Table 4.** Kinetic and mass transfer parameters obtained by mathematical regression analysis (k are in \((\text{cm}^3/\text{mol})^2/\text{min}, \beta \text{ in min}^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>ASPA</th>
<th>GLUA</th>
<th>CYS</th>
<th>GA</th>
<th>DGA</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>1.56E+04</td>
<td>3.47E+04</td>
<td>1.61E+03</td>
<td>2.71E+04</td>
<td>1.95E+04</td>
<td>0.98E+05</td>
</tr>
<tr>
<td>(k_2)</td>
<td>1.14E+03</td>
<td>1.91E+03</td>
<td>1.62E+02</td>
<td>1.78E+03</td>
<td>8.20E+02</td>
<td>6.41E+03</td>
</tr>
<tr>
<td>(k_3)</td>
<td>1.69E+03</td>
<td>6.72E+03</td>
<td>2.65E+02</td>
<td>2.28E+03</td>
<td>2.69E+03</td>
<td>5.37E+03</td>
</tr>
<tr>
<td>(k_4)</td>
<td>2.59E+00</td>
<td>8.28E-01</td>
<td>9.81E-01</td>
<td>6.56E-01</td>
<td>1.38E+00</td>
<td>9.20E-01</td>
</tr>
<tr>
<td>(k_{-1})</td>
<td>1.44E-05</td>
<td>6.05E-13</td>
<td>3.19E-06</td>
<td>2.61E-12</td>
<td>5.17E-06</td>
<td>1.06E-05</td>
</tr>
<tr>
<td>(\beta)</td>
<td>0.0211</td>
<td>0.0534</td>
<td>0.0458</td>
<td>0.0682</td>
<td>0.0390</td>
<td>0.0501</td>
</tr>
</tbody>
</table>
\[ r_i = [\text{CAT}](k_i' [\alpha \cdot \text{MCH}] [\text{HCl}]) \] (4)

As simplifying assumption, the reverse of reaction (3) has the same kinetic constant of reaction (1). With this approach the model contains less adjustable parameters. Moreover, it has been verified that the use of different reverse rate constants does not improve significantly the fitting of experimental data and the two obtained constants (k-1 and k-3) have practically the same value.

In order to describe the evolution with the time of each chemical compound, it is possible to write the mass balance as it follows.

\[
\frac{1}{V} \cdot \frac{dn_m^i}{dt} = \sum r_k + \sum J_m - F_m 
\] (5)

Where \( n_m^i \) stands for moles of the \( m \)-th chemical specie, \( i \) for the phase (gas or liquid), \( V \) is the reaction volume, \( r_k \) the reaction rate expression, \( J_m \) the volumetric mass transfer rate and \( F_m \) the contribution of the sample withdrawn from the system. Therefore, for what concerns the gas-liquid HCl mass transfer, the Whitman two films theory has been adopted, by imposing the following mass transfer rate expression.

\[
J_{\text{HCl}} = kL \cdot a \cdot ([\text{HCl}]^* - [\text{HCl}]) = \beta \cdot ([\text{HCl}]^* - [\text{HCl}]) = \beta \cdot ([\text{HCl}]^* - [\text{HCl}]) \text{ mol/(L·min)}
\] (6)

The mass transfer coefficient \( \beta \) is considered as an additional adjustable parameter, while the solubility has been calculated by using the UNIFAC model (see [1] for details). In this way, by solving the ODE (Ordinary Differential Equation) system (5) it is possible to obtain, by mathematical regression analysis on the collected experimental data, the
kinetic constants reported in Tab. 4 and the parity plot reported in Fig. 5.

Figure 5. Parity plot for all catalysts studied in this chapter.

As it can be appreciated from these diagrams, the fitting can be considered satisfactory. By observing the profiles reported in Fig. 6 and Fig. 7 it is possible to observe that the model is able to describe quite correctly also the runs made at different pressure and different catalyst concentration.
Figure 6. α,γ-DCH production and glycerol consumption for the runs at different pressures.

Figure 7. α,γ-DCH production and glycerol consumption for the runs at different catalyst concentrations.
For what concerns gas-liquid mass transfer coefficient $\beta$, the values obtained (reported in Tab.4) are all of the same order of magnitude with an average value of $5.42 \times 10^{-2}$ min$^{-1}$ that results lower than the average value obtained in our previous work (about 3 min$^{-1}$) [1] for different catalysts. This difference in gas-liquid mass transfer behaviour can be justified by considering that the catalysts investigated in the present work are much more active, so a more limiting value of $\beta$ can be considered reasonable.

A further interesting consideration can be pointed out by observing the kinetic constants obtained by mathematical regression. These constants are related to the activity and selectivity of the studied catalysts and this effect can be better appreciated if we consider their ratios as reported in Tab.5.

The ratio $k_1/k_2$ indicates that all the tested catalysts are very selective toward the production of $\alpha$-MCH with respect to $\beta$-MCH in the first chlorination step. This represent a significant advantage because high concentration of $\beta$-MCH involves serious separation problems from $\alpha$-MCH in industrial plants and in our case we have always observed $\beta$-MCH molar concentrations lower than acetic acid (see Tab.2). A very similar, even more pronounced behaviour, can be appreciated for the ratio $k_3/k_4$ that emphasizes for all the catalysts the high selectivity toward $\alpha,\gamma$-DCH with respect to $\alpha,\beta$-DCH.

**Table 5.** Ratios between the kinetic constants obtained by mathematical regression on the experimental runs performed by using different catalysts. (*) reactivity index expressed as ratio between kinetic constant of i-th catalyst and that of glutamic acid.

<table>
<thead>
<tr>
<th>Run</th>
<th>$k_1/k_2$</th>
<th>$k_3/k_4$</th>
<th>$k_1/k_{1GLUA(*)}$</th>
<th>$k_3/k_{3GLUA(*)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.68</td>
<td>652.5</td>
<td>0.4496</td>
<td>0.2515</td>
</tr>
<tr>
<td>2</td>
<td>18.17</td>
<td>8115.9</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>3</td>
<td>9.94</td>
<td>270.1</td>
<td>0.0464</td>
<td>0.0394</td>
</tr>
<tr>
<td>4</td>
<td>15.22</td>
<td>3475.6</td>
<td>0.7810</td>
<td>0.3393</td>
</tr>
<tr>
<td>5</td>
<td>23.78</td>
<td>1949.3</td>
<td>0.5620</td>
<td>0.4003</td>
</tr>
<tr>
<td>6</td>
<td>15.32</td>
<td>3.41E+8</td>
<td>2.8301</td>
<td>0.8001</td>
</tr>
</tbody>
</table>
In Tab.5 are also reported two reactivity indexes referred to glutamic acid, expressed as ratio between kinetic constant of the generic catalyst and that of glutamic acid, for the first and the second chlorination respectively (reactions 1 and 3). From these ratios, it is evident that in the first chlorination reaction, TGA catalyst is the most active while for the second chlorination glutamic acid resulted the best.

3. Conclusions

The amino acids catalysts have shown a good activity and selectivity, that are strongly depends on the pKa value and the molecular structure. By comparing their performances, ASPA and GLUA catalysts, which contain two carboxylic groups and have a similar pKa values, show higher activity in glycerol conversion than CYS, that is characterized by a higher pKa and by only one carboxylic group. However, the difference in terms of total carboxylic groups is not sufficient to justify the catalytic behaviour of GLUA and CYS. In particular, at this purpose we can compare runs 3 and 8 (Tab.2, 3) that were conducted with the same carboxylic groups concentration. In run 3 (CYS) glycerol residue after 4h of reaction is about 40% while a total conversion was obtained in run 8 (GLUA).

By using amino acids as catalyst, it has been demonstrated that catalyst pKa plays an important role on the selectivity, as in ref. [5]. In fact, even if ASPA has a pKa slightly lower than GLUA, the selectivities to MCHs and DCHs are strongly affected: ASPA showed a relatively high selectivity to MCHs while GLUA has a high selectivity to DCHs.

The series of glycolic acids seems characterized by higher catalytic activity with respect to amino acids, giving place, for all the tested catalysts, to a total conversion of glycerol in the same reaction conditions. For this series, different selectivities to MCHs and DCHs have been observed. Their values are not closely related to the pKa of the corresponding catalysts, as occurred for the previous series of homologues.
Finally, a reliable kinetic model has been applied to the description of isothermal fed-batch runs and a good agreement between experimental data and model prediction has been obtained in all cases.

4. References


Chapter 9- A new class of catalysts: Acyl Chlorides
1. Introduction

In the present chapter, present the results on a completely new class of catalysts for glycerol chlorination, represented by acyl chlorides, never reported in the literature before the patent [1].

The catalysts studied in this work are acetyl chloride, propanoyl chloride, adypoyl chloride, butandioil di-chloride, propandioil di-chloride and phenylacetyl chloride and more precisely it is reported a comparison between the acyl chlorides respect to corresponding carboxylic acid. The influence of some reaction parameters are studied as for example the effects of the pressure on activity and selectivity. In this chapter we studied also the possibility of using crude glycerol coming from the biodiesel production.

2. Experimental Section

The reagents used for the experimental runs were all purchased from Sigma Aldrich at the highest purity (glycerol anhydrous > 99.0% and catalyst > 99.0%) and used as received without further purification. The hydrochloric acid has been purchased from Sol spa (>99.8 vol. %).

As reported in previous works [2,1] all experimental runs were carried out in a 300 cm3 hastelloy steel reactor and the system was described elsewhere in more details [2].

Glycerol and catalyst were loaded into the reactor and this was rapidly closed. In this case we do not eliminate the air in the reactor, with a vacuum pump, to avoid removing also the hydrochloric acid which may be formed from the reaction between acyl chloride and glycerol. In this way after the reactor was closed and the reaction mixture was heated up to the reaction temperature, HCl was fed into the reactor from an external cylinder.
2.1 Experimental runs

All tests were carried out, for 4 hours of reaction, in the same conditions of temperature, stirring speed and catalyst concentration (T=100°C, stirring speed= 1000 rpm, catalyst concentration= 8mol%) ; the tests were carried out at different pressures. During the runs some samples were taken, more precisely at 30 minutes, 1, 2, 3, 4 hours. These samples, after neutralization with an excess of sodium bicarbonate, were analyzed on a gas chromatograph to measure the glycerol conversion and chlorinated products distribution. At the end of the run, after 4 h of reaction, the HCl in excess was discharged from the system by bubbling into a neutralizing trap containing NaOH. Stirring was then stopped and the system was cooled to room temperature. The GC column used for the analysis was a CHROMPACK CPWax, with a stationary phase of 100% polyethylene-glycol, length of 30 m, I.D. of 0.25 mm and film thickness of 0.25 µm. The GC was equipped with a FID detector and helium was used as carrier gas. The other parameters were: injector temperature = 250 °C, detector temperature = 280 °C, temperature program = 1 min at 40 °C, heating rate 20 °C/min to 100 °C then 40 °C/min up to 200 °C, finally hold for 10 min. The withdrawn sample was first diluted with methanol in a volumetric ratio of 1:30 and 1 µL of the resulting solution was injected into the GC. The quantitative analysis was expressed as mole percent normalized with respect to the sum of known components.

The catalysts studied in this work were carboxylic acids with the corresponding acyl chlorides with the scope to show the comparison between them for both activity and selectivity. The catalysts studied were acetic acid, acetyl chloride, propionic acid, propanoyl chloride, adipic acid, adypoyl chloride, succinic acid, succinyl chloride, malonic acid, malonyl chloride, phenylacetyl chloride. In the table 1 the properties of the used catalysts are reported.

All tests were carried out with the use of the acyl chlorides and in comparison with the corresponding carboxylic acid. Comparing the results obtained, in the same operating conditions, the initial measured reaction rate are higher in every case when chloride are used as catalysts. In table 2 the results obtained used the catalyst previously listed are reported. The temperature and the stirring rate of the runs reported in the Table 2 were the same for all tests, 100°C, 1000 rpm and 4h of overall reaction time, respectively.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Molar mass (g mol⁻¹)</th>
<th>Boiling point (°C)</th>
<th>Acidity (pKa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>60.05</td>
<td>118-119</td>
<td>4.79</td>
</tr>
<tr>
<td>Acetyl chloride</td>
<td>78.49</td>
<td>52</td>
<td>-</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>74.08</td>
<td>114</td>
<td>4.87</td>
</tr>
<tr>
<td>Propanoyl chloride</td>
<td>92.52</td>
<td>77-80</td>
<td>-</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>146.14</td>
<td>337.5</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.41</td>
</tr>
<tr>
<td>Adypoyl chloride</td>
<td>183.03</td>
<td>105-107</td>
<td>-</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>118.09</td>
<td>235</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.6</td>
</tr>
<tr>
<td>Succinyl chloride</td>
<td>154.98</td>
<td>190</td>
<td>-</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>104.06</td>
<td>-</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.69</td>
</tr>
<tr>
<td>Malonyl chloride</td>
<td>140.95</td>
<td>53-55</td>
<td>-</td>
</tr>
<tr>
<td>Phenylacetyl chloride</td>
<td>154.59</td>
<td>94-95</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2. Experimental run: operative conditions and glycerol conversion after 1 h of reaction (mol %)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Pressure (bar)</th>
<th>Catalyst (% mol)</th>
<th>Gly conversion after 1h of reaction (% mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic Acid</td>
<td>4.5</td>
<td>8</td>
<td>84.2</td>
</tr>
<tr>
<td>2</td>
<td>Acetyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Acetyl Chloride</td>
<td>10</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Acetyl Chloride</td>
<td>4.5</td>
<td>2</td>
<td>87.9</td>
</tr>
<tr>
<td>5</td>
<td>Acetyl Chloride</td>
<td>4.5</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>Propionic Acid</td>
<td>4.5</td>
<td>8</td>
<td>81.9</td>
</tr>
<tr>
<td>7</td>
<td>Propanoyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>Adipic Acid</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>Adypoyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Succinic Acid</td>
<td>4.5</td>
<td>8</td>
<td>86.3</td>
</tr>
<tr>
<td>11</td>
<td>Succinyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>Malonic Acid</td>
<td>4.5</td>
<td>8</td>
<td>81.9</td>
</tr>
<tr>
<td>13</td>
<td>Malonyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>95</td>
</tr>
<tr>
<td>14</td>
<td>Phenylacetyl Chloride</td>
<td>4.5</td>
<td>8</td>
<td>100</td>
</tr>
</tbody>
</table>

Only for the run 11 and run 14 it was possible to observe after 30 minutes the presence of residual glycerol, more precisely for the run 11 the residual glycerol after 30 minutes
was 7.3 mol % and for the run 14 the glycerol was 10.9 mol%. For the others runs (2, 3, 5, 7, 8, 9) also after 30 minutes of reaction the glycerol conversion was total.

In the figure 1 was reported, a first comparison between acetyl chloride and acetic acid. Using these catalysts the glycerol completely disappears in a much shorter time and the final yield in α,γ-dichlorohydrin is higher than in the presence of acetic acid as catalyst.

![Figure 1: Comparison between the performances obtained by using, as catalysts, acetic acid (---□---, ---○---) and acetyl chloride (---▲---, ---▼---).](image)

Observing the values of final yields we have found that higher selectivity to dichlorohydrins can be obtained in a considerably shorter reaction time.

In this chapter we studied also the influence of HCl pressure on the reaction rate, when an acetyl chloride is used as catalyst. By doubling approximately the HCl pressure from 4.5 bars to 10.0 bars, all the glycerol was converted in less than 15 minutes, while, the maximum yield of α,γ-dichlorohydrin is reached in about 30 minutes. On the contrary, in the run performed at 4.5 bars using acetyl chloride as catalyst (run 2), the glycerol was completely converted after 60 minutes. A run performed in the same condition in the
presence of acetic acid as catalyst (run 1) requires more than 180 minutes for a total conversion of glycerol. In figure 2 was reported this comparison.

![Figure 2. Effect of pressure: comparison between the performances obtained by using, as catalysts, acetyl chloride at 4.5 bars (--- ▲ --, --- ▼ --) and acetyl chloride at 10 bars (--- □ --, --- ○ --)](image)

For the acetyl chloride we studied also the influence of catalyst concentration. The concentration used for the comparison were 2, 4 and 8 % by mole. By reducing the catalyst concentration the reaction rate decrease but not very much, because in all cases glycerol was converted in less than 60 minutes. On the contrary \( \alpha \)-monochlorohydrin concentration was 18.8 % mol after 60 minutes for the run performed with 8% mol of acetyl chloride, 43.1 % mol using 4 % mol of catalyst and finally 78.2 % mol for 2% of catalyst. The time to reach the maximum yield was longer for the run performed with 2 % mol of catalyst while was similar for the run performed with 4 and 8 % mol of catalyst respectively.

The influence of an inorganic salt, such as NaCl, has also been studied on activity and selectivity (to dichlorohydrins) using acetyl chloride as a catalyst. Usually the salt
content in crude glycerol, from biodiesel production via homogeneous alkaline catalysts, ranged from 5% to 7%. In this way, using an amount of salt 8 wt%, we wanted to simulate crude glycerol coming from other industrial processes like biodiesel production. This study showed that the results obtained using NaCl, both in activity and in selectivity, are very similar to those obtained by performing the same reaction without NaCl. This aspect could represent a potential advantage, from an industrial point of view, because it opens the possibility for use as a feedstock of crude glycerol from the biodiesel plants without having to expensive additional purification operations.

Also in this case the chlorination reaction of glycerol with hydrochloric acid was carried out at 100 °C and 4.5 barg and in the figure 3 was reported the comparison using acetyl chloride as catalyst with NaCl and without NaCl.

![Graph showing the effect of NaCl on the chlorohydrin formation](image.png)

**Figure 3.** Effect of NaCl: comparison between the performances obtained by using, as catalysts, acetyl chloride (--- ▲ ---, --- ▼ ---) and acetyl chloride with NaCl (--- □ ---, --- ○ ---)

The results obtained for the synthesis of chlorohydrins, and in particular of all products obtained in the presence of acyl chlorides as catalysts are summarized in the table 3.
Table 3. Experimental run: products distribution after 4h of reaction (mol %)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>α-MCH</th>
<th>β-MCH</th>
<th>α,γ- DCH</th>
<th>α,β- DCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic Acid</td>
<td>23.6</td>
<td>7.0</td>
<td>52.6</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>Acetyl Chloride</td>
<td>18.8</td>
<td>4.9</td>
<td>74.0</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Acetyl Chloride</td>
<td>0</td>
<td>8.8</td>
<td>86.1</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>Acetyl Chloride</td>
<td>78.7</td>
<td>9.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Acetyl Chloride</td>
<td>43.1</td>
<td>4.9</td>
<td>50.8</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>Propionic Acid</td>
<td>51.3</td>
<td>5.3</td>
<td>23.2</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>Propanoyl Chloride</td>
<td>14.1</td>
<td>7.1</td>
<td>75.9</td>
<td>2.9</td>
</tr>
<tr>
<td>8</td>
<td>Adipic Acid</td>
<td>27.0</td>
<td>7.0</td>
<td>64.0</td>
<td>2.0</td>
</tr>
<tr>
<td>9</td>
<td>Adypoyl Chloride</td>
<td>0.9</td>
<td>3.6</td>
<td>92.8</td>
<td>2.7</td>
</tr>
<tr>
<td>10</td>
<td>Succinic Acid</td>
<td>33.2</td>
<td>9.0</td>
<td>40.3</td>
<td>3.8</td>
</tr>
<tr>
<td>11</td>
<td>Succinyl Chloride</td>
<td>26.6</td>
<td>8.2</td>
<td>62.9</td>
<td>2.3</td>
</tr>
<tr>
<td>12</td>
<td>Malonic Acid</td>
<td>66.3</td>
<td>7.4</td>
<td>8.6</td>
<td>0.2</td>
</tr>
<tr>
<td>13</td>
<td>Malonyl Chloride</td>
<td>40.2</td>
<td>7.6</td>
<td>46.2</td>
<td>1.0</td>
</tr>
<tr>
<td>14</td>
<td>Phenylacetyl Chloride</td>
<td>37.1</td>
<td>7.8</td>
<td>53.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Run 6 and run 7 (Table 3) were a comparison of the performance obtained in the same operative conditions by respectively propanoic acid and propanoyl chloride. In this
case this comparison confirms the superiority as catalyst of acyl chloride respect to the corresponding carboxylic acid. For this catalysts the final yield of $\alpha,\gamma$- dichlorohydrin, after 4h of reaction, is higher, 93.6 mol% for the propanoyl chloride and 92.5 mol% for the propionic acid. The glycerol, instead, whit propanoyl chloride as catalyst was completely converted in less than 30 minutes, while, whit propionic acid requires about 3h.

Using adipic acid and corresponding acyl chloride (run 8 and run 9 table 3), esandioil di-chloride, the kinetic advantage to use the acyl chloride was more evident in this case. By using esandioil di-chloride as catalyst a yield of 92.8 mol% of $\alpha,\gamma$- dichlorohydrin was obtained in about 60 minutes, while, using adipic acid a similar quantity of $\alpha,\gamma$-dichlorohydrin was obtained after 180 minutes of reaction. Also in this case it was confirmed that acyl chloride were more active as catalysts than the corresponding carboxylic acid. In particular, the presence of two acyl chloride groups in the same molecule enhances the catalytic effect.

In the run 10 and run 11 (table 3) were reported the performances of succinic acid and the butandioil di-chloride. Also in this case it was possible to observe a superiority of the catalyst butandioil di-chloride respect to the succinic acid. For succinic acid the time necessary to convert totally the glycerol was 180 minutes, while, also in this case in presence of butandioil di-chloride the time was less than 60 minutes.

By using malonic acid and propandioil di-chloride (run 12 and 13) it was possible to observe than in this case propandioil di-chloride was less efficient than the other aacyl chloride previously reported but it was more active than malonic acid confirming the superiority of the acyl chloride to respect to corresponding carboxylic acids.

In the following figure (Fig.4) is reported a comparison between all catalysts used in this part of work. In all cases it is possible to note that the acyl chlorides are more active than corresponding acid.
Figure 4. Comparison between all catalysts used after 1h of reaction.

The adipic acid chloride (Esandioil di-chloride), contemporary is the most active catalyst and the most selective to form dichlorohydrin.

3. A new process for chlorination reaction of glycerol: Acyl Chloride to produce HCl

3.1 Introduction

In this part of the thesis work, the attention has been focused on the use of acyl chlorides. These compounds are used in the same molar concentration respect to glycerol and they give place to higher activity and selectivity respect to the traditional catalysts based on carboxylic acids [4].

We have studied the catalytic performance of these compounds and it has been observed surprisingly that they can give place to the desired reaction product, $\alpha,\gamma$-dichlorohydrin, without the necessity to feed hydrochloric acid; this gas, however, is formed in situ by the reaction between glycerol and acyl chloride.
From the reaction between acyl chloride and glycerol, the catalytically active species, the ester, and HCl are formed.

Then, the hydrochloric acid reacts with the ester to give the reaction product and the carboxylic acid as a byproduct rather than water as in the traditional process. Carboxylic acid is a good catalyst for this reaction and for this reason the reaction proceeds quickly with good selectivity, while it is known that water has a negative effect on the reaction rate. Carboxylic acid, which is formed as a byproduct, can be separated, purified and then reused with obvious economic advantages.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OCR} \\
\text{CHOH} & \quad \text{CHOH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OCR}
\end{align*}
\]

Glycerol \quad \text{Glycerol esters}

HCl reacts with esters to produce:

\[
\begin{align*}
\text{CH}_2\text{OCR} & \quad \text{CH}_2\text{Cl} \\
\text{CHOH} & \quad \text{CHOH} \\
\text{CH}_2\text{OCR} & \quad \text{CH}_2\text{Cl}
\end{align*}
\]

Glycerol esters \quad \alpha,\gamma\text{-dichlorohydrin}
In order to obtain mainly α, γ- dichlorohydrin, a stoichiometric ratio of glycerol/acyl chloride = 1/2 has been used. In these conditions it is possible to achieve a high reaction rate that characterizes the catalytic action already observed by using chlorides as catalysts.

**3.2 Experimental runs**

The aim of this part of work is the study of a new process to produce chlorohydrins, starting from glycerol and acyl chloride without feeding HCl. The acyl chlorides, in stoichiometric ratio, are both reagents and catalysts.

The reaction between acyl chloride, of general formula RCOCl, and glycerol is very fast at room temperature and at 100-120°C is almost instantaneous. For this reason, if we put in contact directly the two reactants, the pressure in the reactor increases considerably due to the instantaneous production of HCl.

It is therefore appropriate to gradually add a reagent to another (preferably feeding the acid chloride to glycerol).

In this way, pressure keeps a moderate value and constant value, in our case about 4-6 bars; the pressure value can be also adjusted by varying the feeding time, by adjusting the acid chloride flow rate.

Then, the process can be conducted in a semi-continuous reactor, with continuous feeding of the acyl chloride to the reactor as it is consumed. The process can also be conducted in a continuous reactor, with continuous feed of glycerol and acyl chloride. The reaction temperature may be kept between 100 and 175°C. In the present work the acyl chloride previously reported as catalysts are used.
As reaction test in the laboratory, I used acetyl chloride as reference. The acetyl chloride is fed with an hplc pump in a stirred reactor in which has been previously loaded glycerol. Also in this case samples were collected at different times in order to follow the time evolution of the distribution of the reaction products.

The results obtained from the reaction between glycerol and acetyl chloride are reported as it follows (Tab. 4 and Tab.5).

In the first example, glycerol (100g) is loaded in the reactor and the acetyl chloride is fed by hplc pump with a flow of 1 ml/min for 154 minutes, but the reaction time is 4 hours. In this operative conditions, the reactor pressure is the pressure generated from HCl formation reaction and the consumption to produce chlorohydrins.

As the pressure in the reactor is constant, the reaction proceeds but when the pressure increased the reaction is stopped.

In the following table are reported the results obtained using acetyl chloride with a flow of 1 ml/min; in this case the pressure in the reactor is about 7 barg and the results confirmed that at the end of chloride alimentation the reaction is completed.

Table 4. Results after 180 and 240 minutes of reaction (mol % distribution)

<table>
<thead>
<tr>
<th>Time</th>
<th>α-MCH</th>
<th>β-MCH</th>
<th>α,γ-DCH</th>
<th>α,β-DCH</th>
<th>Glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>180</td>
<td>1.8</td>
<td>8.2</td>
<td>81.4</td>
<td>8.6</td>
<td>0</td>
</tr>
<tr>
<td>240</td>
<td>0.5</td>
<td>5.9</td>
<td>82.3</td>
<td>11.3</td>
<td>0</td>
</tr>
</tbody>
</table>

In the second test, glycerol (100g) is loaded in to reactor and the acetyl chloride is fed by hplc pump with a flow of 2 ml/min for 80 minutes, but the reaction time is 4 hours. In this operative conditions the reactor pressure is the pressure generated from HCl formation reaction is faster than the previous but the final value is 6 barg instead of 7 barg.

In the table 5 are reported the results obtained using acetyl chloride with a flow of 2 ml/min.
Table 5. Results after 180 and 240 minutes of reaction (mol % distribution)

<table>
<thead>
<tr>
<th>Time</th>
<th>α-MCH</th>
<th>β-MCH</th>
<th>α,γ-DCH</th>
<th>α,β-DCH</th>
<th>Glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>180</td>
<td>0</td>
<td>4.0</td>
<td>91.9</td>
<td>4.1</td>
<td>0</td>
</tr>
<tr>
<td>240</td>
<td>0</td>
<td>3.7</td>
<td>92.3</td>
<td>4.0</td>
<td>0</td>
</tr>
</tbody>
</table>

This test demonstrate that it is possible to reduce the time of reaction changing the operative conditions as amount of glycerol, feed rate of acyl chloride or reaction temperature.

4. Conclusions

From all results reported it is possible to conclude that the acyl chlorides are much more active as catalyst than the corresponding carboxylic acids. The use of the acyl chloride in place of the corresponding acid leads to an improvement both in the activity and in the selectivity in α,γ-dichlohidrins. This results are probably due to the enhanced reaction rate of intermediate esters formation, which in this case is practically immediate. A further effect was noticed by studying the influence of the presence of NaCl in the reaction mixture, on the distribution of the reaction products; this compound promotes the reaction and this opens the possibility to the use of crude glycerol, coming from biodiesel plants, as raw material for this process. Other factor that positively affect the reaction rate was the catalyst concentration. This kinetic advantage, of acyl chlorides with respect to carboxylic acids, is further accentuated by increasing the partial pressure of HCl. Finally acyl chlorides in stoichiometric amount have been studied in order to open new opportunities for chlorination process of glycerol with hydrochloric acid performed in situ and also in this case the activity and selectivity to DCHs is high.
5. References


Conclusions

The aim of this PhD thesis was the study of catalytic processes in biorefinery and in particular the biorefinery that uses as feedstock waste vegetable oils.

The biodiesel production process was studied in the first part of this PhD work. For what concerns the pretreatment, the use of a new acid resin (syndiotactic polystyrene-co-1,4-cis-polybutadiene resin) stable at high temperature, has been studied. This has shown high activity in esterification reaction and a good resistance to the deactivation. The obtained results are very promising and further study will be done to define its microstructure and to test the performance of the resin in a continuous reactor. For the direct use of waste oils, niobia supported on silica has been studied. This catalyst is active in both esterification of FFA and transesterification of triglycerides, with no loss of activity in the continuous run for 100 h. However, the characterization of the used catalyst revealed the slow leaching of niobia, which reduces its potential of industrial application in biodiesel production, if this problem will be not solved.

Finally, a new catalysts based on Zn(II) have been studied, in particular using a homogeneous catalyst supported on silica or the dendrimeric species it is possible to note high activity in both esterification of FFA and transesterification of triglycerides. Further studies will be dedicated to improving the robustness of the catalysts for enhancing their activity and durability.

The second part of this thesis was devoted to study of new catalysts for chlorination reaction of glycerol recovered from biodiesel production process. The behavior of three series of homologous catalysts, chloroacetic acid series (acetic acid, monochloroacetic, dichloroacetic and trichloroacetic acid), glycolic acid series (glycolic acid, di-glycolic acid and thio-glycolic acid) and amminoacid series (glutamic acid, aspartic acid and cysteine), were investigated for their activity and selectivity to produce dichlorohydrins, important intermediates for epichlorohydrin production. For what concerns the first series of catalysts the acetic acid catalyst is the reference molecule; in this case the effect of introducing one, two or three chlorine atoms in the molecule on the activity and selectivity in glycerol hydrochlorination reaction has been investigated. In particular, we observed that pKa of the catalyst has an important role in defining activity and selectivity. The homologue series of acetic, mono-, di- and tri-chloroacetic acid give interesting results in terms of selectivity: acetic acid resulted selective in the production
of 1,3-dichlorohydrin while chloro-substituted acids have produced a mixture of mono- and dichlorohydrins. For this set of catalyst a decreasing activity has been observed in the order acetic>monochloro>dichloro> trichloroacetic acid. A kinetic model has been applied to the description of isothermal fed-batch runs obtaining a good agreement.

By comparing their performances, aspartic acid (ASPA) and glutamic acid (GLUA) catalysts, show higher activity in glycerol conversion than cysteine (CYS). ASPA showed a relatively high selectivity to monochlorohydrins (MCHs) while GLUA has a high selectivity to dichlorohydrins (DCHs). However, the difference in terms of total carboxylic groups is not sufficient to justify the catalytic behaviour of GLUA and CYS. The series of glycolic acids seems characterized by higher catalytic activity with respect to amino acids, giving place, for all the tested catalysts, to a total conversion of glycerol in the same reaction conditions. For this series, different selectivities to MCHs and DCHs have been observed instead.

In the present study we explored also a completely new class of catalysts for glycerol chlorination, represented by acyl chlorides, never reported in the literature. From all results reported it is possible to conclude that the acyl chlorides are much more active as catalyst than the corresponding carboxylic acids. The use of the acyl chloride in place of the corresponding acid leads to an improvement both in the activity and in the selectivity in α,γ-dichlohidrins. This result is probably due to the enhanced reaction rate of intermediate esters formation, which in this case is practically immediate. A further positive effect was noticed by studying the influence of catalyst concentration and partial pressure of HCl. Finally acyl chlorides in stoichiometric amount have been studied in order to open new opportunities for chlorination process of glycerol with hydrochloric acid performed in situ and also in this case the activity and selectivity to DCHs is high.
**List of symbols and acronyms**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA</td>
<td>Free Fatty Acids</td>
</tr>
<tr>
<td>MCH</td>
<td>Monochlorohydrin</td>
</tr>
<tr>
<td>DCH</td>
<td>Dichlorohydrin</td>
</tr>
<tr>
<td>-R</td>
<td>Fatty acids chains</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acids methyl esters</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethylamine</td>
</tr>
<tr>
<td>DMAE</td>
<td>Dimethylethanol amine</td>
</tr>
<tr>
<td>TEMED</td>
<td>Tetramethyldiaminoethane</td>
</tr>
<tr>
<td>TMAH</td>
<td>Tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>WCO</td>
<td>Waste cooking oil</td>
</tr>
<tr>
<td>sPSB-SA</td>
<td>Sulfonated multiblock copolymers syndiotactic polystyrene-co-1,4-cis-polybutadiene</td>
</tr>
<tr>
<td>sPSB</td>
<td>Multiblock copolymers syndiotactic polystyrene-co-1,4-cis-polybutadiene</td>
</tr>
<tr>
<td>TAA</td>
<td>Thiolacetic acid</td>
</tr>
<tr>
<td>BZP</td>
<td>Benzopenone</td>
</tr>
<tr>
<td>DMSO-d6</td>
<td>Dimethylsulfoxide-d6</td>
</tr>
<tr>
<td>TCDE</td>
<td>1,1,2,2-tetrachloroethane-d2</td>
</tr>
<tr>
<td>λ</td>
<td>Conversion</td>
</tr>
<tr>
<td>5NbSi</td>
<td>Catalyst with 5% by wt of Nb$_2$O$_5$</td>
</tr>
<tr>
<td>12NbSi</td>
<td>Catalyst with 12% by wt of Nb$_2$O$_5$</td>
</tr>
<tr>
<td>PAMAM</td>
<td>Poly(amidoamine)</td>
</tr>
<tr>
<td>HPA</td>
<td>Heteropolyacids</td>
</tr>
<tr>
<td>α-</td>
<td>Cl in position 1</td>
</tr>
<tr>
<td>β-</td>
<td>Cl in position 2</td>
</tr>
<tr>
<td>α,β-</td>
<td>Cl in position 1,2</td>
</tr>
<tr>
<td>α,γ-</td>
<td>Cl in position 1,3</td>
</tr>
<tr>
<td>AA</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>MCA</td>
<td>Monochloroacetic acid</td>
</tr>
</tbody>
</table>
\textit{DCA} \quad \text{Dichloroacetic acid}

\textit{TCA} \quad \text{Trichloroacetic acid}

\textit{K}_{\text{HCl}^j} \quad \text{HCl solubility in the } j \text{ compound [mol/cm}^3\text{]}

\gamma \quad \text{Solubility correction factor}

\textit{J}_{\text{HCl}} \quad \text{Mass transfer rate for HCl in the aqueous film [mol/(cm}^3\text{*min}])}

\beta \quad \text{Mass transfer rate constant [min}^{-1}\text{]}

[J] \quad \text{Concentration of the } J \text{ component [mol/cm}^3\text{]}

[HCl] \quad \text{HCl film concentration [mol/cm}^3\text{]}

r_i \quad \text{Kinetic rate [mol/(cm}^3\text{*min}]}

n_j \quad \text{Moles of the } j \text{ component [mol]}

x_j \quad \text{Molar fraction of the } j \text{ component [-]}

J_i \quad \text{Mass transfer flux of component } i, \text{ [mol/min]}

F_j \quad \text{Rectangular-pulse function molar flow-rate of the } j \text{ component [mol/min]}

F_{\text{HCl}}^{\text{IN}} \quad \text{Molar HCl flow-rate [mol/min]}

P \quad \text{Pressure [bar]}

V \quad \text{Volume [cm}^3\text{]}

T \quad \text{Temperature [°C]}

\textit{ASPA} \quad \text{Aspartic acid}

\textit{GLUA} \quad \text{Glutamic acid}

\textit{CYS} \quad \text{Cystein}

\textit{GA} \quad \text{Glycolic acid}

\textit{DGA} \quad \text{Diglycolic acid}

\textit{TGA} \quad \text{Thioglycolic acid}

\textit{Cat} \quad \text{Generic catalyst}

\textit{Gly} \quad \text{Glycerol}

\textit{RPM} \quad \text{Stirring rate, [rpm]}

w \quad \text{Weight, [g]}