Abstract

In this Doctoral Thesis, several catalytic routes have been developed with the aim of obtaining chemical products of high added value and of interest to the food, pharmaceutical and plastic petrochemical industries, under the principles of *Green Chemistry* and through heterogeneous catalysts both chemical and enzymatic. Specifically, enzymatic hydrolysis of naringin (a flavonoid which is widely present in citric wastes) has been developed to obtain prunin and naringenin flavonoids, which have food and pharmaceutical applications. For this purpose, the commercial naringinase from the fungus *Penicillium decumbens* has been purified in a simple way in one step, and it has been obtained a purified enzyme which allows obtaining selectively the citric flavonoid prunin. Both enzymes, the commercial and the purified one, have been covalently immobilized over an organic support (graphene oxide) and over a bidimensional zeolite (ITQ-2) modified with aldehyde groups on its surface. The enzymatic derivatives have been characterized, and it has been shown that they have high thermal stability and more affinity for the substrate than the free enzyme. The enzymatic derivatives have been used successfully in the hydrolysis of naringenin, showing high conversions and selectivities. Additionally, the immobilized naringinase over the ITQ-2 zeolite has been used to treat the grapefruit juice to reduce the bitter taste (which is in part due to the presence of naringin) through a process in a fixed bed continuous reactor. It has been shown that is possible to maintain the catalytic activity through 300 hours, obtaining high quantities of released sugars, the lose of the bitter taste and, what is more, increasing the antioxidant capacity of the grapefruit juice.

A chemoenzymatic process has been developed with the aim of obtaining chiral alcohols with pharmaceutical applications, through a continuous process in two steps (oxidation-reduction). The first step is the Oppenauer oxidation of a racemic alcohol using Zr-Beta zeolite and acetone as hydride acceptor, and as a result, the corresponding prochiral ketone and isopropanol as by-product are obtained. The second step is the enantioselective reduction of the prochiral ketone using the alcohol dehydrogenase enzyme (ADH) electrostatically immobilized on the ITQ-2 zeolite and the isopropanol produced in the first step, which regenerates the cofactor; this process presents both a high yield and enantioselectivities to the chiral alcohols (R or S). It has been shown that both catalytic systems are highly actives, selectives and stables: with both of them it is possible to keep a yield higher than 90 % during at least 100 h in continuous reactors with fixed bed. Finally, both steps have been combined in continuous, and this reaction has been kept during at least 40 h with a yield to the chiral alcohol higher than 90 %.

A chemoenzymatic process in a continuous fixed bed reactor has been developed in two steps to obtain diesters of 2,5-bis(hydroxymethyl)furan (BHMF) from 5-hydroxymethylfurfural (HMF), which are useful as plasticizers in the polymer industry. The first step consists of the chemoselective reduction of the HMF using a catalyst based on cobalt nanoparticles covered by carbon, which allow obtaining high yield and selectivities to

BHMF. In the second step, the BHMF has been esterified/transesterified using the immobilized enzyme (Novozym 435). Both steps have been optimized separately (temperature, hydrogen pressure, solvent, acyl donor compound, etc.) in discontinuos and continuous reactors. The optimum solvent for the first step is methanol, which allow obtaining high yield and selectivity to BHMF, approximate 90 %. Moreover, it has been shown that the solvent and the acyl donor compound have strong influence on the enzymatic deactivation. The optimization of the solvent and acyl donor allowed to obtain yields of diesters of around 90 % in the global chemoenzymatic process, while the activity and selectivity of the continuous process was maintained during at least 60 h.