_____

Testing Set-Up and Analytical Methodology

Catalytic Testing Set-Up

Once the thermal stability of oleic acid and ethyl linoleate (see *Chapter 3.1*) had been determined, a continuous catalytic-testing system for vapour-phase experiments was designed and built up (Fig. 2.1.1). The dashed pointed areas stand for homogenously heated zones performed by suitable furnaces. Due to the
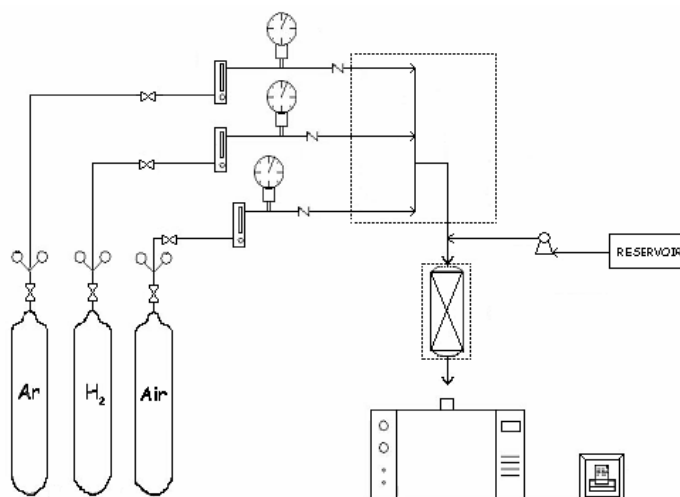
Figure 2.1.1 Catalytic testing system.

sensitive behaviour of these materials in the presence of stainless steel and light, the flow lines and reservoir were Teflon® and/or Pyrex - made. Since the reactor had to be subjected to high temperatures, the reactor was made of quartz. New reactors had to be designed along the research work to satisfy the experimental requirements, embodying an evaporating chamber and the catalytic reactor, such as that shown in Fig. 2.1.2.

This system allowed the activation of the catalysts (50-100mg) *'in situ'*, either by dehydrogenation, oxidation or thermal procedures under inert conditions. The gas flows were controlled by flowmeters with needle valves. Bottles of argon (Ar, C-

50), hydrogen (H_2, C-50) and air (air, C-50) were used as gas supplying sources. The system lines set-up allowed the mixture of these gases, which was useful in several cases. All gases were previously heated in order to avoid temperature gradients in the reactor. Thermocouples in the reactor and pre-heating furnace were necessary as temperature controllers. The furnace temperature controllers were able to perform different heating-rate programs. Manometers were likewise used to guarantee that the system was working under 1 bar pressure and to detect and to over-pressures caused by any anomaly during the catalytic testing.
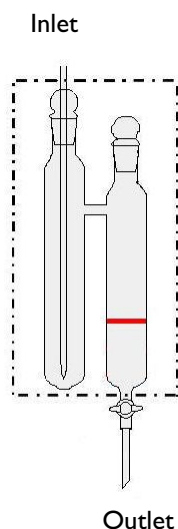
Inlet

Outlet

Figure 2.1.2 Detailed catalytic reactor.

The starting material (ethyl linoleate) was fed by a peristaltic pump connected to a Pyrex reservoir in the absence of light. The starting material was injected to the reactor and mixed with argon at the entrance of the reactor. Depending on the furnace temperature, ethyl linoleate was either directly evaporated and conducted to the catalytic bed, or it was directed to the bed by inert gas dragging.

The sample was collected by placing a cold trap at the reactor exit so that the condensation of the products was ensured in all cases. It was immediately analysed by GC analysis, as described below.

Analytical Methodology

The reaction products were analysed by GC using a Shimadzu G-17 gas chromatograph equipped with a highly polar column (HP FFA-P) with a FID detector. The specific chromatographic settings and the analytical method are

Table 2.1.1

Gas chromatograph settings and analytical method.

Gas	Column calculator	Method
He@400Kpa	Set P press=1.01972	$T_{inicial}$=175 °C
	Set P flow=3.0	T_{final}=230 °C
	Velocity=45cm/sec	Heating rate =10 °C/min
Total flow=29ml/min	Col flow=1.9ml/min	$T_{detector}$=230 °C
	Septum purge=7.6	$T_{injector}$=220 °C

detailed in Table 2.1.1.

Calibration curves were found by analysing a mixture of different concentrations of standards of ethyl oleate (99 %), linoleate (99 %), α-linolenate (99 %) and γ-linolenate (99 %) in ethanol. All these materials were provided by Aldrich (Germany). The response factor of the detector was calculated considering that the peak area (A_i) is generally defined as:

$$A_i = \delta_i * n_i$$

where n_i is the number of moles of a determined compound *i* and δ_i is the detector response factor corresponding to determined conditions. This factor depends on the other present products and their relative amount. The quotient of the response factors of two compounds *i* and *j* can be expressed as:

$$\delta_i/\delta_j = A_i * n_i / A_j * n_j$$

A sequence of coefficients for the different product concentrations is calculated, which allows finding the moles from the area and response factors quotient. The value of the different compound moles allows determining the conversion and selectivity.

Since aromatic FAEE and FAEE, whose was m/z = 302, (see *Chapter 3.2*) were both non-commercially available, an approximated response factor was assumed by

observing the trend of response factors with the number of unsaturations in the system.