

Active Carbon at 200 °C

The proposal of a mechanism for the obtaining of aromatic FAEE (see *Chapter 3.6*), consisted in a sequential reaction with three steps: a) dehydrogenation reaction of starting material, b) cyclation to give a ring and, finally, c) a second dehydrogenation reaction. Apparently, the cyclation was promoted, partially or totally, by thermal effects. Therefore, reaction products under higher temperatures were to be avoided, which meant a new reactor design (see *Chapter 2.1*). Re-hydrogenation of tri-unsaturated FAEE was also considered. The influence of reactor design into the resulting products was studied and is presented in the following chapter. The importance of this chapter is based on the novel detection of tri-unsaturated FAEE, some of them being ω -3 FAEE, which was the main goal of this work.

3.7.1 Experimental

The catalytic tests were performed at 200 °C with $0.055 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$ using argon as inert carrier with a flow of 0.225 mL/s. The samples were diluted in ethanol

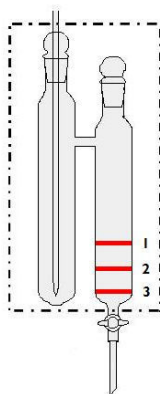


Figure 3.7.1 Quartz reactor with catalytic bed in the three positions at the outlet.

before being analysed by GC. The catalytic bed was set in three different positions separated from the reactor outlet (Fig. 3.7.1).

3.7.2 Results and Discussion

The first experiment was performed with the catalyst on the plate in position I (Fig. 3.7.1), which implied that product reaction were longer exposed to temperature effects. The position 2 and 3 were located 4 and 8 cm lower to position I, respectively. Thus, position 3 entailed the performance of the experiment with the lowest reaction-product exposure to temperature. In all cases, a substantial

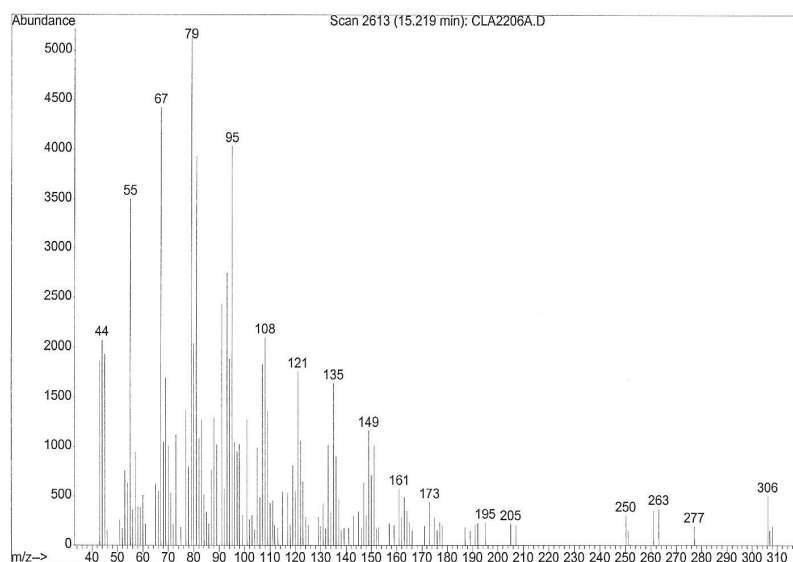


Figure 3.7.2 A mass spectrum of tri-unsaturated FAEE.

variation regarding the reaction products was detected: tri-unsaturated FAEE were identified by GC-MS analyses for the first time (Fig. 3.7.2). Due to the complex structure of the molecule consisting in long tri-unsaturated hydrocarbonate chains and an ethylic ester group, several isomers were obtained. Concerning the structural determination of tri-unsaturated FAEE isomers, no further analyses were performed given that it was not the aim of our work. Nevertheless, the detection of several peaks whose mass spectrum presented a molecular peak at $m/z = 306$ proofed the presence of several isomers (see Annex III). In some cases, the mass spectro-library could directly be determined the compound indicating that ω -3 tri-unsaturated FAEE had been obtained. In other cases, mass spectra required some interpretation. It is worth clarifying that some GC peaks with $m/z = 306$ may

correspond to the diene compound. Although this fact may dangerously be considered as negative information, it is recommendable to consider it, since this observation strengthened and confirmed the mechanism proposal in Chapter 3.3. Anyway, all compounds with $m/z = 306$ are considered as being dehydrogenation products for the purpose of selectivity values.

The total conversion of ethyl linoleate and the selectivity values in the different reactor positions are shown in Fig. 3.7.3. The conversion value was increasing from position 3 to position 1. Regarding the selectivity, the most relevant difference was

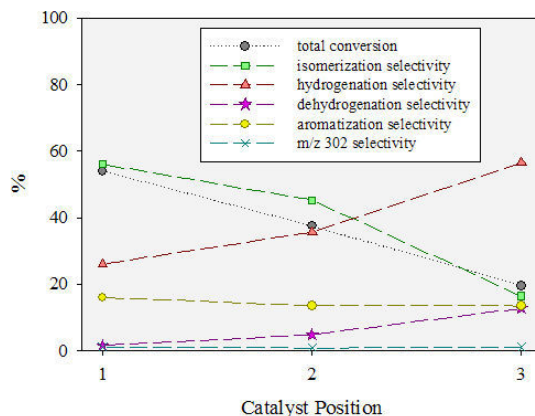


Figure 3.7.3 Total conversion and selectivity towards different products at 200 °C in three different reactor locations.

observed for the catalytic bed in position 3. As the catalytic bed was nearer to the reactor exit, dehydrogenation and hydrogenation selectivities incremented, aromatization slightly decreased and, finally, isomerization and m/z 302 clearly decreased. This fact evidenced that there was an evolution of the products after the catalytic bed and the minor change in the catalyst location in the reactor supposed a substantial variation in the reaction products. It also proofed that aromatic FAEE were already formed in the catalytic bed. The opposite trend followed by isomerization and hydrogenation reaction was also reported by Bernas et al. [1, 2], who affirmed that these two reactions were parallel competing reactions and assigned to the presence of chemisorbed hydrogen, so that if a low concentration of chemisorbed hydrogen on the catalyst surface is present, then it favours isomerization; while a high concentration favours hydrogenation. However,

chemisorbed hydrogen increases the isomerization reaction rate. The isomerization and hydrogenation selectivity are related to hydrogen chemisorbed by a complex relation.

3.7.3 Conclusions

By decreasing temperature reaction to 200 °C, tri-unsaturated FAEE (some of them being ω -3 compounds) were detected using AC as a catalyst. Although its selectivity was not very high (1.6 %), its meaning was relevant, especially because it supported the mechanism proposal in Chapter 3.3. and the obtaining for the first time of such compounds.

The exposure of reaction product to thermal effects along the outlet of the reactor showed that the evolution of the products is an important fact, even by minor distance exposure. Tri-unsaturated FAEE evolved towards other products, probably aromatic FAEE. Hydrogenation and isomerization reaction were competing reactions which followed opposite trends.

References

- [1] A. Bernas, P. Laukkanen, N. Kumar, P. Mäki-Arvela, J. Väyrynen, E. Laine, B. Holmbom, T. Salmi, D. Y. Murzin, *J. Catal.* 210 (2002) 354.
- [2] A. Bernas, N. Kumar, P. Mäki-Arvela, N. V. Kul'kova, B. Holmbom, T. Salmi, D. Y. Murzin, *Appl. Catal. A: Gen.* 245 (2003) 257.