
Active Carbon at Low Temperature

Once the obtaining of tri-unsaturated FAEE had been achieved not only by AC, but also by HSAG-100, it was decided to decrease even more the reaction temperature from 70 °C to 120 °C. At these temperatures, aromatization of FAEE was expected to occur in a much lower extent, so that the selectivity towards tri-unsaturated FAEE increased. The minimization of product-reaction thermal exposure after the catalytic bed ensured that no product evolution occurred (see Annex V).

3.7.1 Experimental

Active carbon was supplied by Fluka (Germany). The feed consisted ethyl linoleate (>97 %) supplied by Fluka (Germany). Argon has been used as carrier gas (13.5 mL/min). A reaction temperature range of 70-120 °C has been set in all cases. The catalyst weight in all cases has been 0.2 g. Under these experimental conditions no diffusion limitations were detected. For further information concerning experimental, please, consult other previous chapters or/and Annex V.

3.7.2 Results and Discussion

First, a blank experiment of running ethyl linoleate without catalyst at 120 °C was run giving no conversion at all, under the conditions given in the experimental section.

The reaction, using active carbon as a catalyst, was performed at a temperature range between 70 °C and 120 °C. The conversion of ethyl linoleate and selectivity towards the same different products (as in previous chapters) are plotted vs. the reaction temperature in Fig. 3.9.1. Then, conversion of ethyl linoleate to tri-unsaturated FAEE followed an increase on lowering temperature from 120 °-70 °C. The non-oxidative dehydrogenation to tri-unsaturated FAEE became more important than the isomerization and hydrogenation reactions at 70 °C. The selectivity to isomers presented a minimum value at the lower temperature with a plateau region in between, the selectivity to aromatic FAEE yielded a maximum value at 120 °C, and selectivity to mono-unsaturated FAEE gave a maximum value at 120 °C.

The values of total conversion increased, as expected, with temperature rise. At 120 °C, the conversion reaches a value of 59%. At the lowest temperature of 70 °C, the conversion is 20%. The reaction rates of conversion of ethyl linoleate at 70 °C and 120 °C were $0.007 \mu\text{mol}\cdot\text{g}^{-1}_{\text{cat}}\cdot\text{s}^{-1}$ and $0.02 \mu\text{mol}\cdot\text{g}^{-1}_{\text{cat}}\cdot\text{s}^{-1}$, respectively. Up to a 35% of tri-unsaturated FAEE was obtained synthetically at 70 °C, to our knowledge,

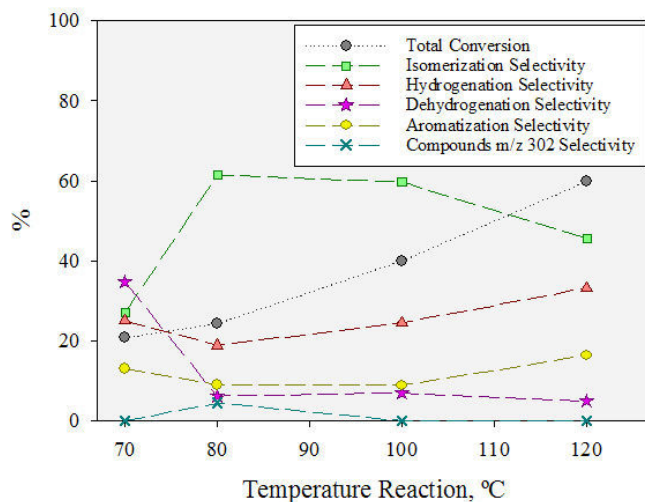


Figure 3.9.1 Total conversion and selectivity towards different products vs. temperature.

for the first time. The increase in the concentration to tri-unsaturated FAEE might be associated to the decrease of the isomerization of ethyl linoleate.

The amount of mono-unsaturated FAEE obtained, may be accounted for the hydrogenation of ethyl linoleate, using the hydrogen from reactions aromatization and dehydrogenation reactions. Therefore, either the formation of tri-unsaturated FAEE or the detection of mono-unsaturated FAEE proved the capability of AC to dehydrogenate FAEE. The mono-unsaturated compounds could either come from the hydrogenation of the starting material, ethyl linoleate, or the hydrogenation of the previously formed tri-unsaturated FAEE or from both hydrogenation reactions. Some hydrogenation experiments performed at 120 °C using active carbon as a catalyst and ethyl linoleate (di-unsaturated FAEE) as starting material in one case, and ethyl linolenate (tri-unsaturated FAEE), in the other case, showed that ethyl linoleate hydrogenates kinetically easier than the tri-unsaturated ester. Moreover,

the hydrogen balance was consistent with this fact: on one hand, the formation of one mol of aromatic FAEE implied the formation of two moles of hydrogen. On the other hand, the hydrogenation of ethyl linoleate to give a mono-unsaturated FAEE used one mol of hydrogen. So, the formation of one mol of aromatic FAEE gave enough hydrogen to form two moles of mono-unsaturated FAEE from ethyl linoleate, which may explain the fact that the conversion to mono-unsaturated FAEE was about double than the conversion to aromatic FAEE.

The observed catalyst stability for a long time and the fact that the dehydrogenation takes place under non-oxidative conditions seem to indicate that the surface functionality of the catalyst did not play a crucial role, in this case.

3.7.3 Conclusions

Active carbon showed dehydrogenation activity at low temperatures such 70 °-120 ° C under non-oxidative conditions. Active carbon kept its dehydrogenation activity (zero conversion from a blank non-catalyzed reaction) at least after 24 hours.

The dehydrogenation of ethyl linoleate gives tri-unsaturated FAEE, isomers of ethyl linoleate, aromatic FAEE and mono-unsaturated FAEE. The selectivity of ethyl linoleate to the tri-unsaturated FAEE was favoured at lower temperatures. The non-oxidative dehydrogenation to tri-unsaturated FAEE became more important than the isomerization and hydrogenation reactions at lower temperatures such as 70 ° C. Up to a 34 % of tri-unsaturated FAEE had been obtained synthetically for the first time.