

# Monitoring of biodiesel synthesis reactions by isothermal microcalorimetry

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## INTRODUCTION

Biodiesels are synthesized from a transesterification reaction of triglycerides by low molecular weight alcohols leading to the formation of fatty acid alkyl esters. This reaction requires the use of a liquid catalyst (KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>...) or of a solid catalyst (zinc aluminates, zeolithes, silica mesostructured materials or immobilized enzymes [1-3]).

The base-catalyzed ethanolysis of colza oil was studied by isothermal microcalorimetry, which is an analytical technique in which the heat released or absorbed by a reacting sample is monitored against time and temperature. In the specific case of isothermal calorimetry, temperature remains constant and reaction kinetics drive the heat release of the sample.

## EXPERIMENTAL SET-UP

A C80 microcalorimeter was used under isothermal conditions at 30°C, 40°C and 50°C with membrane mixing vessels as shown on figure 1. They allow in-situ mixing and stirring.

Tested materials: commercial colza oil (~1.3g / test) mixed with 3.4w% NaOH in EtOH (~0.45g / test), with 10.72w% K<sub>2</sub>CO<sub>3</sub> in EtOH, or with solid NaOH.

Samples were mixed at experimental temperatures and stirred during 20 minutes at a rate of 10 rpm.

The sample surrounding calorimetric sensor (thermopile) allowed measuring quantitatively the heat released by the reaction during its occurrence.

A reference vessel filled with ethanol and colza oil was used to compensate the phenomena of heat accumulation, heat of stirring and heat losses through the stirrer.

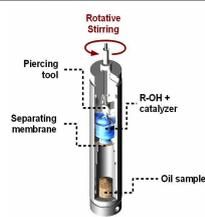


Figure 1 – Hastelloy made reaction vessel

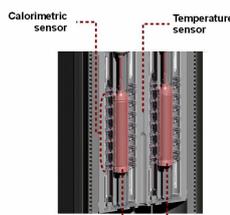


Figure 2 – Inside the C80 calorimeter

## INFLUENCE OF TEMPERATURE

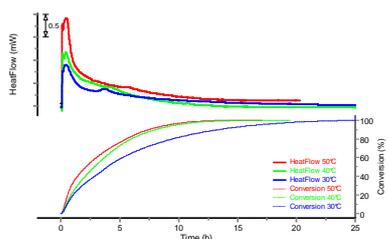


Figure 3 – Comparison of isothermal tests at 30°C, 40°C, and 50°C

Heat release data (figure 3) during the transesterifications are integrated in order to reach the reaction enthalpy. It is equal to  $-10.9 \pm 0.6$  J/g of ethanolate (NaOH + EtOH solution).

Thermal conversion  $\alpha$  is obtained from partial integration:

$$\alpha = \frac{1}{\Delta H_R} \cdot \int_{t_{start}}^t \frac{dH_R}{dt} \cdot dt$$

Both maximum heat release rate and conversion data confirm the acceleration of the reaction with increasing temperature. The thermal conversion reaches 98% after 10.8h at 50°C, 11.7h at 40°C and 20.0h at 30°C.

Reaction Temp (°C)	Enthalpy (J/g EtONa)	Conversion after 2 hours (%)	Max heat release rate (mW/g)
30	-10.3	31.8	0.69
40	-10.9	39.0	0.89
50	-11.5	48.6	1.37

Table 1 – Integration of exothermic peaks

## INFLUENCE OF THE CATALYST

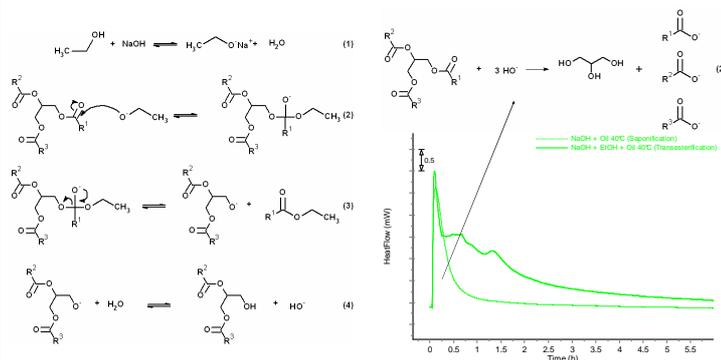


Figure 4 – Typical base-catalyzed transesterification of a triglyceride by ethanol

Figure 5 – Direct saponification tests at 40°C

The reaction goes through a first step of alcoholate formation (Figure 4), leading to the formation of water. It gives rise to the hydrolysis of some of the produced ester, with subsequent soap formation, reducing the ester yields [4]. Moreover, the presence of unreacted NaOH in the ethanolate solution leads to direct saponification of the triglyceride (step 2').

This fast exothermic reaction is clearly showed on figure 5. The green solid line was obtained by placing fresh NaOH and EtOH in the mixing vessel instead of using previously prepared EtONa solution. Unlike the other tests showed on Figure 3, an intense, sharp peak appears at the beginning of the reaction. The green dashed line corresponds to a solid NaOH (8.44mg) + colza oil mixing leading only to direct saponification and perfectly fitting the first half hour of the solid line.

This was confirmed by the run of the same transesterification reaction using K<sub>2</sub>CO<sub>3</sub> as a catalyst (Figure 7) which does not lead to saponification, and thus to initial high exotherm. The reaction is also faster and less energetic (-0.55 J/g EtOK).

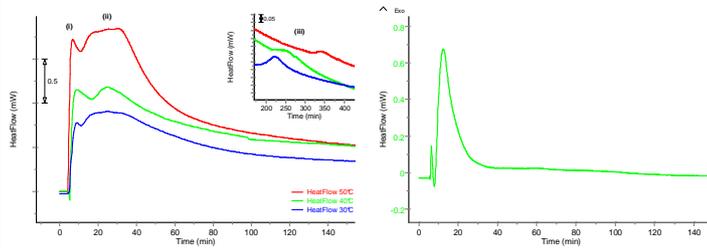


Figure 6 – Thermal steps of NaOH catalyzed reaction

Figure 7 – K<sub>2</sub>CO<sub>3</sub> catalyzed transesterification at 40°C

## CONCLUSION

Transesterification reaction of colza oil by ethanol using sodium hydroxide as a catalyst could be followed up by calorimetry. The high sensitivity and stability of the instrument allowed to get accurate data even with long term experiments.

Three main thermal steps could be noticed: (i) fast direct saponification, (ii) ethanolate diffusion rate-limited step, (iii) Heat production acceleration that may be linked with the hydrolysis of some of the produced ester (could be confirmed by simultaneous spectroscopic methods).

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