

# **Microwave-Assisted Catalyst-Free Transesterification of Triglycerides with 1-Butanol under Supercritical Conditions: supporting information.**

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## **Experimental section**

### **Transesterifications in Discover reactor**

For the first experiment, a 100 mL round-bottomed flask was loaded with 10 mL of rapeseed oil, 40 mL of butanol and 0.1 g of KOH. In the second experiment, the same flask was loaded with 10 mL of rapeseed oil, 25 mL of butanol and 0.1 g of KOH. In both cases, a magnetic stirring bar was added, the flask was placed into the microwave reactor and a reflux condenser was attached. After 30 min of reaction at reflux temperature (117°C), the reaction mixture was analyzed by GPSEC analysis. In both cases, all of the triglycerides were converted to FABE.

### **Transesterifications in the MARS reactor**

In the first experiments, a 100 mL quartz vessel was loaded with 10 mL of rapeseed oil, 0.1 g of KOH and 25 mL (first experiment) or 40 mL (second experiment) of butanol. After adding a magnetic stirring bar, the vessel was closed properly and was put into position one of the rotor. After 30 min of reaction at 150°C, the reaction mixture was analyzed by GPSEC analysis. In both cases, all of the triglycerides were converted to FABE.

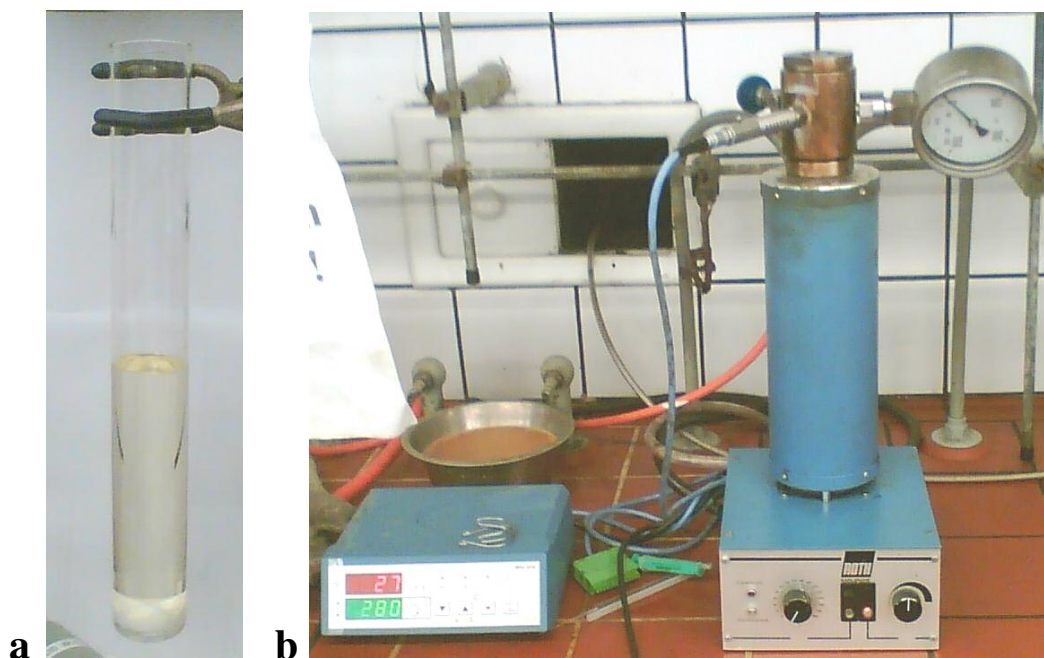
In the subsequent reactions, the vessel was loaded with the same amounts of butanol and rapeseed oil, but no KOH catalyst was added. After 150 min, no conversion of triglycerides to FABE was observed.

### **Transesterifications in the Synthos 3000 reactor**

An 80 mL quartz vessel was loaded with 10 mL of rapeseed oil and 25 mL of 1-butanol. After adding a stirring bar to the reaction mixture, the glass support was loaded with 6 SiC cylinders, attached to the cap and the vessel was sealed properly (see Figure 1) before fixing it in the 8-position rotor at position 1. For technical reasons, another 80 mL quartz vessel (filled with the same reaction mixture and equipped with the same glass – SiC assembly) was placed on the opposite position of the carousel (position 5). Additionally two empty sealed vessels were placed on position 3 and 7 (as the rotor top plate contains the hydraulic system for simultaneous pressure sensing it is important to charge the rotor symmetrically; four equipped positions are necessary to achieve a flat position of the plate to guarantee accurate pressure measurement). After 4 hours at 310 °C (280 °C monitored surface vessel temperature), the reaction was cooled down to room temperature and analyzed using GPSEC.

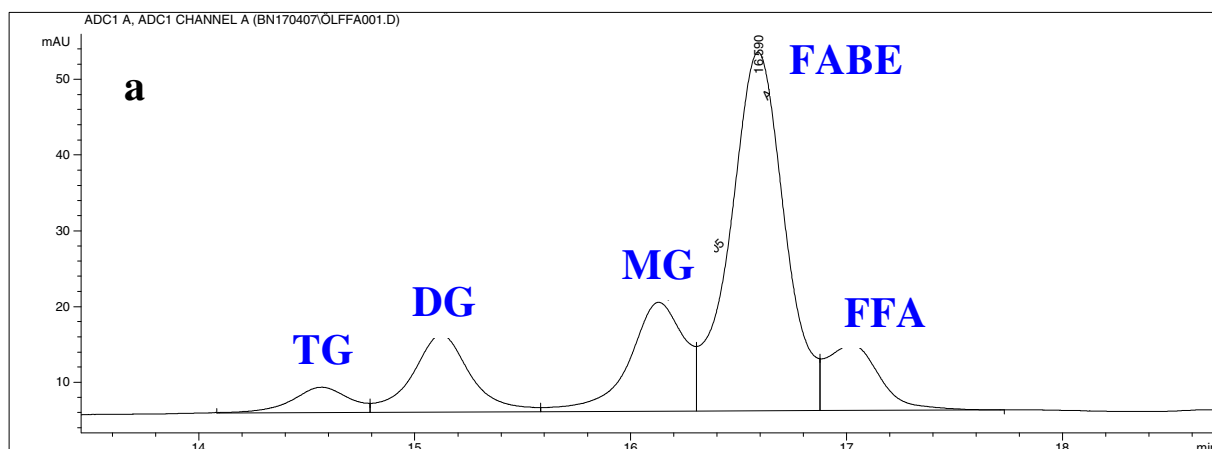
### Transesterifications in the high pressure autoclave

The steel autoclave vessel was equipped with a stirrer and filled with 30 mL rapeseed oil and 75 mL of 1-butanol. The reaction mixture was heated to 280 °C and after 4 hours the heater was switched off. When the autoclave had cooled down to ca. 150 °C the vessel was taken out and cooled further in a water bath. After evaporating the remaining butanol, GPSEC analyses showed 65% conversion to FABE.

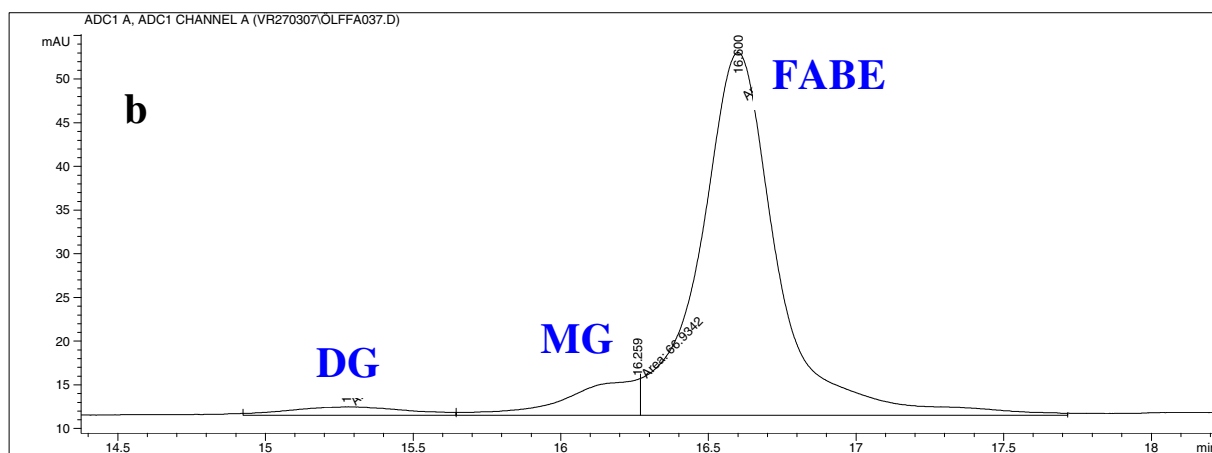


**Figure S1** Shown is (a) the vessel used for the autoclave experiments already filled with the reaction mixture; (b) the autoclave assembly.

## Analytical data



**Figure S2** GPSEC of the reaction mixture after transesterification in a high pressure autoclave



**Figure S3** GPSEC of the reaction mixture after transesterification in the Synthos 3000 microwave reactor.