

Biodiesel from waste cooking oil: highly efficient homogeneous iron(III) molecular catalysts

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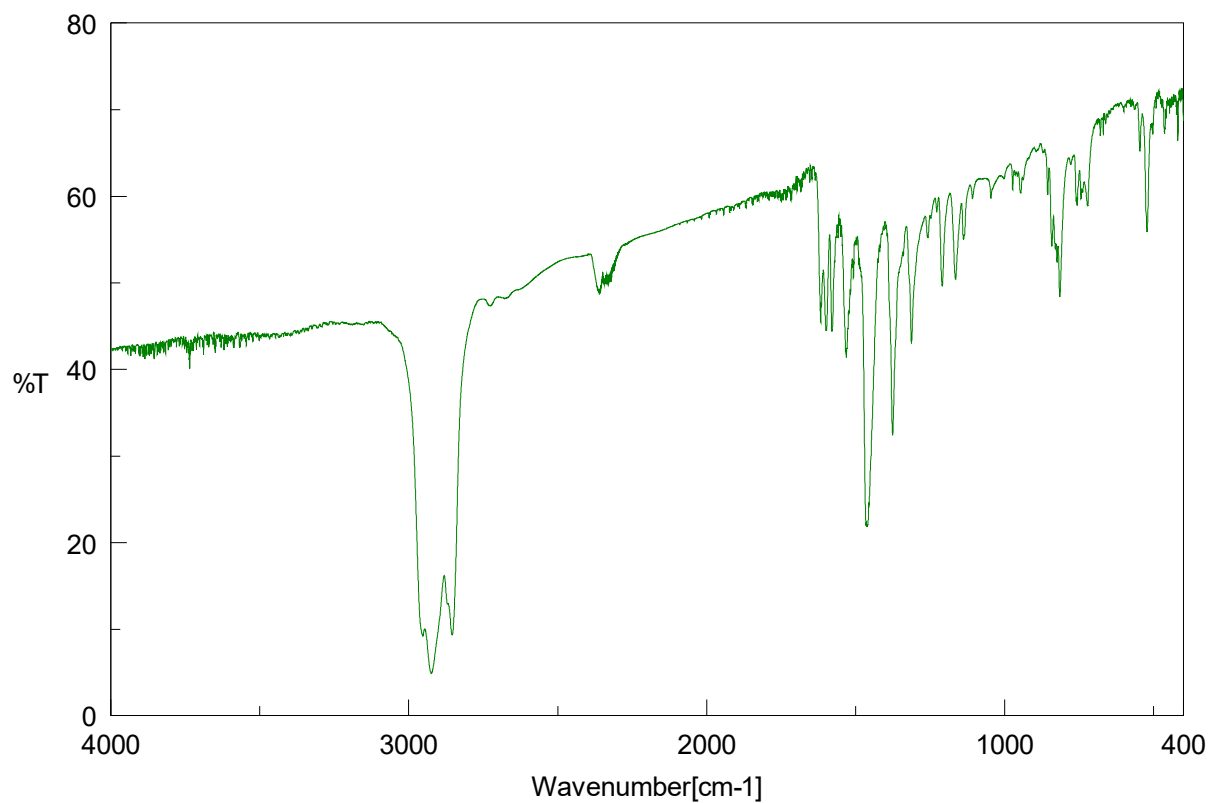


Figure S1 – FT-IR spectrum, in nujol, of complex **2Me-OAc**.

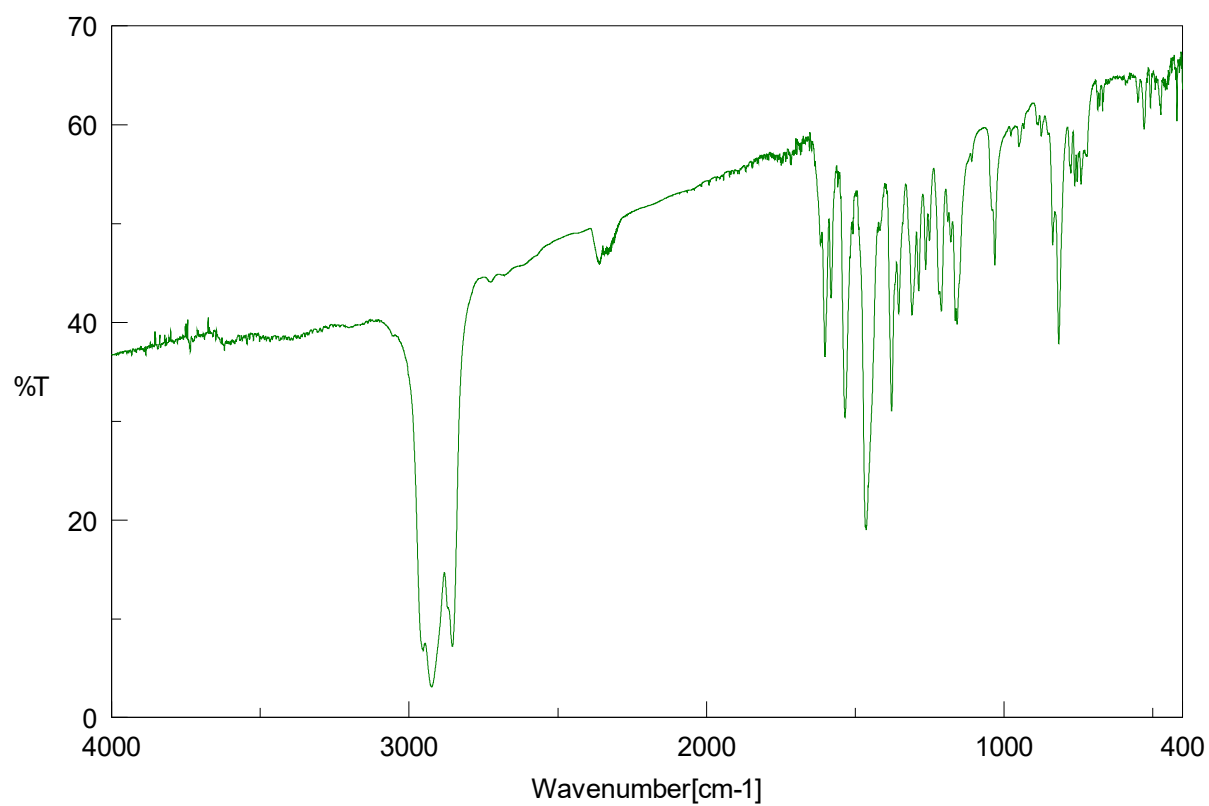


Figure S2 – FT-IR spectrum, in nujol, of complex **2OMe-OAc**.

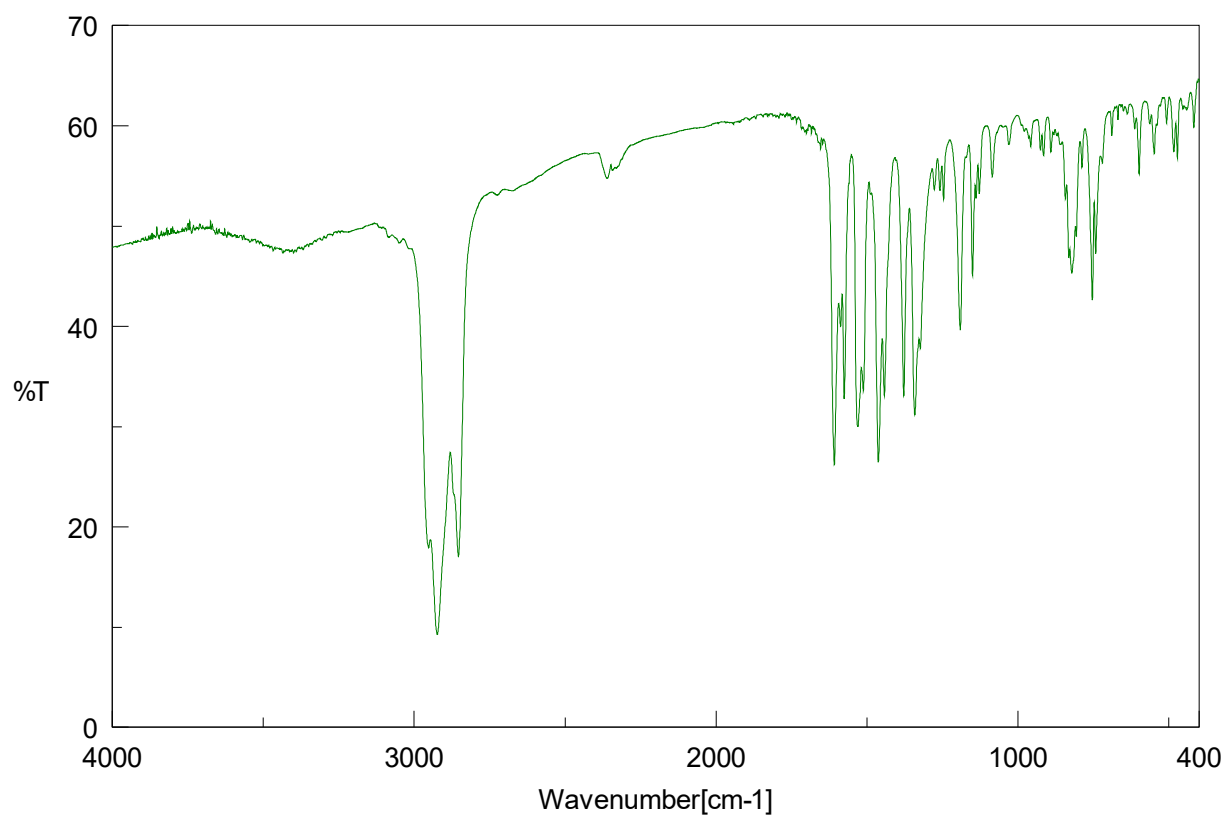


Figure S3 – FT-IR spectrum, in nujol, of complex **2'H-OAc**.

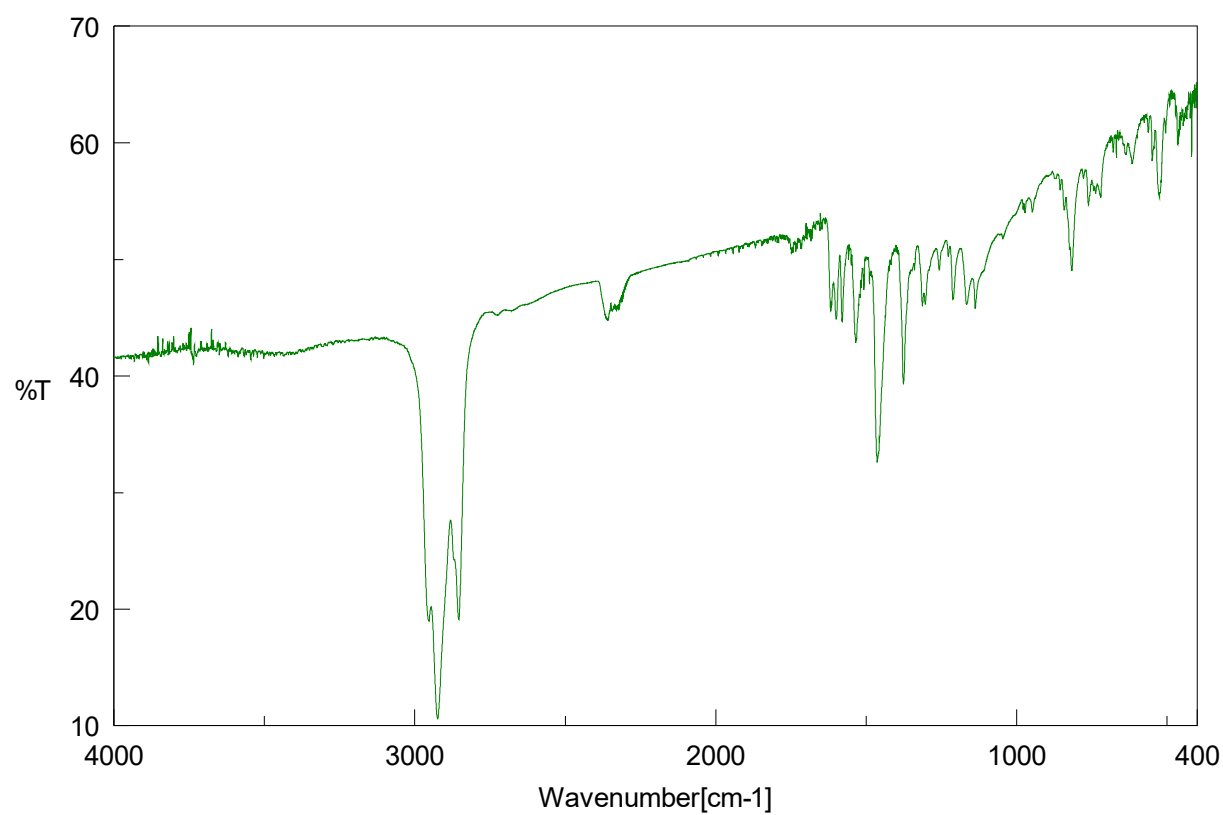


Figure S4 – FT-IR spectrum, in nujol, of complex **2Me-Cl**.

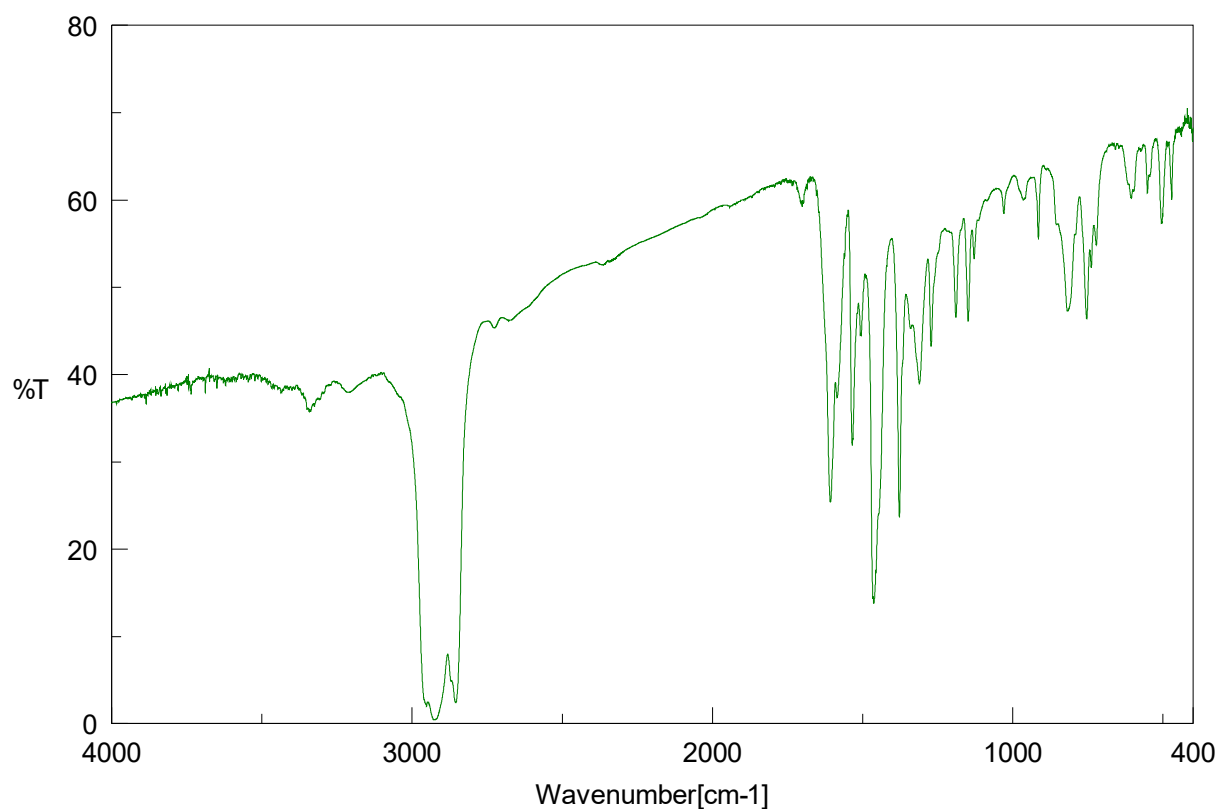


Figure S5 – FT-IR spectrum, in nujol, of complex **2''H-OAc**.

Table S1 - Melting points (decomposition) of the catalysts

Entry	Catalyst	Mp(decomposition)
1	2H-OAc	335 °C
2	2H-Cl	277 °C
3	2Me-OAc	321 °C
4	2Me-Cl	271°C
5	2OMe-OAc	305 °C
6	2OMe-Cl	264 °C
7	2'H-OAc	332 °C
8	2''H-OAc	308 °C

Paragraph S1. Vegetable oils characterization methods

The following abbreviations were used: V_t , titrating volume (mL); V_b , titrating volume blank test (mL); $[C_x]$, titrating concentration; Mw_x , formula weight (for KOH 56.11 gmol^{-1}); m_{oil} , sample mass (g); Pe , conversion factor (12,69).

- **Acidity Value (AV) determination:** 10-20 g of vegetable oil were diluted in 50 mL of a solvent mixture (ethanol-diethyl ether 1:1 in volume). The solution was titrated with 0.1 M KOH vigorously stirring and using phenolphthalein solution as an indicator. The acidity value (or neutralization number) is expressed following equation (1) as potassium hydroxide milligrams needed to neutralize the acidity of one gram of sample.

$$AV = \frac{(V_t - V_b) \cdot [C_{KOH}] \cdot Mw_{KOH}}{m_{oil}} \quad (1)$$

- **Peroxide Value (PV) determination:** 1.2 g of vegetable oil were diluted in 10 mL of chloroform and 15 mL of acetic acid. After a few minutes under magnetic stirring, 1 mL of a potassium iodide saturated solution was added. The flask was closed and left to react for 5 min protected from the light. Then 75 mL of distilled water and 1 mL of a starch solution as indicator were added. The produced free iodine was titrated with a 0.01 M sodium thiosulphate solution under vigorous stirring. The peroxides value is expressed following equation (2) as milliequivalents of active oxygen per kg of oil.

$$PV = \frac{(V_t - V_b) \times [C_{Na_2S_2O_3}] \times 1000}{m_{oil}} \quad (2)$$

- **Iodine Value (IV) determination:** 1.2 g of vegetable oil were diluted in 20 mL of a solvent mixture (cyclohexane-acetic acid 1 : 1 in volume). Then, 25 mL of Wijs reagent were added, the solution was placed in the dark, and a blank test was prepared as well. After 2 hours, 20 mL of a potassium iodide solution (100 g/L) and 150 mL of water were added to each flask. The solution was titrated with 0.1 M sodium thiosulphate using a starch solution as an indicator. The iodine value is expressed following equation (3) as the amount of iodine in grams that can be set in 100 g of fatty substance.

$$IV = \frac{Pe \times [C_{Na_2S_2O_3}] \times (V_b - V_t)}{m_{oil}} \quad (3)$$

- **Fatty acids composition determination:** the molar fractions of saturated (SFAs), monounsaturated (MUFAs) and polyunsaturated (PUFAs) fatty acids were estimated for fresh soybeans oil and sunflower oil by ^1H NMR (example in Figure 6) setting at 2 the integral from signal d and using the following equations (4-6):

$$MUFAs, \%_{mol} = \frac{(\int a - \int c \cdot 2)}{2} \cdot 100 \quad (4)$$

$$PUFAs, \%_{mol} = \frac{(\int c \cdot 2)}{4} \cdot 100 \quad (5)$$

$$SFAs, \%_{mol} = 100 - (MUFAs + PUFAs) \quad (6)$$

In this approximative composition, the PUFAs value refers to di-unsaturated fatty acid.