# Heterogeneously Catalytic Hydrogenation of Animal Fatty Acids in Supercritical $CO_2$

Stefania Muto[1,2]*, F. Zaccheria[1], N. Ravasio[1] and R. Bogel-Lukasik[2]

[1]*CNR-ISTM, Via Golgi 19, 20133 Milan, Italy,*

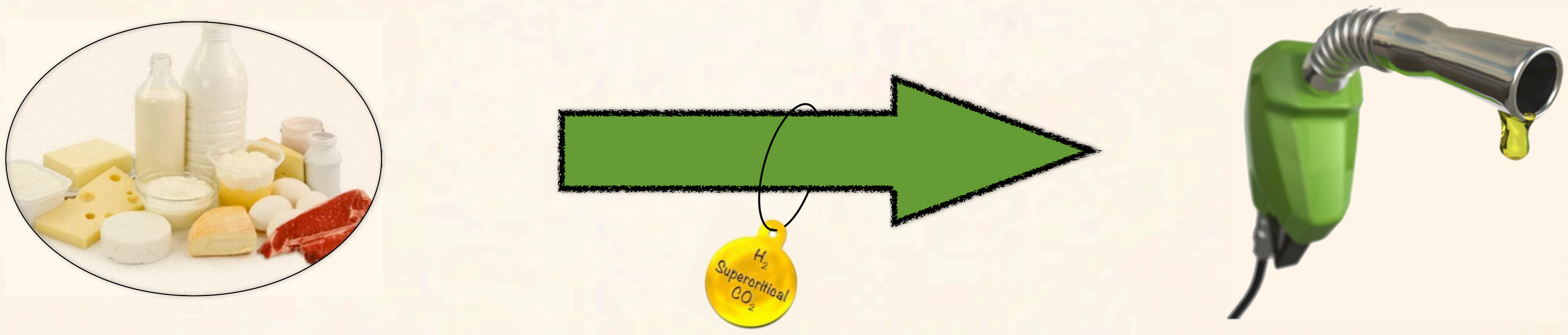
[2]*Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia, 1649-038, Portugal,*

* stefania.muto@istm.cnr.it

The heterogeneous catalytic hydrogenation of fatty acids is a possible system to obtain biodiesel from renewable resources[1], because they are not chemically very different from some petroleum fractions [2]. Non conventional solvents as supercritical fluids can be investigated to develop a process that follows the principles of green chemistry and environmental sustainability. Carbon dioxide is readily available, cheap, recyclable, non-toxic and non-flammable and for these reasons it is used as solvent in many types of catalytic reactions [3].

The LNEG laboratory is optimizing a green process to obtain chains of C16-C18 hydrocarbons by catalytic hydrogenation of animal fats using $H_2$ pressure and supercritical $CO_2$.

**Animal Fatty Acids** → **Biodiesel**




The catalytic reactions were performed varying the temperature and $CO_2$ and $H_2$ pressures. The raw material used was a mixture of animal fatty acids and the catalyst was a Fluid Catalytic Cracking **(**FCC) one, used in industry for the cracking of high-molecular weight hydrocarbon fractions. The data of the optimization reactions are reported in **Table 1**.
The system used for the hydrogenations of fatty acids is shown in **Figure 1**.

**Table 1**. Reactions of hydrogenation of animal fatty acids, catalyzed by FCC in supercritical $CO_2$: optimization of the temperature and the $H_2$ and $CO_2$ pressures.

| Run | T (°C) | $H_2$ p (bar) | $CO_2$ p (bar) | Catalyst Recovered (g) | Liquid phase (g) | Solid phase (g) | Total yield (g) | Total percent yield (%) |
|---|---|---|---|---|---|---|---|---|
| R14 | 340 | 11 | 140 | 5.351 | 4.706 | 5.821 | 10.527 | 94 |
| R15 | 320 | 11 | 140 | 5.541 | - | 14.829 | 14.829 | 132 |
| R16 | 300 | 11 | 140 | 5.339 | - | 10.687 | 10.687 | 95 |
| R17 | 340 | 5.5 | 140 | 5.222 | 5.274 | 2.903 | 8.177 | 73 |
| R18 | 340 | 22 | 140 | 5.070 | 4.819 | 3.205 | 8.024 | 72 |
| R19 | 340 | 5.5 | 160 | 4.999 | 2.750 | 4.582 | 7.332 | 65 |

Experimental conditions: FCC catalyst = 4.8 g, raw material = 11.2 g.


**Figure 1**. The reactor and the system used to hydrogenate the animal fats with $CO_2$ and $H_2$ pressures.

The mixture constituted by chains of C16-C18 alkanes should be liquid in the reactor at the end of the reaction and so we can suppose that the optimal conditions of temperature and pressure of $H_2$ and $CO_2$ are those reported in **Run R17**, because there was a higher amount of liquid phase than in the others.
These assumptions can be confirmed by GC analysis.

**Aknowledgements**
The autors would like to thank the COST program for STSM grant and the LNEG laboratory for the hospitality and the opportunity to work with them.

**References:**

[1] F. Zaccheria, R. Psaro, N. Ravasio, Green Chem., 2009, 11, 462–465.
[2] A. Corma, S. Iborra, A. Velty, Chem. Rev., 2007, 107, 2411–2502.
[3] M. G. Hitzler, F. R. Smail, S. K. Ross, M. Poliakoff, Org. Process Res. Dev., 1998, 2, 137-146.