Final Draft
of the original manuscript:

Bengtson, G.; Fritsch, D.:

Catalytic membrane reactor for the selective hydrogenation of edible oil: Platinum versus Palladium catalyst

In: Desalination (2006) Elsevier

DOI: 10.1016/j.desal.2006.03.476

Catalytic membrane reactor for the selective hydrogenation of edible oil: Platinum versus Palladium catalyst

Gisela Bengtson and Detlev Fritsch
GKSS-Forschungszentrum Geesthacht, Institute of Polymer Research,
21502 Geesthacht, Max-Planck-Str.1, Germany, gisela.bengtson@gkss.de

Introduction

For many purposes in food industry edible oil has to be hardened by hydrogenation. The commercially preferred low-cost Ni-catalyst requires temperatures of up to 200 °C causing high amounts (>50%) of trans-fatty acids [1]. These are objectionable because of health reservations. Noble metal catalysts allow working at lower temperature [2] and can be easily incorporated into the porous polyamideimide (PAI) membranes developed for high oil permeability at 100 to 140°C [3]. Operation in the membrane reactor affords the extended use of the expensive noble metals. Hydrogenation of sunflower oil was catalyzed by palladium and platinum, the results were compared in regard to reactivity and degree of trans-isomerization.

Experimental

Preparation of PAI membranes and their catalytic activation is described in [3]. The membranes have N_2-fluxes of up to 2800 m³/m²h bar, water fluxes (20°C) of 10000 to 50000 L/m²h bar and oil fluxes (60°C) of 500 to 1500 L/m²h bar. Metal content of the activated membranes was in the range of 0.1 to 2 g/m². *Membrane reactor conditions:* Membrane reactor tests were done in the flow-through mode with permeate recycling at 100°C and 4 bar of H_2 pressure. Membrane area was 100 cm² and 500 ml refined sunflower oil was treated in each run.

Results

Fig. 1 shows two typical hydrogenation runs with Pd resp. Pt catalysis. The reactivity is measured by the decrease of the iodine value (IV), summing up all included double bonds. The IV is roughly proportional to the major (65%) fatty acid component linoleic acid (C18:2 = octadecane chain /2 double bonds). Isomerization was observed by the increase of the trans-fatty acids, mainly trans-isomers of C18:1. Full hydrogenation leads to stearic acid (C18:0).

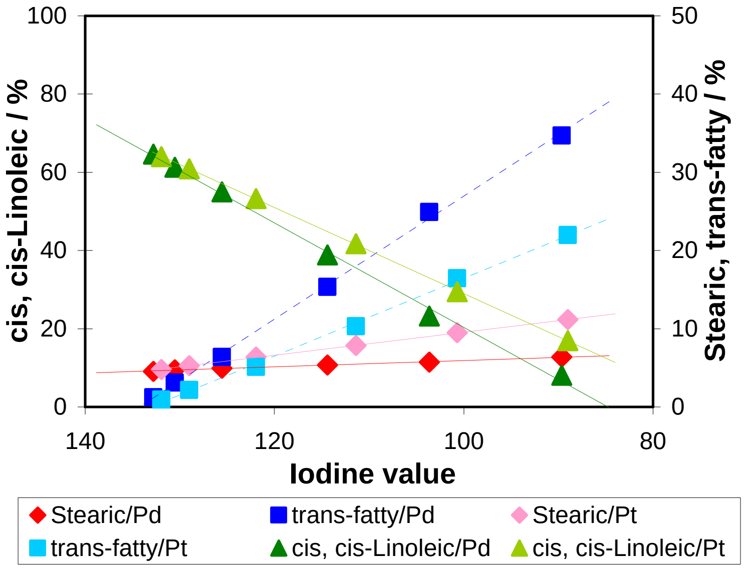

Fig. 2. Hydrogenation of sunflower oil in the catalytic membrane reactor.
Pd-catalyst = dark symbols, Pt-catalyst = light symbols. Metal content: 1g/m².

With both catalysts an IV of about 90 was achieved, however, the product composition was quite different. The degree of isomerization was definitely higher with Pd (35%), compared to 22% with Pt. Complete hydrogenation to C18:0, however, was higher with Pt (11%) but only slightly increased by Pd (from 4 to 6%). C18:1 increased in both cases from 23 to 29%. Reactivity was Pd>Pt: 88% of the linoleic acid has reacted within 8h, compared to 74%.
To verify the different results obtained by Pd and Pt, a simple test using supported catalysts for hydrogenation of methyl oleate (cis-C18:1) in solution at 1 bar H_2 was invented. It showed that catalysis by Pd proceeded exclusively via the trans-isomers, which are subsequently hydrogenated (Fig. 2). Pt catalysis is less reactive; it hardly worked on the trans-isomer methyl elaidate, but hydrogenated methyl oleate directly to methyl stearate.

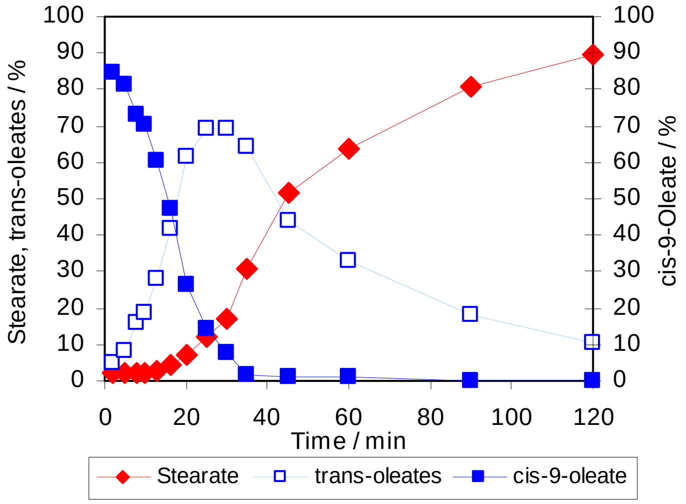

Fig. 2. Pd catalyst (2% on alumina) in methyl oleate test. Conditions: 100°C, n-decane. 5g methyl oleate / 2mg Pd, 1bar H_2.

Conclusions

Hydrogenation of sunflower oil was performed in a catalytic membrane reactor with highly porous membranes and a high throughput rate. At 100°C/4bar H_2 the iodine value of 500ml oil decreased from 130 to 90 within 8h using 100cm² of membranes activated by 1g Pd resp Pt/m². The isomerization to trans-fatty acids was higher with Pd catalysis (35%) compared to 22% with Pt. The latter produced more saturated stearic acid (11% compared to 6% by Pd). The suitability of Pt catalyst was proved by comparison of the supported catalysts in a simple test using methyl oleate in solution.

References

[1] D. Jovanovic, R. Radovic, L.Mares, M. Stankovic, B. Markovic, Nickel hydrogenation catalyst for tallow hydrogenation and for the selective hydrogenation of sunflower seed oil and soybean oil, Catalysis Today 43 (1998), 21-28.

[2] B. Nohair, C.Especel, P.Marecot, C.Montassier, Le Chien Hoang, J. Barbier, Selective hydrogenation of sunflower oil over supported precious metal, Comptes Rendus Chimie 7 (2004) 113-118.

[3] G. Bengtson, D. Fritsch, Development of catalytically reactive membranes for the selective hydrogenation of sunflower oil, Catalysis Today (2006), accepted.

Acknowledgement: Financial support by the EU program Quality of Life and Management of Living Resources: FP5-QoL-2001 QLK1-CT-2002-02234, contract QLK1-CT-2002-02234 is greatly acknowledged.