The Hydrogenation of Rapeseed Oil

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The influence of process conditions and feedstock qualities on the course and result of the hydrogenation.

1. Introduction

From an economical point of view it is essential to carry out both the hydrogenation and the subsequent filtration of the catalyst in the shortest possible time. Therefore, both activity and filterability of the catalyst are of great importance.
It is equally important of course to process the oil to the required product quality. The selectivity behaviour of the catalyst is an important factor in this respect.
Activity and selectivity are not only dependent on the quality of the catalyst, but also on the process conditions and the quality of the oil to be hydrogenated.
Taking rapeseed oil as an example it is shown, how the course of the hydrogenation and the properties of the endproduct can be influenced by varying the process conditions.

2. Basic theory and description of the tests

To a certain extent the hardening of rapeseed oil is comparable to that of fish oil. Contrary to other oils, both these oils contain relatively high contents of impurities, which can hinder the effect of the nickel catalyst. It is possible to distinguish between

- mechanical poisoning of the catalyst by impurities and gums in the oil, that can reduce the total surface of the catalyst.
- chemical poisoning of the catalyst by reactions with the nickel, e.g. by sulphurous compounds, giving nickel sulphides; this leads to a reduction of the surface of the active nickel.

The mechanical poisons can be removed effectively by refining the oil; the chemical poisons, however, can only partially be removed.

There are differences in the effect of the poisons on the course of the hydrogenation and on the quality of the hardened products. Mechanical poisons have only little influence on selectivity, however, activity will be diminished. Chemical poisons will also strongly affect the selectivity of the process. For instance, nickelsulphides will promote the formation of trans-isomers, a reaction which occurs to some extent in any hardening.

Especially in rapeseed oil higher sulphur contents are found, varying between 2 and 100 ppm depending on type and pretreatment.

Figure 1 shows the influence of various catalyst poisons on reaction rate. Clearly sulphur can be seen to have the most negative influence.

Poisoning Effect, related to several Elements

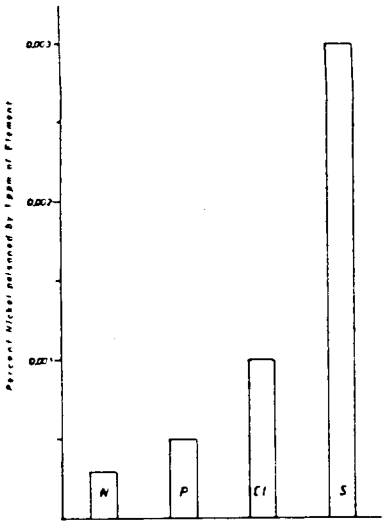


Figure 1

Survey on the Series of
Rapeseed Oil Hydrogenation Trials

Catalyst : PRICAT 9906

Type of Oil : Canola Rapeseed Oil

Trial No	Influences tested	Hydrogenation Conditions			
		Cat Conc (% mass)	Temperature (°C)	H_2-Pressure (bar)	Agitation (min⁻¹)
1	Catalyst Re-use	fresh 0.10 used --	200	2	750
1a		fresh -- used 0.15	200	2	750
1b		fresh 0.02 used 0.18	200	2	750
1c		fresh 0.02 used 0.18	200	2	750
1d		fresh 0.02 used 0.18	200	2	750
1e		fresh 0.02 used 0.18	200	2	750
1	Catalyst Concentration	0.10	200	2	750
2		0.20	200	2	750
1	Hydrogenation Temperature	0.10	200	2	750
3		0.10	140	2	750
1	Hydrogen Pressure	0.10	200	2	750
4		0.10	200	4	750
1	Catalyst Poisons	0.10	200	2	750
5		0.10	200	2	750

Figure 2

While a complete removal of the poisons by pre-refining is not usually possible, varying the hardening conditions will partially offset their influence. Using rapeseed oil, the effect of such variations on activity and selectivity is shown.

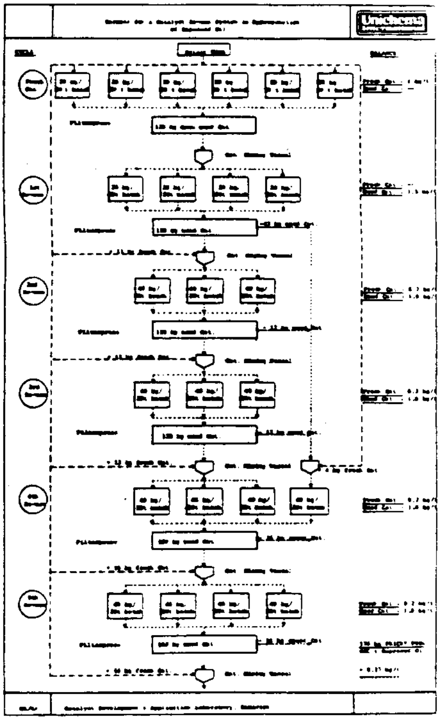
Figure 2 summarizes the tests and their respective process conditions.

2.1 Effect of re-use of the catalyst

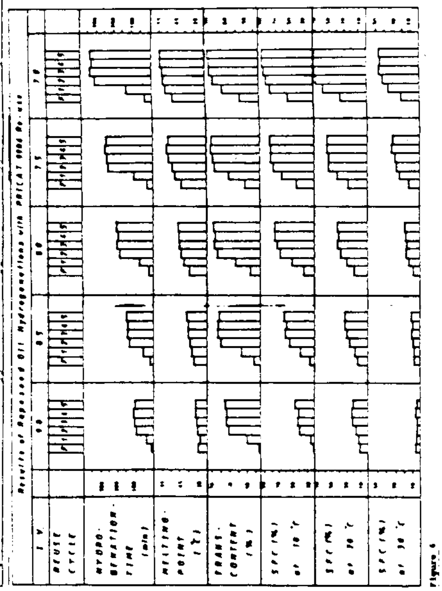
Multiple re-use of the catalyst not only gives a saving in catalyst consumption, but also more constant product qualities between different hydrogenation batches.

The Ni-content in the re-used catalyst depends on the filtration conditions applied. If no filter aid was used, approx. 15-20 % can be expected. Usually with every cycle abt. 10 % of the re-used

catalyst is replaced by fresh one.
As shown in figure 3, six cycles were done subsequently. The results are given in figure 4.



← figure 3



Although the gas-time is increasing, the results such as melting point, trans- and solids contents stabilize with increasing number of cycles to a constant level, yielding a constant product quality.

With this technique variations in raw material quality are levelled out, since the relatively high total amount of catalyst adsorbs part of the poisons and impurities in the oil to be hydrogenated, as well as catalysing the hydrogenation.

2.2 Effect of catalyst concentration (figure 5)

As can be expected higher catalyst concentrations will reduce the gas-time. Apart from the activity, the selectivity is also affected. In spite of the higher trans-isomer build up by higher concentrations, the melting point and solids contents at higher temperatures will be lower at same iodine values. This is due to the better polyene selectivity S 1.

Influence of the Catalyst Concentration on the Hard Fat Properties

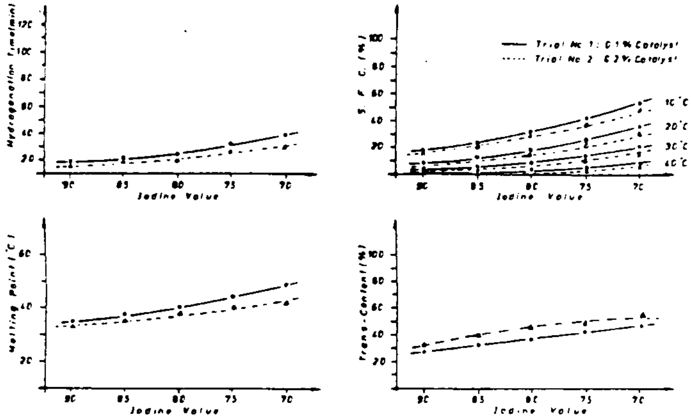


Figure 5

2.3 Effect of the hydrogenation temperature (figure 6)

Lower temperatures will increase the reaction time, i.e. the catalyst's activity will be reduced. Moreover, by keeping the hydrogenation temperature low, both the trans-isomerisation and the polyene selectivity will be diminished, resulting in a hydrogenated fat with a lower trans isomer content but an increased amount of stearine. Because there are considerable differences between the melting points of pure trans isomers (below 40°C) and of pure stearine (abt. 70°C) the solid fat contents of low temperature hydrogenated oils are lower at measuring temperatures of less than 30°C, but somewhat higher at temperatures of and above 30°C. The higher melting points are caused by the increased stearine formation, which is favoured during low temperature hydrogenation.

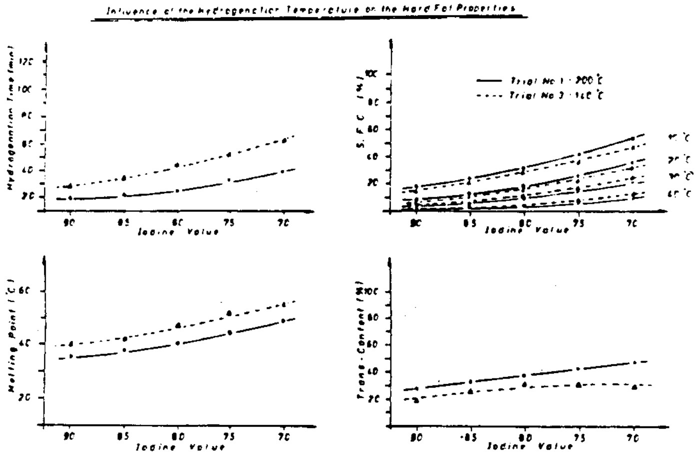


Figure 6

2.4 Effect of hydrogen pressure (figure 7)

A higher hydrogen pressure leads to a faster hydrogenation reaction. Despite the lower trans-isomerization under these conditions, the melting point and solid fat contents are not decreased. On the contrary, the actual higher melting point and S.F.C. data found are caused by a high stearine formation due to a worse polyene selectivity S 1. Thus at a higher H_2-pressure this effect superposes the lowered trans-influence.

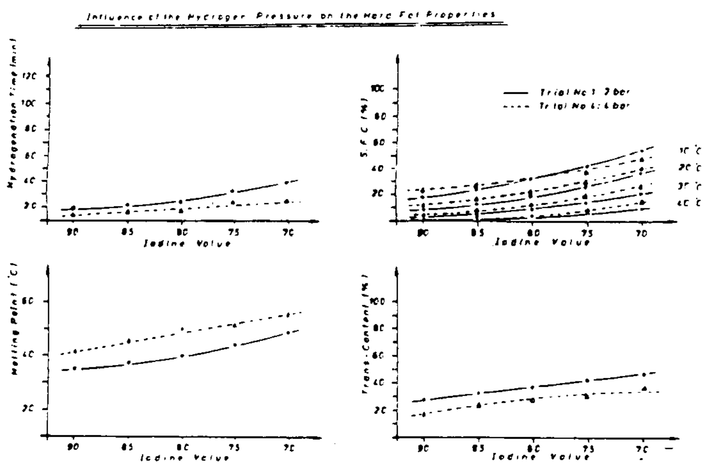


Figure 7

2.5 Effect of catalyst poisons (figure 8)

With a part of the rapeseed test oil the sulphur contents was deliberately lowered from 6.3 to 2.4 ppm. Under constant process conditions this clearly gives shorter gas-times, lower trans- and solids contents as well as lower melting points.

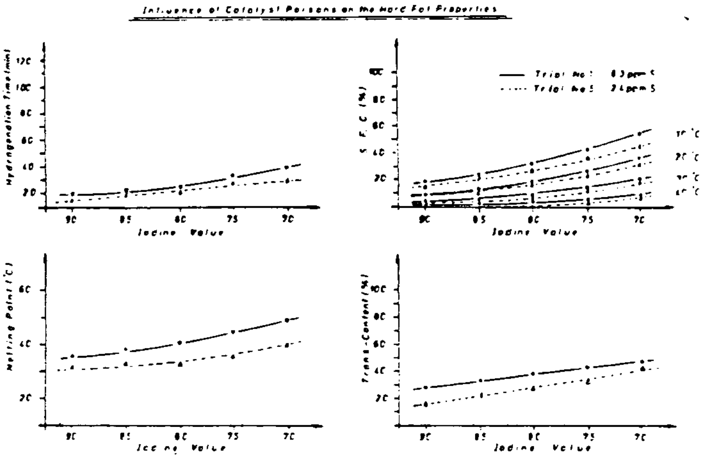


Figure 8

In summary it can be remarked that in spite of the permanently improving activity and selectivity of commercially available catalysts, the know-how of an experienced hydrogenation plant manager will rema remain essential for smooth processing to obtain the required product quality.

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