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The Use of Bleaching Earth in Fatty Acid Production

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ABSTRACT

Pretreatment of crude tallow or fish oil fatty acids with bleaching clays considerably improves the rate of hydrogenation with several different catalysts. Several series of tests were run to demonstrate these effects, and the data are presented.

To produce triglyceride-based fatty acids with a low iodine value (IV), a number of considerations have to be made. There exist, for instance, two principal routes: (a) hydrogenation of the neutral or slightly acidic oil followed by splitting and distillation; and (b) splitting of the triglyceride, followed by hydrogenation of the fatty acid and final distillation. The route chosen depends on the crude material available and on the facilities in the plant. Further aspects to be considered deal with some necessary purification steps.

For the splitting, followed by hydrogenation, one has also to consider whether the fatty acid should be distilled prior to the hydrogenation to remove impurities and poisons, as otherwise the hydrogenation would stop at rather high IV or the catalyst consumption would be too high. However, that means that the fatty acids are distilled twice, once before and once after the hydrogenation, which is costly. The decision for either route (a) or route (b) and for all the necessary purification steps also depends largely on the cost comparison for the possible variations. Especially for today's market, the end-product must be as cheap as possible in order to be competitive.

This paper deals with a type of purification step which we regard as interesting, as one can start from crude oils or crude fatty acids. The only necessary pretreatment is a clay treatment. For our tests, we used a crude tallow and a crude fish fatty acid.

HYDROGENATION OF CRUDE TALLOW

The crude tallow used is described in Table I. The hydrogenation of the crude untreated tallow was performed at 120-190 C under a pressure of 20 bar with 0.05% as Ni catalyst, and 1,000 rpm agitation.

Pretreatment of the crude tallow was done in the same autoclave as the hydrogenation, to simulate the cheapest way for this treatment. The conditions were with 1% Tonsil Optimum FF, at 110 C, for 30 min, at 50 mm Hg pressure.

After the clay treatment we added 0.025 and 0.050% of Ni catalyst, heated to 120 C under vacuum, and started addition of hydrogen. The temperature was then increased in 30 min to 190 C. Pressure was 20 bar and agitation 1,000 rpm.

RESULTS

To find the optimum amount of clay for the pretreatment, we performed a series of tests with no clay treatment and with different amounts of clay. Figure 1 shows the results of these tests. It is evident that a pretreatment with 1% clay improves the hydrogenation time dramatically. The hydrogenation time down to an IV of 2.5 is reduced from 5 hr to 1 hr while, with no pretreatment, the final IV after 6 hr is 1.5 and a further reduction is almost impossible. Under these conditions, we obtained an IV of less than 1 in 1 hr 20 min with 1% clay, and in 1 hr with 2% clay. As the difference between 1 and 2% of clay is not very significant from a practical point of view, we decided to use 1% of clay for all the other tests.

To perform the hydrogenation down to a maximum IV of 1 within 3 hr, we reduced the amount of nickel by 50%. The result is shown in Figure 2. Curves 1 and 4 belong to one catalyst and curves 5 and 6 to another catalyst. The difference between curves 1 and 4, and curves 5 and 6, respectively, is still quite significant, even as the catalyst concentration is reduced by 50% down to 0.025% Ni for this type of tallow. It is interesting to note that the hydrogenation time down to an IV of 2 for the different catalysts shows a difference of ca. 25% in the case of the crude tallow, whereas with pretreatment the hydrogenation time is about the same. With pretreatment and a reduced amount of catalyst, the final IV was even lower than without pretreatment. Furthermore, the hydrogenation time was ca. 1/3 shorter, respectively, half as long for the two catalysts applied.

HYDROGENATION OF CRUDE FISH OIL FATTY ACIDS

Characteristics of the fish oil fatty acids are shown in Table II. The tests were done under similar conditions as mentioned for tallow, but in addition we also performed tests on bleached fish oil fatty acids. Bleaching of the crude fatty acids was with 1% Tonsil Optimum FF for 30 min at 95 C and 50 mm Hg pressure. Under these conditions we obtained bleached fatty acids with the characteristics shown in Table II.

The conditions for the pretreatment of the crude fish oil fatty acid were slightly different from the bleaching operations and were with Tonsil Optimum FF clay for 20 min at 110 C and at 20 mm Hg pressure.

Hydrogenation of the crude, the pretreated and the bleached fish oil fatty acids was performed under identical conditions with variable concentrations of Ni catalyst at 75-200 C and 20 bar pressure with 1,000 rpm agitation. The only difference is the fact that, in the case of the pretreated fatty acid, the bleaching earth was not removed before hydrogenation.

To determine the advantages of a pretreatment or a separate clay treatment prior to the hydrogenation step, we first performed a series of hydrogenations with different amounts of catalyst added to the crude fish oil fatty acid. Furthermore, we performed tests with pretreated fish oil fatty acids. The pretreatment was done with 0.5, 1 and 2% of a highly activated clay.

Results for the hydrogenation of the crude fish oil fatty acid with varying amounts of catalyst are shown in Figure 3. It is evident from this graph that, for this type of catalyst

TABLE I

Characteristics and Color of Crude Tallow

Characteristics	
FFA	3.8%
Phosphorus	61 ppm
POV	5.2
AnV	4.6
Polyethylene	280 ppm
Color (5¼" Lovibond cell)	
Red	10.7
Yellow	70.0
Blue	0.2
White	1.0

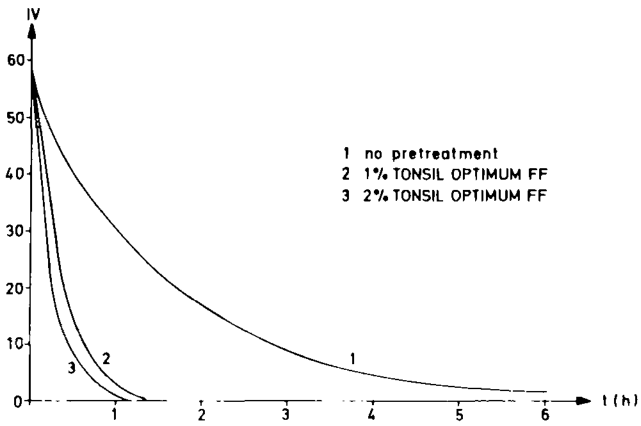

FIG. 1. Hydrogenation of tallow. Concentration: 0.05% Ni; temperature: 120-190 C; pressure: 20 bar.

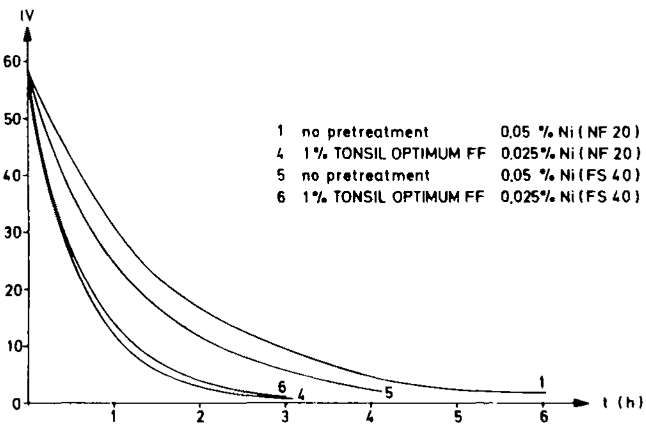

FIG. 2. Hydrogenation of tallow. Temperature: 120-190 C; pressure: 20 bar.

TABLE II

Characteristics and Color of Crude and Bleached Fish Oil Fatty Acids

Crude fish oil fatty acid		Bleached fish oil fatty acids	
Characteristics		Characteristics	
Phosphorus	7.7 ppm	Phosphorus	6.1 ppm
POV	13.2 meq/kg	POV	1.8 meq/kg
AnV	48.9 meq/kg	AnV	30.7 meq/kg
Color (5¼" Lovibond cell)		Color (5¼" Lovibond cell)	
Red	21.3	Red	11.3
Yellow	70.0	Yellow	40.0
White	1.0	White	1.0

and for this type of fish fatty acid, 0.1% is necessary to reach a final IV of <5 within 4 hr. Due to the fact that we started the hydrogenation at 75 C, with a heating rate of ca. 2 C/min, the slope at the beginning of the hydrogenation gives information about the starting point of the reaction. As the same catalyst is always used, with different concentrations, we can see in Figure 3 the influence of all the poisons or deactivating substances present in the crude fish fatty acid. The dotted lines in this and in the following figures show the IV reduction during a 4-hr period and the solid line shows the decrease of the IV in a period of 1 hr. It is obvious that 0.2% Ni is far too much catalyst as the IV goes down within 15 min to less than 10. It was almost impossible to control the reaction temperature even with the internal cooling system which was installed in our 5-L autoclave. At the lower catalyst concentrations, however, we can well observe the influence of the deactivating substances. This becomes clearest for the 0.05% Ni curve.

We have plotted four curves for hydrogenation tests with 0.05% Ni, but with a different treatment of the crude fish oil fatty acid in Figure 4. Curve 1 is identical with the 0.05% Ni line in Figure 3. We can conclude that the hydrogenation becomes faster and goes to lower IV with an increasing amount of clay. With pretreatment with 1% clay we obtained an IV of ∿15 after 4 hr; with 2% clay, the IV after 4 hr was ∿10.

It is questionable whether the bleaching clay acts as a cocatalyst or if it just adsorbs deactivating substances as phospholipids or soaps. It will also decompose oxidized fatty acids which have a poisoning effect on the hydrogenation catalyst. The answer to this question is given in Figure 5. We can conclude from these curves, which were obtained with 0.075% Ni, that the standard bleaching operation with a filtration step prior to the hydrogenation gives even better results than the clay pretreatment, wherein we did not remove the clay before the hydrogenation.

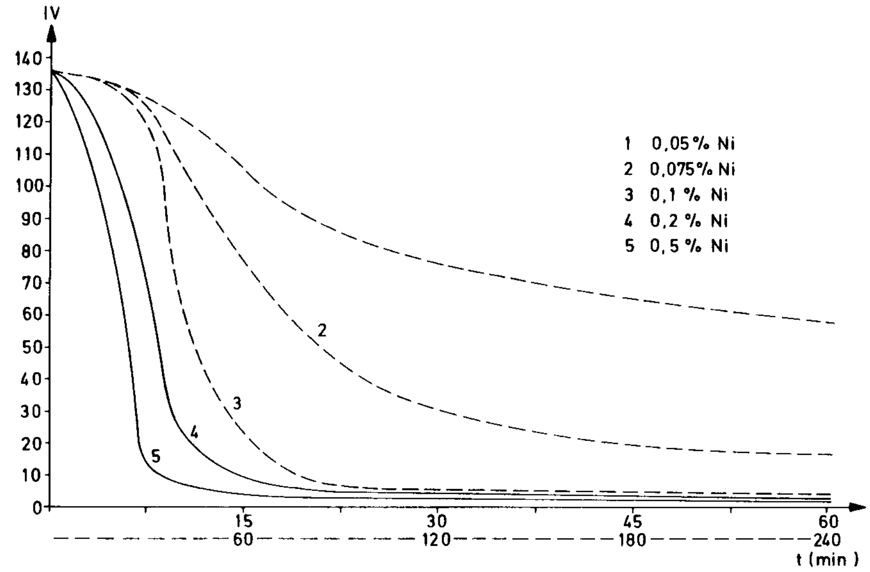

FIG. 3. Hydrogenation of crude fish oil fatty acid. Catalyst: FS 40; temperature: 75-200 C; pressure: 20 bar.

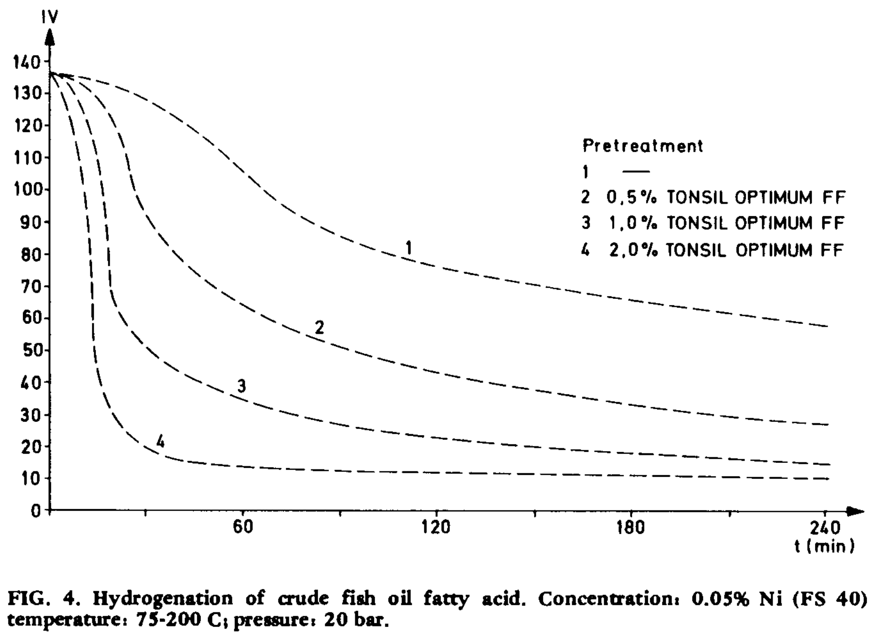

FIG. 4. Hydrogenation of crude fish oil fatty acid. Concentration: 0.05% Ni (FS 40); temperature: 75-200 C; pressure: 20 bar.

The final IV after 1 hr was slightly above 5 and changed little with prolonged hydrogenation time of 4 hr. With no pretreatment the hydrogenation was much slower, but we see during the whole 4-hr treatment a reduction of the IV, reaching ca. 17 after 4 hr.

Figure 6 shows the results based on an addition of 0.1% Ni. Curve 1 is plotted twice, first for the 4-hr hydrogenation cycle and secondly for the first hour only. Influence of the clay treatment can be observed mainly during the first 30 min. A fast hydrogenation without pretreatment starts just after 30 min when the temperature reached ca. 140 C. Using just 0.5% of clay a fast reduction of the IV was observed after only 8 min, as there was a very rapid temperature increase of the oil up to 195 C within 10 min. For higher clay concentrations, this temperature increase started after only 2 min. It was even steeper than for the 0.5% clay treatment.

This test series showed that, for hydrogenation of a crude fish oil fatty acid as used in our experiment, a quantity of ca. 0.1% Ni is necessary. The hydrogenation will lead in ca. 2 hr to an IV of ca. 5 with the tested catalyst. When lower IV are necessary, pretreatment or a bleaching step has to be made. A separate bleaching step or a clay pretreatment also allows reduction of the catalyst concentration of ca. 25% to achieve the same final IV. Furthermore, the bleaching or pretreatment step reduces the hydrogenation time by a factor of 2-3 as most of the reaction is performed during the first 30 min. A further advantage is the low starting temperature of the hydrogenation and consequently the energy savings.

The series on the crude tallow were made with 2 catalysts designed for neutral fats and fatty acids, but the series on the crude fish oil fatty acids was performed only with one catalyst designed for fatty acids. To see if other catalysts show the same positive influence on a clay pretreated oil or fatty acid we did further tests which are

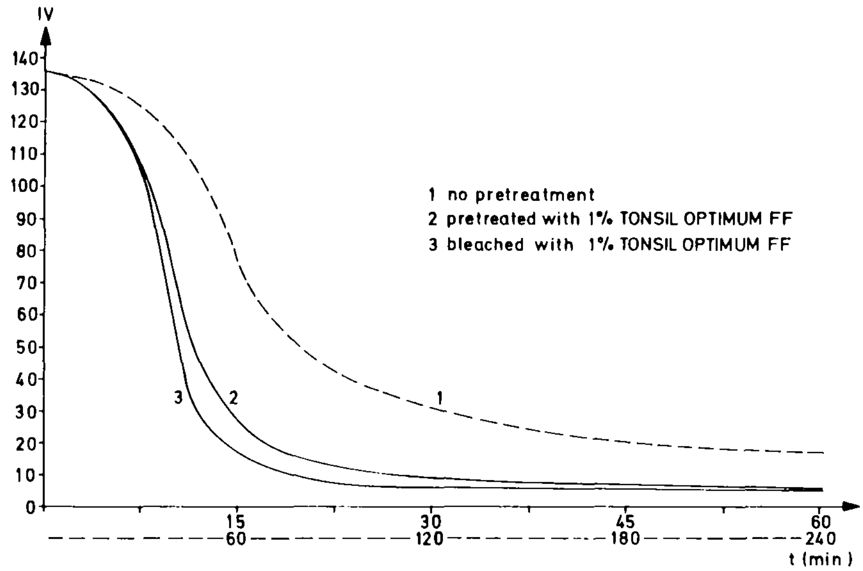

FIG. 5. Hydrogenation of crude fish oil fatty acid. Concentration: 0.075% Ni (FS 40); temperature: 75-200 C; pressure: 20 bar.

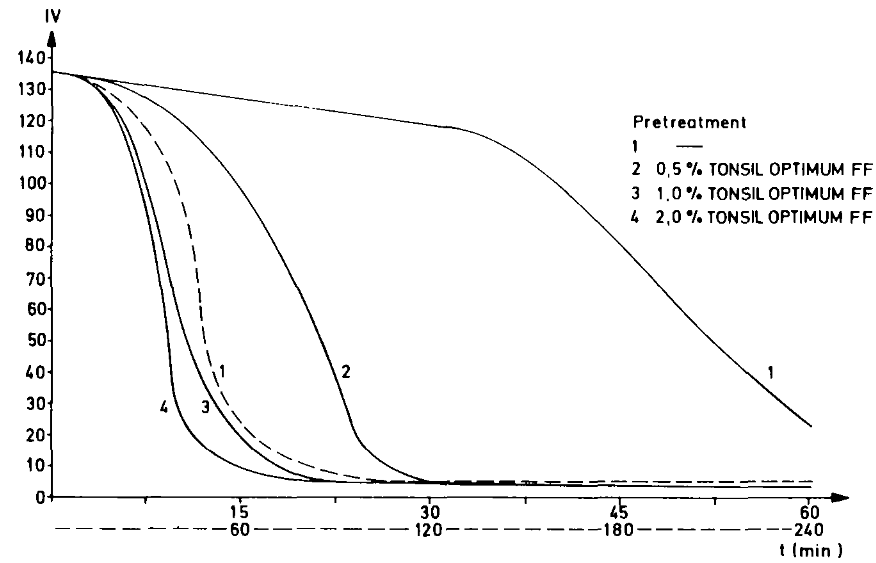

FIG. 6. Hydrogenation of crude fish oil fatty acid. Concentration: 0.1% Ni (FS 40); temperature: 75-200 C; pressure: 20 bar.

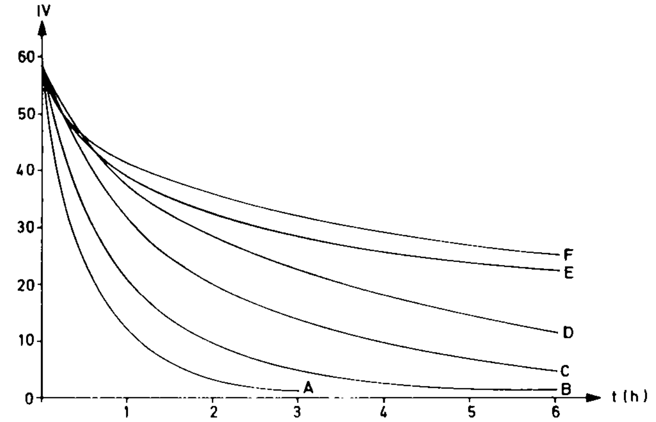

FIG. 7. Hydrogenation of tallow: pretreatment with 1% Tonsil Optimum FF at 110 C. Concentration: 0.025% Ni; temperature: 120-190 C; pressure: 20 bar.

shown in Figure 7 for hydrogenation of the crude tallow pretreated with 1% clay. Considering the extremely low Ni level and the curves shown in Figures 1 and 2, it can be concluded that a pretreatment or a separate bleaching step improves the rate of hydrogenation remarkably. The positive influence of bleaching clay becomes even more obvious when we look at Figures 8 and 9. In Figure 8 the hydrogenation curves for a number of different catalysts are shown. Remarkable is the curve for catalyst D which starts the hydrogenation after ca. 25-30 min when the temperature was 125-135 C. But after that late start it hydrogenated the crude fish fatty acid down to an IV of 6, the second-best result.

Another interesting curve is that of catalyst H. This catalyst showed quite a high activity at 75 C, but after ca. 1 hr the slope became flatter. In Figure 9, we compare catalysts G and H which were the two extremes in Figure 8. Curve 1 is based on 240 min hydrogenation time, whereas curves 2 and 3 show the IV during the first hour of the hydrogenation only. We learn from these curves that the active catalyst H is very easily poisoned by the crude fish oil fatty acid. But when the acid was pretreated it became similar to catalyst G and when the acid was bleached, both catalysts became identical after 15 min hydrogenation time. From this result we learn that it is almost impossible to distinguish between different catalysts when the concentration is above a certain level, as can be seen from Figure 3.

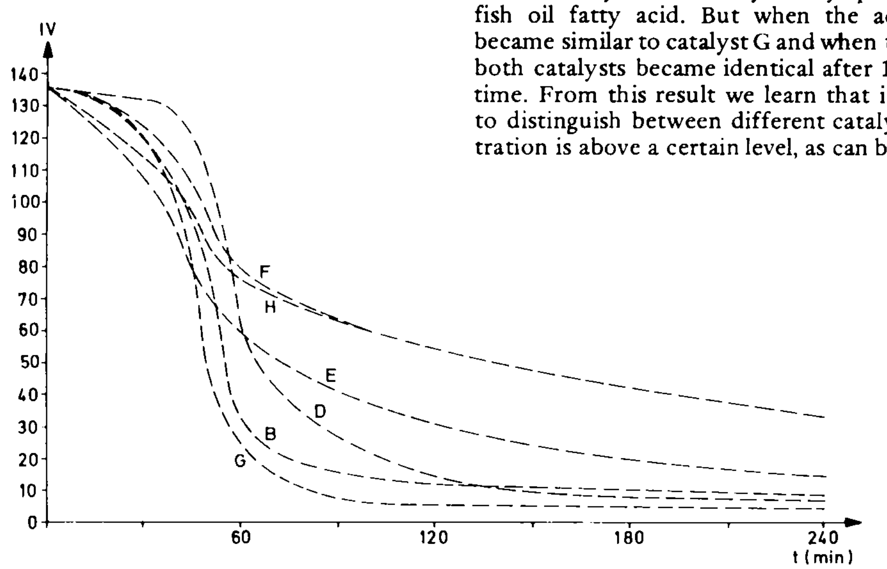

FIG. 8. Hydrogenation of crude fish oil fatty acid. Concentration: 0.1% Ni; temperature: 75-200 C; pressure: 20 bar.

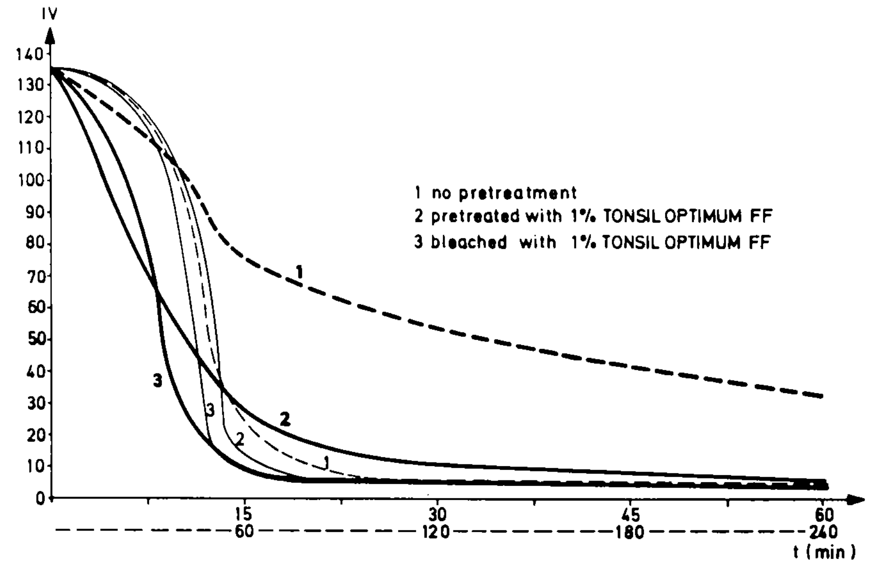

FIG. 9. Hydrogenation of crude fish oil fatty acid. Concentration: 0.1% Ni (catalysts G and H); temperature: 75-200 C; pressure: 20 bar.