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Catalyst characteristics and performance in edible oil hydrogenation

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Abstract

Hydrogenation of vegetable oils was first discovered in the beginning of this century and quickly became a major processing step in the fats and oils industry. Hydrogenation changes a liquid oil made of triglycerides of polyunsaturated fatty acids to one containing mostly monounsaturated fatty acids. This procedure improves the functionality and flavor stability of the oil. The process is a complex series of reactions occurring in a three-phase slurry reactor in a batch mode primarily utilizing supported Ni catalysts and can result in a variety of products. A good catalyst for edible oil hydrogenation must have good activity, selectivity, poison resistance and filterability. The physical characteristics of the catalyst affect these attributes greatly. This paper discusses these attributes and how a catalyst and the operating conditions affect them.

Keywords: Hydrogenation; Edible oils; Nickel

1. Introduction

Hydrogenation of vegetable oils has been around since the beginning of this century. In that time, it has become a major processing step in the fats and oils industry. The process is defined as converting a liquid oil to a solid or semisolid product by means of a multi-phase catalytic reaction with hydrogen. There are two main reasons why hydrogenation is important to the industry. The first is increasing the stability of the oil. A highly unsaturated oil is susceptible to autoxidation, thermal decomposition and other reactions that affect the flavor. Consequently, it is desired to partially hydrogenate the oil to improve shelf life. The second reason to partially hydrogenate vegetable oil is to improve its utility. For most products, such as shortenings, margarines or confectionery fats, the desired softening and melting characteristics correspond to oils that are partially hydrogenated. The choice of catalyst to use for hydrogenation greatly affects the properties of the final product.

In order to understand how catalysis of the hydrogenation reaction helps the oil processor, we must first understand the properties of vegetable oil and how hydrogenation can enhance them. Vegetable oils are primarily composed of triglycerides, which are esters of glycerol and fatty acids. Fig. 1 shows the basic structure of a triglyceride molecule. The most common fatty acid chains in vegetable oils include, but are not limited to, the saturated palmitic and stearic acids and the unsaturated oleic, linoleic and linolenic. These fatty acid chains are randomly distributed among the triglycerides, making the separation of specific triglycerides virtually im-

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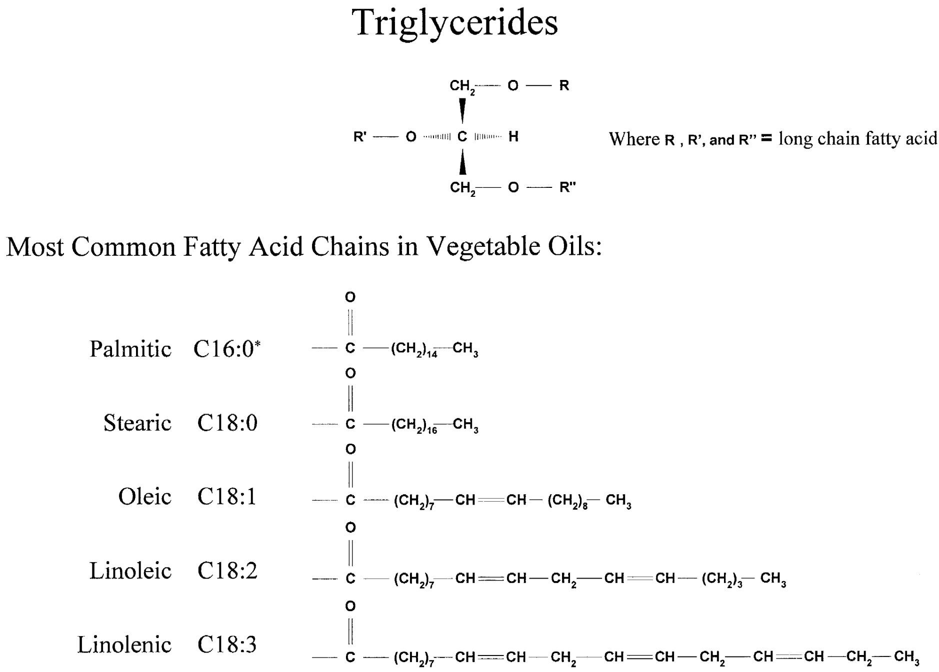


* Nomenclature: C16:0 indicates a 16 carbon chain with 0 double bonds.

Fig. 1. Basic structure of a triglyceride molecule and the most common fatty acid chains in vegetable oils.

possible. Further complicating matters is the fact that different varieties of seeds yield oils with different overall composition of fatty acid chains. Table 1 shows the typical fatty acid composition of common vegetable oils. By partial hydrogenation of the unsaturated bonds, it is possible to manipulate the fatty acid composition and achieve the desired properties of the oil. The properties that oil processors are concerned with when hydrogenating are the final Iodine Value (IV), fatty acid composition, melting point and the solid fat content. The IV is a measure of the unsaturation of the oil and is expressed as the centigrams of iodine absorbed per gram of oil. Therefore hydrogenation decreases the IV. The melting point and the solid fat content of the oil is indicative of the utility of the oil.

Table 1
Fatty acid composition of common vegetable oils

	Soybean	Canola	Corn	Peanut
C16:0	10.5	4.9	11.5	11.0
C18:0	3.2	1.9	2.2	2.3
C18:1	22.3	57.0	26.6	51.0
C18:2	54.5	24.0	58.7	30.9
C18:3	8.3	10.4	0.8	0.7
C20:0	0.2	1.5	–	–
IV	130	115	124	84–100

The use of heterogeneous catalysts has proven to be most effective in achieving the desired fatty acid composition and melting properties. By definition, a heterogeneous catalyst is one that is present in a different physical state than the reactants. In this case, the catalyst is a solid while the reactants are in liquid and gas states. The reaction is conducted as a batch slurry reaction in industry. The active metal in these types of catalysts is supported on a porous material. This material affects the mass transfer of the reactants, allowing the manipulation of the properties of the final hydrogenated product. This is possible by selecting the catalyst according to its intrinsic characteristics and the operating conditions to be used in the reaction. This paper will examine the properties of hydrogenated vegetable oil and the characteristics of the catalyst that affect these properties.

2. Catalyst manufacture

A great number of tests have been carried out with many metals on triglyceride hydrogenation with the final conclusion that Nickel is the most appropriate because it has the best benefits to cost ratio. Current technology in catalyst manufacture uses a dry reduction method shown in Fig. 2. The nickel salt solution is deposited on the support material. The support materials can be silica, alumina, or silica–alumina. Once the nickel has been deposited on the carrier, it is washed, dried, calcined and then reduced in hydrogen at appropriate temperatures. About 60% of the nickel is reduced to zerovalent metal, which is responsible for catalytic activity. The resulting black powder is pyrophoric and therefore should be stabilized to prevent contact with air. Soybean stearine (fully hydrogenated soybean oil) is commonly used for this purpose. The soybean stearine is added to the catalyst while still in the hydrogen atmosphere. This prevents the nickel metal from oxidation and lowering its catalytic activity. Once the catalyst has been stabilized, it is cooled, formed and packaged.

3. Physical characteristics of the catalysts

The physical characteristics of the catalysts play an important role in the development of the reaction. The pores of the support should be sufficiently large enough so that the active metal, in this case nickel, is accessible to the triglyceride molecules and allow enough movement within the pores to allow the normal progress of the reaction.

Considering that the reactions involved take place on the surface of the catalyst, a large surface area is fundamental in the achievement of good performance. The support is the medium in which the metal is distributed over a large surface. As an example, 1 g of nickel as a solid cube has a surface area of lower than 1 cm^2. The same gram of nickel in 50–100Å particles can occupy approximately 100 m^2. If we were to disperse these particles uniformly on a porous material, we could have an area of 200–600 m^2

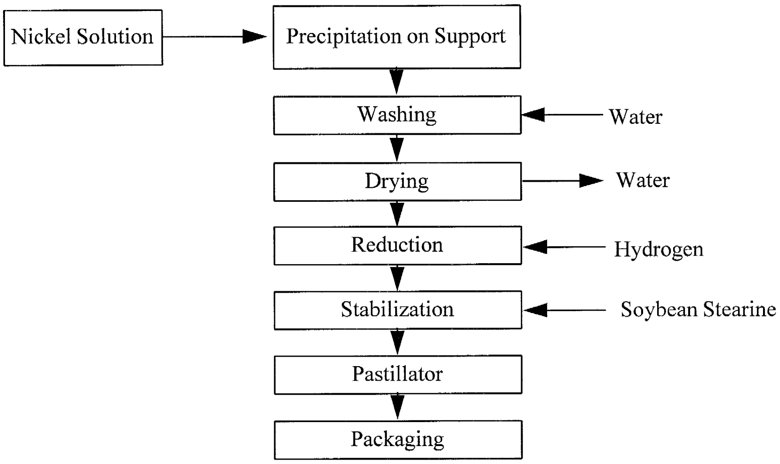


Fig. 2. Schematic of the manufacturing process of Nickel catalysts.

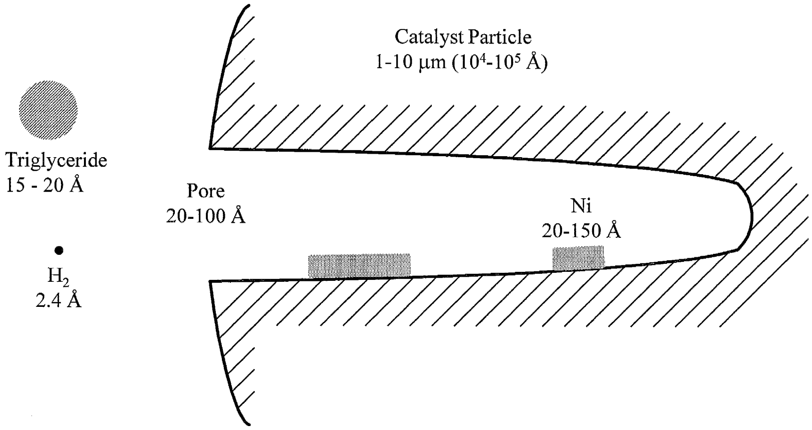


Fig. 3. Relative sizes of reaction components taking place in the reaction.

covered with nickel. Fig. 3 is an example of the relative sizes of the reaction components taking place in the reaction.

These physical characteristics of a catalyst, independent of the operating conditions of the hydrogenation, affect the course of the reaction. Therefore, they have an important influence on the activity, selectivity, poison resistance and filterability during the hydrogenation process. Each of these reaction attributes will be discussed in more detail.

4. Effect on activity

The total surface area of the catalyst, its particle size and the physical characteristics of its pores, are of great importance on the rate of the reaction. These factors are directly related to the diffusion of the reactants and their accessibility to the active sites of the catalyst.

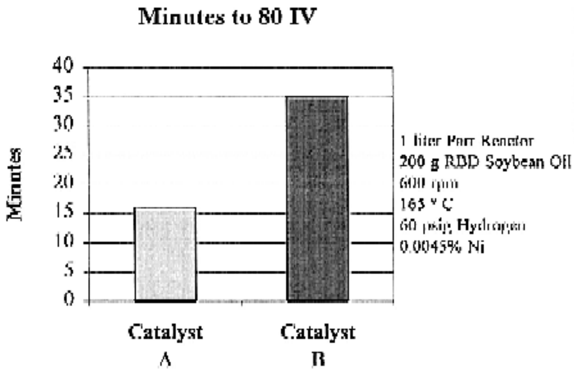
The active sites are the actual nickel surface atoms on which the reactions occur. Table 2 summarizes the affect of the physical characteristics of catalysts on the activity of hydrogenation. Pores with diameters smaller than 20Å do not contribute to the progress of the reaction since the triglyceride molecules cannot reach the active sites within them. Following the same principle, the faster the diffusion of the triglyceride molecules through the pores of the catalyst, the faster the rate of the reaction. This is obtained with relatively short pores and with medium to large diameters such as 40Å to 100Å. At the same time, increasing the number of small particles increases the global surface area of the catalyst and the possibility of having more active centers. Increasing the number of smaller catalyst particles also decreases the length of the pores.

Besides diffusion factors, the distribution and size of the nickel crystallites on the support play an important role in the activity of the reaction. The small nickel crystallites and their uniform distribution throughout the surface of the catalyst allow for a larger number of surface Ni atoms and, in turn, a larger number of active centers where the reaction can take place, resulting in a higher rate of the reaction.

To illustrate the effects of the physical parameters of the catalyst on activity, we can compare the activity of two different catalysts on the hydrogenation of soybean oil. This com-

Table 2
Effect of the physical parameters of the catalyst on activity

Increasing parameter	Effect on activity
Pore volume	+
Pore length	−
Particle size	−
Surface area	+
Ni crystallite size	−



Physical Properties

	A	B
Surface Area, m^2/g	312	252
Pore Volume, cm^3/g	2.02	1.36
Particle Size, μm	1.6	4.1
Crystal Size, μm	26	41

Fig. 4. Comparison of the activity of two catalysts with different physical parameters.

parison is shown in Fig. 4. This is a standard test in our laboratory, using a 1 liter Parr reactor, with 200 g of refined, bleached and deodorized (RBD) Soybean Bean Oil (SBO), 600 rpm, temperature of 165°C and hydrogen pressure of 60 psig. The quantity of catalyst used was 0.0045 weight% as nickel in oil. With Catalyst A, an 80 IV in 16 minutes was obtained whereas 35 minutes was needed for obtaining the end point with Catalyst B. Analyzing the physical characteristics of the two, Catalyst A had a larger surface area and pore volume and smaller particle size and crystallite size.

The larger surface area, smaller particle size and smaller crystallite size for catalyst A indicate the possible larger number of active sites and, hence, higher activity. Also the larger pore size allows faster diffusion of the reactants, allowing a higher reaction rate.

5. Effect on selectivity

Selectivity in fats and oils hydrogenation is defined in a number of ways. Types of selectivity include Linoleic Selectivity Ratio, Linolenic Selectivity Ratio, Specific Isomerization and Triglyceride Selectivity. The characteristics of the catalyst affect each type of selectivity and, in turn, the quality of the hydrogenated product.

There is preference for the hydrogenation of the most unsaturated fatty acids, with maximum formation of oleic fatty acid and minimum increase of stearic. When hydrogenation of linolenic is favored over the hydrogenation of linoleic, it is called Linolenic Selectivity. When hydrogenation of linoleic over the hydrogenation of oleic is the favored reaction, it is called Linoleic Selectivity. The selectivity ratios, defined by Albright [1] and the basis of the AOCS method TZ 1B-79 for selectivity determination, is simply the ratios of the pseudo-first order rate constants of the hydrogenation reaction. If the reactions are written as

$$\text{linolenic} \xrightarrow{k_1} \text{linoleic},$$

$$\text{linoleic} \xrightarrow{k_2} \text{oleic},$$

$$\text{oleic} \xrightarrow{k_3} \text{stearic}.$$

Then the selectivity ratios are defined as

$$\text{Linolenic selectivity ratio} = \frac{k_1}{k_2},$$

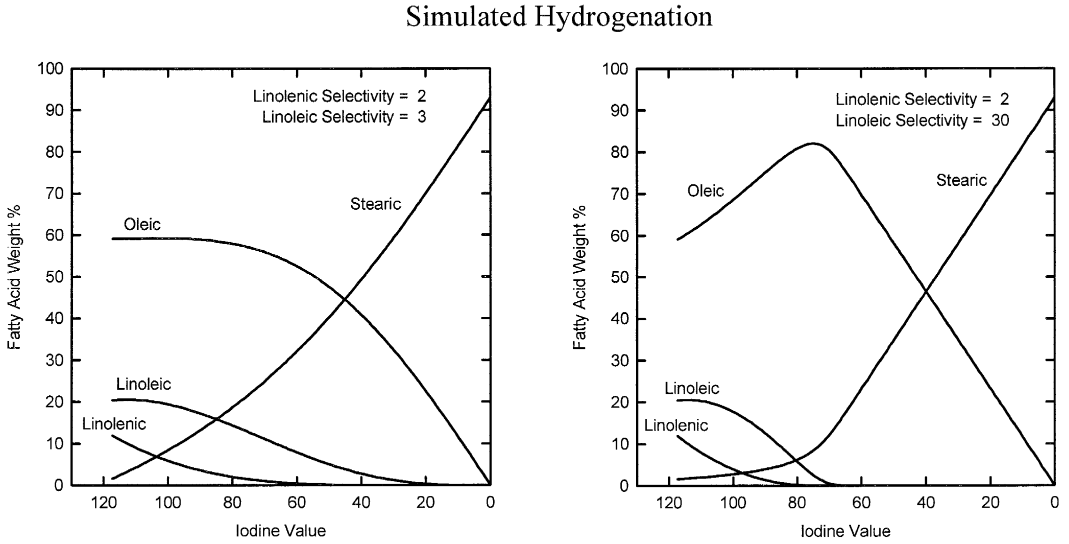


Fig. 5. Illustration of the importance of selectivity in the hydrogenated product.

and

$$\text{Linoleic selectivity ratio} = \frac{k_2}{k_3}.$$

Fig. 5 illustrates the importance of selectivity on the hydrogenated product. A high linoleic selectivity indicates that one of the double bonds in the linoleic fatty acid chains are preferentially hydrogenated before those on the oleic fatty acid chains, resulting in a more desirable product.

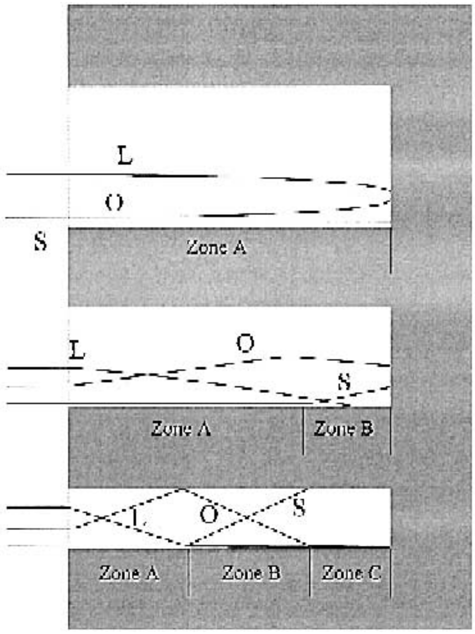


Fig. 6. Effect of pore size on the selectivity of hydrogenation.

The extent of reactant diffusion to the surface of the catalyst will characterize the final selectivity. Therefore, the physical characteristics of the catalyst determine its selectivity performance. Fig. 6 illustrates the effects of pore width on selectivity. According to Coenen [2], in Zone A, the pore width is many times the size of the triglyceride molecules. Therefore, oil and hydrogen molecules can move freely in and out without much hindrance. In this situation, hydrogenation favors the most unsaturated fatty acids. In pores of medium width, a point will be reached where the polyunsaturates will be almost fully hydrogenated. In this zone (Zone B), the hydrogenation of monounsaturates starts to occur. Finally, in pores where access is highly restricted (Zone C), there exists a semi-stagnant population of fully hydrogenated material.

A side reaction to partial hydrogenation is the formation of *trans* isomers. Their presence imposes a great influence on the melting characteristics of the hydrogenated product and may or

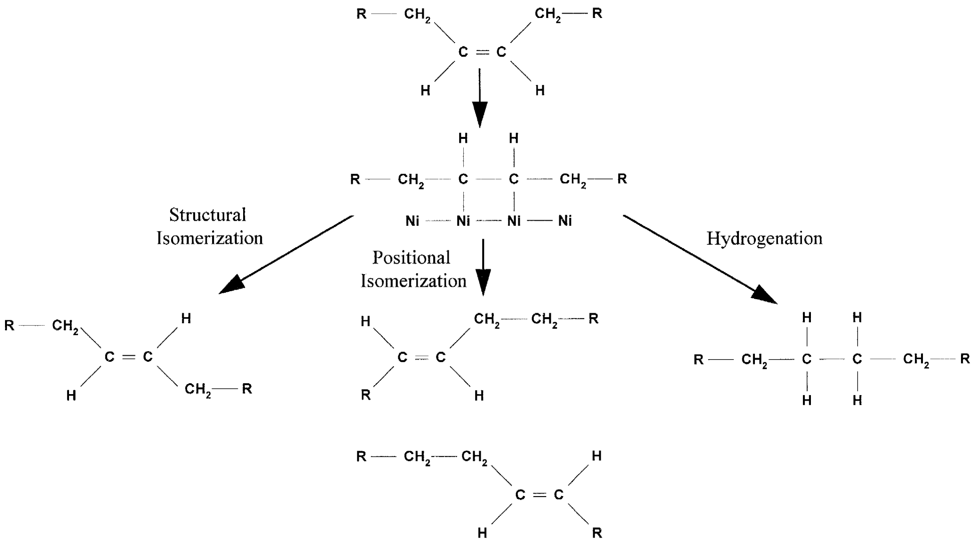


Fig. 7. Hydrogenation and isomerization mechanism.

may not be desirable depending on the application of the final product. *Trans* isomers are formed when the triglyceride desorbs from the catalyst surface without being hydrogenated, as shown in Fig. 7. It is possible to control their formation and, to some extent, control *trans* isomer selectivity.

Coenen [2] mentioned the existence of triglyceride selectivity. This type of selectivity is related to the formation of partially unsaturated triglycerides over the formation of totally saturated ones. The rate of hydrogenation with heterogeneous catalysts is independent of the position of the fatty acid chain on the triglyceride. Triglyceride selectivity type is therefore a consequence of the diffusion rate of the triglyceride molecule within the pores of the catalyst and related to linoleic selectivity. A high linoleic selectivity will indicate a low concentration of unsaturated triglycerides. On the contrary, a low linoleic selectivity will indicate a high proportion of saturated triglycerides.

6. Effect on poison resistance

The poisoning of the catalyst is basically a diffusion process, in which substances other than the triglycerides are attracted to the nickel's active centers, blocking or eliminating completely their catalytic activity. Such poisons may be sulfur or phosphorous containing fatty acids or isothiocyanates. Depending on the size of those substances and the size of the catalyst pores, these substances may or may not enter the pores and block them totally or partially. If the substances are larger than the catalyst pores, isothiocyanates, they will affect only the nickel crystallites present on the external surface of the catalyst particles.

Therefore, we could say that selective catalysts with larger pores are more susceptible to poisoning. On the contrary, catalysts with medium and small size pores should be more poison resistant for larger poisonous compounds. Poison resistance and activity of the catalyst are related phenomena. A catalyst with high poison resistance will be able to maintain good activity throughout the hydrogenation process, especially with ''difficult'' oils having a high poison content like marine oils. This would apply also for fatty acid hydrogenation. We can explain this by the fact that a higher proportion of nickel remains active throughout the course of the reaction. Klimek [3], postulating a relative hydrogenation efficiency, reported that 1 ppm of Cl, S, P and N, poisons 30, 20, 6 and 2 ppm of nickel, respectively.

7. Effect on filterability

Removal of the catalyst particles from the hydrogenated product is an important factor in the economics of the hydrogenation plant. If the Ni can be recovered from the filters in a large concentration, reclaimers will pay the oil processor to take the material for reclamation. However, if the Ni concentration is small, the oil processor must pay the reclaimer to take the material for disposal.

The metallic screen of a pressure leaf filter has openings of about 70 microns. The particle size of a catalyst is on average less than 10 microns. In spite of this difference, it is the catalyst itself that builds up the septum for its separation from the hydrogenated oil. This process is assisted by the use of a small quantity of filter aid for the formation of a pre-coat on the screens of the filter at the beginning of the filtration cycle. This pre-coat helps the formation of a bridge which is then reinforced with the catalyst particles. However, catalyst particles that are too small, such as high amounts of particles smaller than 1 micron, cannot be retained properly in this medium. This causes nickel bleed-through and shorter filtration cycles with more frequent needs for cleaning the filter.

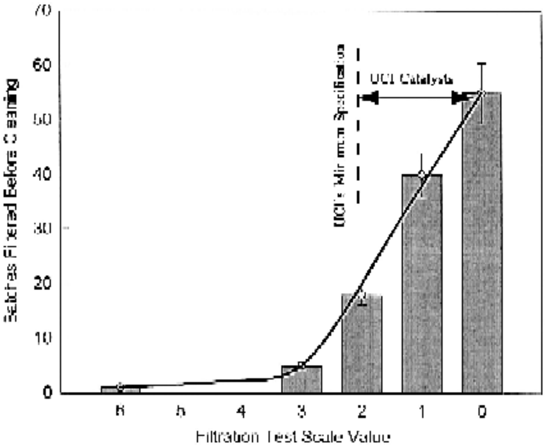


Fig. 8. UCI filtration test scale value versus hydrogenation batches before filter needs to be cleaned.

As was explained, the smaller the particle size, the larger the external surface area and therefore the higher the activity and selectivity expected. However, the filterability of the catalyst is a feature that is continuously gaining importance. The environmental laws are becoming more strict, forcing the industry to use less disposable raw materials and to properly handle those that are absolutely necessary. Better filtering catalysts make it easier for the industry by allowing them to meet low nickel levels in the hydrogenated products with less use of filter aids. Another benefit is the higher nickel content in the filter cake, which makes it easier to dispose of properly. All this translates to a more efficient and lower cost operation. Hence, it is important and responsible for a catalyst manufacturer to produce a good filtering catalyst.

With these concerns in mind, we have developed in our laboratory a test to measure the degree of filterability of Ni catalysts [4]. The test consists of a Soxhlet® type apparatus to extract the vegetable stearine from the catalyst with toluene for two hours. The reservoir solution of the extractor is then vacuum filtered through filter paper with a much smaller pore size. The amount of Ni on the filter paper is the amount of Ni that passed through the Soxhlet® thimble during extraction. The shade of the filter paper is compared to seven standards of differing degrees of filterability numbering 0 to 6, with 6 being a poor filtering catalyst. Using this comparison, the catalyst is assigned a filterability number. As shown in Fig. 8, oil processors can hydrogenate 50 to 60 batches before the filters need to be cleaned with a filterability of 0 as opposed to 1 or 2 batches with a filterability of 6, making good practical sense as well as economic.

A summary of how the physical parameters of the catalyst effect the reaction attributes is shown in Table 3. It is interesting to note the pore length and particle size has an adverse

Table 3
Summary of the effects of the catalyst characteristics on performance

Increasing parameter	Activity	Selectivity	Poison resistance	Filterability
Pore volume	+	+	−	
Pore length	−	−	+	+
Particle size	−	−	+	+
Surface area	+	+	+	
Ni crystallite size	−	−	+	

effect on activity while improving the filterability of the catalyst. In fact, the challenge to catalyst manufacturers is to make an active and selectivity catalyst while maintaining good filtration characteristics.

8. Practical uses of different types of catalysts

We have shown that catalysts can perform in different ways according to their physical characteristics. It is very important then to select the right type of catalyst depending on the desired final product. Besides the catalyst characteristics discussed above, the operating conditions used are critical for the achievement of the expected results.

Table 4 summarizes the effect of the operating conditions on the performance of the catalyst. Pressure, temperature, catalyst concentration and agitation all have a positive effect on the activity. Temperature and catalyst concentration have a positive effect on linoleic selectivity while pressure and agitation have a negative effect. Interestingly enough, the effect of operating conditions on selectivity is the opposite of the H_2 concentration in the oil. The more H_2 in the oil, the more chance for the hydrogenation of the monounsaturates, therefore, selectivity decreases. The steepness of Solid Fat Content (SFC) curve is generally related to the selectivity. The more selective the hydrogenation, the more steep the SFC curve. Increasing temperature and agitation hinder the formation of *trans* isomers while temperature increases their formation. As with selectivity, the formation of trans isomers is related to H_2 absorption into the oil.

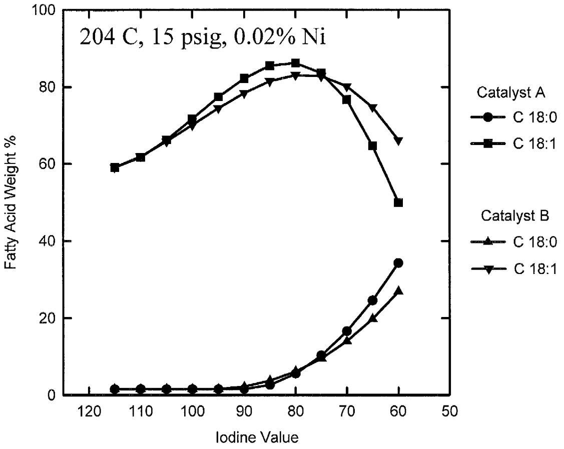


Fig. 9. 18:0 and 18:1 profiles of the hydrogenation of Canola Oil at 204°C, 15 psig and 0.02% Ni.

To illustrate the effects of operating conditions on the selectivity, activity and the SFC curve, the performance of two different types of catalysts in Canola oil were compared. Catalyst A was characterized to have large pores, large surface area and high selectivity. Catalyst B was characterized to have a smaller surface area and medium pore size. Presented here are experiments conducted using the conditions of high temperature, low pressure and high catalyst con-

Table 4
Summary of the effects of the operating conditions on performance

Increasing parameter	H_2 concentration in oil	Activity	Linoleic selectivity	Solid fat content curve	*trans* fatty acids
Pressure	+	+	−	Flat	−
Temperature	−	+	+	Steep	+
Catalyst concentration	−	+	+	+ or −	+ or −
Agitation	+	+	−	Flat	−

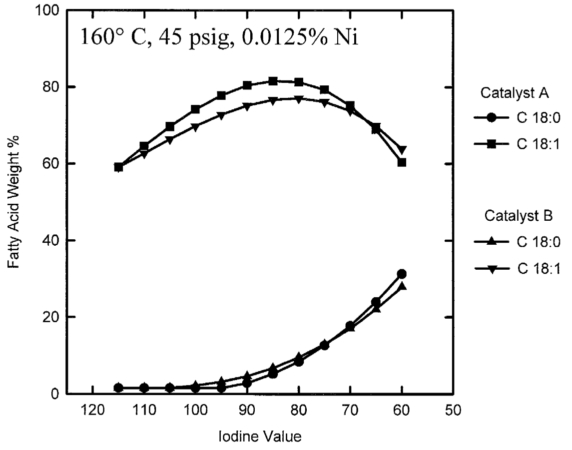


Fig. 10. 18:0 and 18:1 profiles of the hydrogenation of Canola Oil at 160°C, 45 psig and 0.0125% Ni.

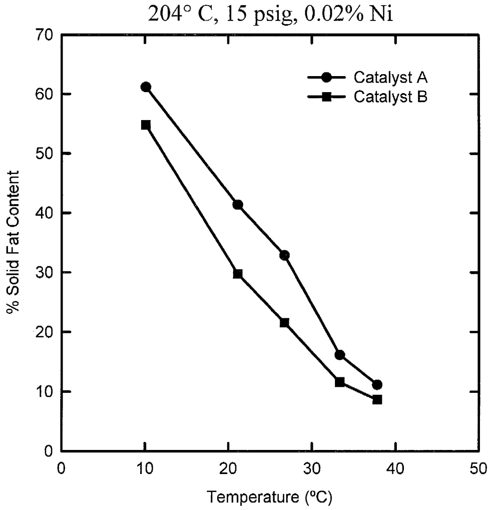


Fig. 12. Solid Fat Content curve for Canola Oil hydrogenated to 70 IV at 204°C, 15 psig and 0.02% Ni.

centration (204°C, 15 psig and 0.02% Ni) and an experiment conducted using low temperature, high pressure and low catalyst concentration (160°C, 45 psig, 0.0125% Ni).

Fig. 9 shows the fatty acid profiles of 18:0 and 18:1 during the hydrogenation of Canola oil at 204°C, 15 psig and 0.02% Ni using Catalyst A and Catalyst B. As expected, the catalyst with larger pores and surface area, Catalyst A, is the more selective of the two.

Fig. 10 is the hydrogenation of Canola Oil at 160°C, 45 psig, 0.0125% Ni. While both catalysts are less selective at these conditions, catalyst A remains more selective than catalyst B. This can be explained by the much faster diffusion of the triglyceride molecules through the pores of Catalyst A than through Catalyst B.

Fig. 11 is the activity of Catalyst A and B at the respective conditions. Higher temperature, lower pressure and higher catalyst concentration

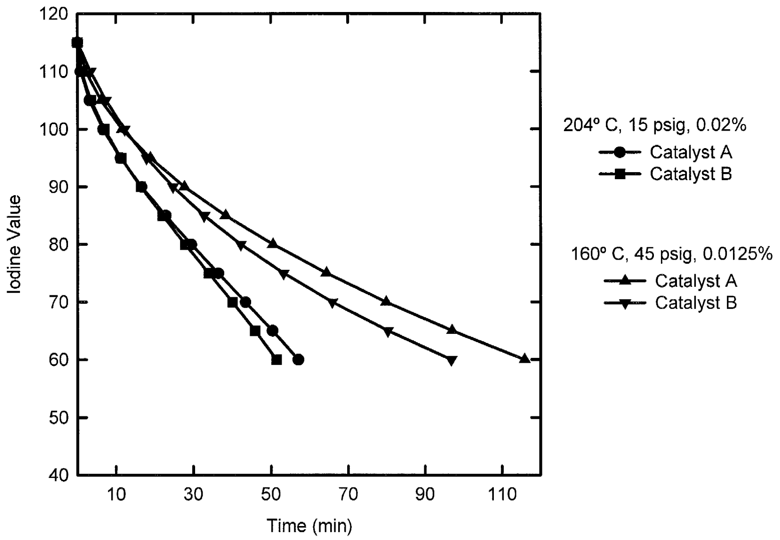


Fig. 11. Iodine value versus time in the hydrogenation of Canola Oil using Nickel catalyst at the respective conditions.

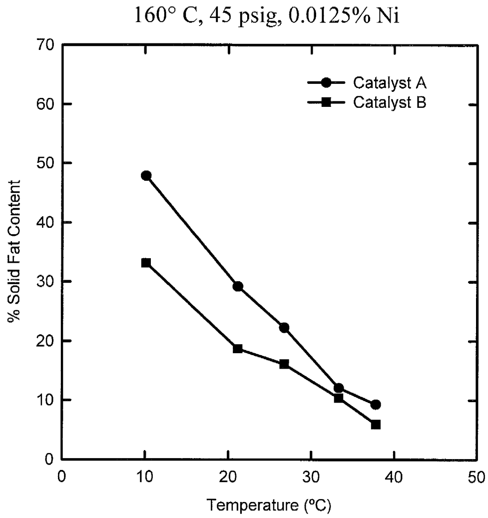


Fig. 13. Solid Fat Content curve for Canola Oil hydrogenated to 70 IV at 160°C, 45 psig and 0.0125% Ni.

result in greater activity. Catalyst A remains more active than Catalyst B with the change conditions. Again, this is attributed to the faster diffusion rate of the oil and hydrogen into the pores of Catalyst A (larger pore volume) than in Catalyst B (smaller pore volume). The larger the pore size, the higher the hydrogen concentration at the crystallite site, producing greater activity.

As a consequence of the above mentioned selectivity differences, the SFC curves of the hydrogenated Canola oil tend to be consistently steeper for Catalyst A. This is shown in Fig. 12 and Fig. 13 for the conditions of hydrogenation studied here and at 70 IV. It is also noted that the high temperature, low pressure and high catalyst concentration produce a steeper SFC curve in both catalysts. As was explained earlier, the steepness of the SFC curve can be related to the selectivity differences observed in the reaction.

The technology for the development of catalysts has improved substantially in the last few years. With a better understanding of how catalysts work, it is possible to obtain catalysts with very high activity and selectivity, excellent filterability and in general better cost/benefit relationships. The challenge for improving what we presently have is permanent and we will always lead our development efforts towards meeting the needs of industry so that they can in turn satisfy the permanently changing consumer and market trends.

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