Hydrogenation and Bleaching Control Procedures[1]

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Abstract

A brief description of various hydrogenation-control tests, including refractive index, congeal points, and Wiley melting-points, will be followed by a discussion of how these analyses are used to control the production of hydrogenated oils to meet certain specifications. The purpose of various bleaching operations will be discussed, including the degree of color reduction necessary in various stages of bleaching to meet specific customer requirements of final color.

Introduction

Plant control of hydrogenation and bleaching procedures requires a considerable amount of skill in the art of processing edible fats and oils as well as adequate technical competence. The term technical competence means not only a knowledge of types and the amount of catalyst to use, hydrogenation temperatures and pressures, necessary hydrogenation endpoints, etc., but also a rather extensive "library" of past performance records, which indicate almost precisely the product changes which will occur as process conditions are varied. Not only is it necessary to know how process variables affect individual analyses, but also how these changes will affect over-all product quality as measured by a complete series of analyses.

For example, generally refractive indices and congeal points are used to control a hydrogenation operation in which the final measure of product acceptance is solid-fat index.

Hydrogenation Control

In discussing hydrogenation control, there will be a division of product classifications into normal shortening and margarine base-stocks, flake products or so-called titer stocks.

Normal Shortening or Margarine Base-stock

This rather broad classification includes hydrogenated base oils from which shortenings of all types are made, base-stocks for straight hydrogenated or blended margarine oils and the host of other partially hydrogenated oils used for frying and other applications, which are all made to individual customer specifications. There are three methods commonly used to control hydrogenation reactions.

Refractive Index. A suitable refractometer equipped with a temperature control bath which is capable of maintaining the prism of 40 ± 0.1C is usually used. After the instrument is standardized, the RI of samples of oils of known iodine value is obtained. These refractive indices are plotted, and a table is prepared so that the iodine value can be read off the chart when the refractive index has been determined on a sample of unknown iodine value.

Congeal Point. A 90-g sample of fat is placed in a 180-ml electrolytic beaker. The dry sample is heated to 65C and placed in a 15C- or 20C-water bath, depending on the estimated congeal point, and is stirred with a titer thermometer, according to the procedure described in the official methods of the AOCS. When the sample has clouded to the extent that the thermometer bulb is still visible at the center of the beaker but not visible at the back of the beaker, the thermometer is immersed to its immersion line in the fat and allowed to remain undisturbed. The beaker is then placed in a 20C-air bath, and the highest temperature reached is recorded.

TABLE I

	Run No.				
	1	2	3	4	5
% Nickel	0.01	0.02	0.04	0.03	0.07
Type of catalyst	Moderately selective			Very selective	
Initial temperature	300F	300F	300F	300F	300F
Hydrogenation pressure	15	15	15	15	15
IV	99.6	99.2	100.1	97.7	98.9
SFI @ 50F.	7.2	7.4	7.0	7.2	7.4
70	2.0	2.3	1.7	2.0	1.9
92	....	....	....	....	....
104	....	....	....	....	....

Wiley Melting-Point. A large tube with an internal diameter of 35-38 mm is first prepared by filling the tube about half-full of boiled water and then carefully pouring boiled alcohol down the side of the tube so that it will float above the water and form a water-alcohol interface. A specially chilled fat disc is then dropped into the tube. This disc floats at the alcohol-water interface. The tube is heated in a water bath at a controlled rate, and the temperature at which the disc becomes spherical is recorded as the Wiley melting-point.

It should be emphasized that Wiley melting-points require about 3 hr from the time the disc is prepared until the time the determination is completed. This is not a satisfactory method of control since plant converters can be tied up for 3 hr waiting for this determination. It is necessary however when the principal customer consistency specifications are iodine value and Wiley melting-point. In these cases the iodine value is closely approximated by determining the refractive index, and then the Wiley melting-point must be run. When the product being hydrogenated is similar to an oil that is in use daily in the plant however, the oil may first be cooled and filtered. If the Wiley melting-point does not meet customer specifications, a second run may be necessary with a slight iodine value adjustment based on the first hydrogenation run.

The most common hydrogenation control tests however are not Wiley melting-points but rather congeal points, and the iodine values as determined by refractive index. For soybean oil products above approximately 95 iodine value, refractive index alone is a satisfactory control for hydrogenation reactions in normal plant hydrogenations.

It will be noted in Table I that marked differences in catalyst concentration had very little effect on the SFI of the final hydrogenated oil. This does not mean that a difference in SFI values cannot be obtained but only that, when an attempt is being made to achieve uniformity, I.V. or refractive index can be used to control the SFI pattern of high iodine-value base oils. Admittedly the I.V. of oils varies from season to season. A 120- I.V. SBO cannot be hydrogenated to the same final I.V. as a 132-I.V. SBO and still obtain the same final SFI pattern. However these data do show that SBO of virtually the same I.V. can be hydrogenated to a given I.V. above 95 and obtain the same, or virtually the same, SFI pattern. There is little difference in the final SFI even with sub-

TABLE II

	Run No.	
	1	2
% Nickel	.02	.02
Hydro. temperature	300F	470F
Pressure, PSIG	15	15
Final IV	96.0	96.0
SFI @ 50F.	8.3	11.2
70	2.4	3.6
92	....	....
104	....	....

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[1] Presented at the AOCS Short Course, East Lansing, Aug. 29–Sept. 1, 1966.

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stantial differences in hydrogenation catalyst concentration and type.

It is possible to obtain differences in SFI pattern even at a 95-I.V. level in hydrogenated SBO. This requires a deliberate attempt to create a difference.

Table II indicates a marked difference in these two oils. One oil was hydrogenated from start to finish at 300F while the other was hydrogenated at 470F. Most plants could not start a hydrogenation at 470F. The point is however that at the same final I.V., using the same refined oil, it was only possible to create a 3% solids difference at 50F in an attempt to make the oil as different as possible. These differences can be achieved in laboratory equipment but are not generally seen in plant equipment. In most instances plant hydrogenators are limited in initial temperature to steam temperature, which is usually around 300–330F.

When oils are hydrogenated to an I.V. less than 90–95, refractive index alone is not sufficient to control the reaction. As the degree of hydrogenation increases, the effect of more selective catalysts in producing increasing amounts of *trans*-isomers increases. Also, as the degree of hydrogenation increases, temperature becomes increasingly important in the degree of *trans*-isomer formation. From the data in Table III it becomes apparent that hydrogenation temperature has a marked effect on the SFI curves of an oil if all other factors remain constant, that the amount and type of catalyst have a marked effect on hydrogenation curves at any given temperature.

Consequently it is essential that, on base oils to be hydrogenated to less than 90 I.V., these oils be hydrogenated to not only a refractive index but also a congeal point. The plant must have not only refractive indices but congeal-point requirements for the various oils to be hydrogenated. Generally, the practice is to hydrogenate to a refractive index as an advisory limit, and actual control or the mandatory control is done by congeal point.

These data cannot be obtained from the literature because hydrogenation equipment, practices, and plant requirements differ. It can only be obtained by maintaining a record of previous plant experience or by a rather laborious pilot-plant evaluation in equipment, which fairly closely duplicates plant results.

Only the hydrogenation of soybean oil has been discussed, but the same general practices apply to corn oil hydrogenated to 95 I.V. and to cottonseed oil hydrogenated to about 90 I.V., i.e., corn oil hydrogenated above 95 I.V. and cottonseed oil hydrogenated above 90 I.V. may be controlled by refractive index. Below these iodine values, refractive index and congeal points are necessary.

Hydrogenation of Hard Stocks

The hydrogenation of hard stocks, flakes or titer stock, as they may be called, is far less critical than any other type of hydrogenation. The iodine value is usually lowered to less than 10, and, at this iodine value, little or no *trans*-isomer remains. If any *trans*-isomer does remain, it is of little consequence because of the hardness of the product. New or used catalyst at any level which will hydrogenate the oil quickly may be used.

Control of hard flakes is simple. True, refractive indices are not often used. The refractometers are generally kept at 40.0 ± 0.1C, and the flakes will solidify on the prism at this temperature. The fat is too hard for a congeal-point determination, and iodine values and titer determinations are fairly time-consuming. A quick titer test is usually used for control work. In this test a sample from the converter is used. A titer thermometer is dipped into the hardened fat and rotated between the fingers until the fat clouds on the thermometer bulb. A correction factor is applied to the temperature at which the fat congeals to obtain a "quick titer." This test is accurate enough for control work and is quite commonly used. Different correction factors are required for cottonseed, tallow, and lard, etc.

There is a direct correlation between iodine value and titer for any given oil. Either the I.V. or titer may later be run to determine the actual titer of the hard flakes. Generally titers are only run on products sold to a customer's specification because a cottonseed oil hydrogenated to a 58C titer will work interchangeably with a slightly softer or harder fat.

TABLE III

	Run No.		
	1	2	3
% Nickel	.04	0.04	0.05
Initial Temperature	300	300	300
Hydro. Temperature	300	450	450
IV	63.7	63	63
Congeal	34.5	33.0	33.0
SFI @ 50F.	54	54	60
70	42	44	45
92	24	22	21
104	9	7	3

[a] Run No. 3 is made with very selective catalyst.

Bleaching Control

If it is concluded that hydrogenation is essentially a science requiring some degree of "skill in the art," then it must also be concluded that bleaching is a skill with some measure of science. The only tools available to the plant in controlling bleaching operations are a colorimeter and the official AOCS bleach test. The problems are that the earth used in the official test in most instances is not representative of the earth used in plant operations, the temperatures and equipment used do not simulate plant conditions, the time used in the official test is far shorter than that used in plant operations, and certain processes such as hydrogenation and deodorization markedly affect oil color and must be taken into account.

If oils are not to be hydrogenated but merely refined, bleached, and deodorized or perhaps refined, bleached, winterized, and deodorized, the plant-processing supervisor or other responsible individual, must decide from the results of the official bleach how much greater or lesser color reduction he will obtain by using the natural or activated clay in the plant.

A typical situation might be like this. The plant is producing a refined bleached and deodorized soybean oil which must meet a color limit of 1.5 red, maximum. The processing supervisor knows that the soybean oil currently in process is dropping 2.5 red color units during deodorization. A color drop on soybean oil of this magnitude is common during deodorization. Then the oil need only be bleached to less than 4.0 R to meet the customer's requirements. Bleaching to a 3.5 R will insure a final color well below the customer's requirements. If the oil is bleached to a 1.5 red, color clay is wasted, excess oil is retained in the extra clay, and some unnecessary damage may be done to the oil on account of the hard bleaching which results from the excessive conjugation of the dienes and trienes. With unhydrogenated cottonseed oil a color reduction in the deodorizer of 1.0 red units is common. Efficient bleaching requires the addition of the clay to the cold oil prior to heating and bleaching. Therefore the processing or bleaching supervisor must decide on the amount and type of clay necessary to reach the bleached color, before deodorization, which will finally meet the customer's requirements. This must be done on the basis of an official bleach, the shortcomings of which have been previously discussed.

When an oil is hydrogenated prior to deodorization, the oil may be "heat-bleached" during hydrogenation. This is particularly true of oils hydrogenated at temperatures of 400–450F, where little or no additional color reduction will be forthcoming during deodorization. Then the oil must be bleached to a color below the final color requirements of the customer.

Often emulsifier may be added to the product after deodorization. Lecithins in particular, may cause a marked color increase in the product. Therefore the oil must exit from the deodorizer at a low enough color to absorb the color increase caused by the addition of the emulsifiers and still not exceed the customer's requirements.

The foregoing does not mean to imply that all of the decisions in a bleaching operation are the responsibility of the bleaching or processing supervisor. Certainly manufacturing specifications should serve as a guide to color

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• *Names in the News*

W. C. Ault

Applied Science Laboratories, State College, Pa., has announced the appointment of W. C. Ault as Technical Consultant to their staff. He will have special responsibilities in connection with various aspects of the Lipid Chemicals produced and sold by Applied Science. Dr. Ault recently retired after 25 years with the USDA, Philadelphia Laboratories, during which time he was in charge of work on fat chemicals and derivatives. The January JAOCS (page 16A) published a detailed account of his career.

Dorothy Rathman (1950) Assistant Director, Institute of Nutrition, Corn Products Co., Argo, Ill., has received a promotional transfer to the Corn Products Food Technology Institute, Waltham, Mass. Louise Morrow (1955) also of Corn Products, has been transferred to the Waltham Plant also, where she will serve as technical librarian.

S. S. Chang (1952) is currently lecturing in Tokyo and Osaka, Japan, on his specialty, the chemistry and technology of edible fats and oils. While he is in the Orient, Dr. Chang will visit processing plants in Hong Kong, Taiwan and Japan. Several food scientists who have taken postdoctorate work at Rutgers' Department of Food Science are employed in some of the Japanese plants he will visit.

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• *Hydrogenation Procedures . . .*

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limits at various stages of processing. However it should be recognized that there will be hard-to-bleach oils or oils that do not heat bleach well in the deodorizer. Manufacturing specifications should be flexible enough to permit changes in color limits to accommodate the handling of these oils.

Basically the hydrogenation of an oil to meet a customer or plant specification must be very precise. If the oil must be straight-hydrogenated to meet consistency specifications, then the oil must meet this requirement when it is hydrogenated and must not be contaminated at any stage of processing. Also, the production of an oil to meet a color limit need not be so exacting, i.e., there are several ways of ariving at the same final color limit. Finally, while there is little freedom of choice in hydrogenation, there must, of necessity, be some latitude in bleaching operations.

Another aspect of bleaching which needs to be discussed is prebleaching. All refined oils should be prebleached, that is, bleached immediately after refining. This is usually done with a low percentage of earth, generally 0.5% or less. The purpose of this is not to obtain a color limit but to remove residual soap and impurities left after refining. High soap contents in the refined oil cause erratic hydrogenation curves and are deleterious to oil stabilities when carried through into the finished product. The efficiency of prebleaching can be checked by determining soap content before and after prebleaching. A good refined oil should have less than 50 ppm soap, and there should be virtually no soap remaining after prebleaching.

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