Controlling quality in an edible oil refinery

In edible oil processing it must be accepted that the raw materials, being natural products, will vary with climate, method of extraction, storage conditions, etc. Thus, application of fixed processing conditions will lead to fluctuation in final product quality or reduced yield. In addition, the requirement that processors can handle a range of oil types and blends can lead to cross-contamination, just by a hold-up in the different types of equipment, all of which makes it apparent that only high frequency of testing can assure quality.

This paper illustrates how the changes in process equipment and process control influence quality control without the introduction of in-line monitoring in a multi-oil refinery handling the range of oils shown in Table 1.

Quality control in edible oil refining is based on planned samples being evaluated by skilled analysts with results reported back to the production staff. This assumes that the following features exist in the scheme: (a) fixed and defined processing conditions are applied; (b) samples are obtained at a correct frequency from a relevant point; (c) analyses carried out are rapid and accurate enough for the purpose; and (d) feedback of data to the process staff is rapid.

Quality control can only be successful if applied against a background of known processing steps for each oil type, and if specified process controls are rigorously applied. Thus, any variations from target values are easier to investigate and correct. This point emphasizes the necessity for good two-way communication.

Sampling frequency is dictated by the size and operation of the process plant and experience of how it varies. Batch operations fix sampling frequency, but continuous operations need sampling at one- to two-hour intervals.

The analytical methods used need to be rapid so that the production staff is in a position to exert real control. A high level of accuracy in many of the methods is not necessary, and in some cases can be qualitative when the in-process product is being examined. The methods principally used are those found in the British Standard BS.684 (1) or the AOCs Methods Book (2), the methods having been selected on the basis of ease of operation, speed and reproducibility.

A major weakness in this type of scheme is that often the quality control chemists can become responsible for making decisions on product quality and subsequent dispatch of borderline product without authorization. The responsibility for achieving the specified quality must stay with the processor, who has a better understanding of the plant being controlled and the oils and fats being processed. However, authority for accept or reject decisions can be taken by the technical staff if properly administered. The authority for final product quality in this particular refinery operation was placed with the technical manager so that he or she was in a position to reject or approve the product.

The scheme also requires that all the people involved have a clear understanding of the quality control standards that are being applied and why they exist.

In the refinery operation to be discussed, the operation has changed from being partially batch processed to being totally continuous and semi-continuous. There has been no attempt to introduce any in-line testing, and standard analytical methods—in some cases slightly modified—continue to be used.

The analytical methods in use are shown in Table 2. Each will be discussed.

Routine control tests

There are a number of key points in monitoring oil quality in refining (Table 3).

(continued on next page)
The first point is crude oil quality. The key step in ensuring good quality in edible oil is the purchase of good quality crude oil, which is subsequently handled and stored in such a way as to minimize deterioration. The oils are purchased on a GMQ basis or with a FOSFA Certificate.

The major tests applied are FFA, Lovibond color, iodine values, (IV) moisture and impurities — these confirm the buying specification. The oxidative status of the oil is judged by applying the peroxide value and anisidine value tests and, where necessary, the specific extinction coefficient. These tests are particularly applied to vegetable oils in order to show the oxidative history of the oil. The peroxide value (PV) is a good guide to quality (3), but the test is empirical and therefore rigid application of test conditions are applied. Since PV measures hydroperoxides (which are transitory), the test is supported by the anisidine value to provide a more complete view of the condition of the oil. The anisidine value (4) gives an estimate of the level of aldehyde, particularly 2-alkenals, in the oil. It does not measure total carbonyls. It is a useful test if this limitation is understood. If a low anisidine value (less than three) is found combined with a low peroxide value, this indicates there has been no significant loss of natural antioxidant from the oil. Where necessary the oxidative history of the oil can be further examined by the specific extinction coefficient at 232 amu and 268 nm. Finally, in the case of vegetable oils the phosphorus content is estimated (5). This is done colorimetrically on the sample after ashing it. The test, therefore, takes a relatively long time to complete, which can be a drawback. Vegetable oils are generally low in FFA content but contain significant amounts of phosphatides (lecithin). Water degumming removes the hydratable phospholipids before the refinery receives the oil, which leaves the nonhydratable phospholipids for removal. The degummed oils are conditioned by phosphoric acid treatment then contracted with alkali. Thus, in the case of vegetable oils the “neutralization” step is more about lecithin removal than removal of acidity, which also can be removed during deodorization.

In the case of palm oil, where the acidity is higher and phosphatides less important, alkali treatment is used to remove acidity. This also has been found with fish oils and animal fats.

The analyses mentioned for vegetable oils are used to define the treatment recommended to the refinery. In the case of palm oil, following the analysis, a laboratory refining is carried out followed by bleaching, and, though this is a simple procedure in glassware, it is possible to indicate the refining treatment to be applied in the plant to produce a neutral, low-colored oil.

In the case of fish oil, which invariably is hydrogenated, laboratory refining, bleaching, hydrogenation and deodorization are carried out prior to evaluation of oxidative and flavor stability of the lowest melting hardened fish oil that is handled in the formulations. The tests used are the Rancimat (6)—an automated oxygen test—and a school oven test, where dishes of the oil are heated at 65°C for seven days and flavor-tested at daily intervals. Following these tests, recommendations are made for the processing of the particular parcel of fish oil.

Tallow is checked qualitatively for the presence of polyethylene and for bleachiability before being accepted.

The next step is that immediately prior to refining the charge of oil is rechecked for free fatty acid (FFA) content, which verifies that the storage stability has been good and confirms the level of alkali to be applied.

In the third step, the refined and washed oil is checked for soap, FFA and color. At this stage the soap should be less than 200 ppm and the Wolff titration is used—though sensitive only to 5 ppm, it is sufficient for control. The dried oil is discharged to intermediate storage and also is tested for moisture (0.1% max), FFA, color and phosphorus (30 ppm max) in the case of vegetable oils if a standard bleach is to be used; otherwise steps need to be taken to modify the bleach to prevent later stability and hydrogenation problems.

The oil from the bleachers routinely is inspected for clarity after recirculation on the press to build up the filter cake. Bleaching earth removes color bodies by chemisorption and, almost as importantly, removes traces of soap, and gums. The peroxides are decomposed and secondary oxidative compounds are dehydrated to form polar compounds which are easily absorbed. Certain animal fats are given a heat test by heating the oil to at least 250°C and if there is an increase in color, this indicates the possible presence of protein fìnes, and remedial action becomes necessary.

The bleached oil is now extremely vulnerable to oxidation and if placed into storage for an extended period (12–24 hr), the peroxide value is checked in order to ensure there is no oxidative damage which will lead to the production of prooxidant secondary oxidation products during deodorization or hydrogenation.
At this point it is worthwhile to consider the problem of cross-contamination in a plant where a wide variety of oils are processed. Since the scheduling of the refining program is arranged so as to minimize cross-contamination, the batch nature of the operation is of great assistance here. However, all crude oils entering the plant are checked for IV, and checked again after refining and bleaching. The IV test used is basically the Wijs method. However, the test is shortened by the introduction of mercuric acetate, which reduces standing time to five minutes. There is a minimal loss in accuracy and, since the test is comparative, the gain in time is a considerable advantage.

Hydrogenation

Up to 35 hydrogenated oil qualities are hardened in four batch vessels which maximizes flexibility with only a minimal risk of cross-contamination.

Hardened oils are defined by their percent solids curve (determined by pulsed nuclear magnetic resonance) (7), slip melting point and IV. There are a number of special oils that also require that the residual levels of certain unsaturated fatty acids be determined. These are determined by gas chromatography of the fatty acid methyl esters. The methyl ester preparation method is a rapid, semi-micro one developed by J.D. Craske (8).

In the case of hydrogenated fish oil, which has a large volume throughput, the principal control analysis is refractive index with the target figure recommended by the laboratory. At the hydrogenation end-point, the oil also is checked for slip point and then discharged to storage. The oil in the storage tank is analyzed for percent solids at two points on the curve.

In the case of a hardened oil where a specific melting curve is required for a customer or for an oil blend, at the hydrogenation end-point the oil is held in the vessel, and the IV and percent solids are determined before release to storage. This practice obviously limits vessel utilization. However, tight specifications now are being demanded by food processors in terms of performance of fat in their end product, and this practice is justified to avoid possible rejection later.

Following filtration to remove the catalyst, the hardened oil is checked for FFA and color. A small increase in FFA is expected; however, the presence of a dark color indicates the presence of residual nickel. This is confirmed qualitatively by the addition of a few drops of ammonium sulphide to the oil. The test is sensitive to 2–3 ppm of nickel by giving a black precipitate. Remedial action may be taken.

The hardened oil receives a clean-up bleach and is then filtered before being discharged to storage. The oil is now checked for percent solids, slip melting point, IV, FFA and color.

Blends are made according to customer specifications and are made prior to or after deodorization depending on complexity. In all cases, the quality control laboratory, using samples of the oils available, prepares test blends and checks pulsed nuclear magnetic resonance profile, and then advises the production staff of blend proportions. Then the prepared blends are checked at two points on the NMR profile to confirm their conformity to the specification.

Not only solids profiles are demanded in the blends. For example where “high in polyunsaturates” claims are being made, a GC trace of the fatty acid methyl esters is required to ensure the required level of linoleic acid is available in the blend. Biscuit-dough fat blends are prepared which require specified levels of particular oil types so that IVs are also needed as well as percent solids. In frying shortenings, percent solids and determination of the unsaturation are necessary to ensure good frying life and palate sensation.

The prepared blends are deodorized and the first product from the deodorizer is checked for FFA, peroxide value, anisidine value, color and flavor before being sent to storage. Once the batch is complete, a full test program can be undertaken with additional analysis to the above being IV, Rancimat test, cold test (where appropriate), slip point and percent solids. These analyses can then be put on the certificate of analysis that goes to the customer with the load.

Finally, a loading sample is taken from the tank car for final confirmation that there has been no change in the oil.

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during the loading procedure. Deodorizer and loading samples are retained against customer complaint.

The in-process target specifications are shown in Table 4.

Ancillary control analyses

These analyses are undertaken by the quality control laboratory and have a greater bearing on refining efficiency than on the final oil quality.

The strength of the caustic used in refining is checked by quality control so that losses are minimized and quality is protected.

The soapstock is checked at intervals to ensure that losses are in control. The total fatty matter and neutral oil can be determined. These results are used to confirm data from mass balance in the process records.

During bleaching, a crude check on the earth usage is made by filtering out the earth from the oil, washing it with hexane and drying it to a constant weight.

The filter cake discharge is checked for oil content to ensure correct blowing procedures are in use so that losses are controlled.

The press cake from the hydrogenated oil filtration is checked at regular intervals to check nickel levels, as this has an effect on the salability of the nickel catalyst cake.

The high level of testing described is necessary to exert control on a partial batch process to ensure a reasonably consistent final product without accepting low yields due to overkill in refining. It requires analysts working in shifts and supported by a day staff. The level of analytical input, particularly on blend control, becomes overwhelming as blends increase in complexity so that a high level of rechecking and adjustment is undertaken.

Influence of plant changes

The equipment changes effected during a refurbishment program were the introduction of two centrifugal refining lines with loss monitoring equipment and C.I.P. plant. These units supplied continuous bleachers with fine control on the bleaching earth addition. The storage capacity for bleached oil was expanded.

The existing hardening plant was updated with improvements in instrumentation such that hydrogenation conditions and gas usage could be controlled closely, as well as vessel utilization improved. Filtered and post-hardening bleached oil is delivered to an expanded range of storage tanks. The decision was made that all oil blends would be prepared prior to deodorization in agitated tanks on load cells, and the system microprocessor would be controlled. Finally, the oil is deodorized in a semi-continuous deodorizer prior to discharge to an outloading tank. The deodorizer is also microprocessor-controlled. Figure 1 shows the layout and the sampling points.

Certain program limits were introduced to minimize risk of deleterious cross-contamination of oils, since it was accepted that in a continuous plant handling a wide range of oil the risks of cross-contamination can be considerable.

All the liquid vegetable oils were refined in one plant. The refining plants never do runs of less than 50 metric tons (MT) of a particular oil type. Blends of less than 12 metric tons (MT) are never handled.

The analytical scheme described above was applied and the experience generated demonstrated that the improvement in the consistency gained in plant operation meant that certain tests could be dropped. The following four paragraphs are examples of these situations.

It was found that the variation in the degumming and refining treatment applied to each liquid vegetable oil type was small; therefore it was decided a certain minimum standard treatment could be applied to each oil type. This meant that regular testing of phosphorus could be dropped, with the knowledge that in certain cases, a certain loss in yield was possible.

Introduction of the loss-monitoring scheme has reduced the frequency of soapstock testing. Total fatty material analysis of soapstock has been modified to a simple fatty acid determination on the acidified soapstock, which is sufficient to confirm control, i.e. a target figure of 70–75% fatty acid is used.

The hydrogenation plant improved consistency to such an extent that it has been possible to make standard blends in the blenders, eliminating the necessity for laboratory pre-blending. It has been found that only 2–3% of blends need to be amended for nonassignable causes. A spin-off advantage has been that blends of the correct size are being made so that “heels” of oil in the tanks no longer pose a major quality problem due to adjustments after checking.

The control on bleaching earth used has improved to the

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<td>In Process Specifications</td>
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<td>1. Refined &amp; dried oil</td>
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<td>2. Bleached oil</td>
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<td>3. Hardened oil</td>
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<td>4. Blended oil</td>
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<td>5. Deodorized oil</td>
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<td>6. Finished batch</td>
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<td>11. Post deodorized refined</td>
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<td>12. Finished batch</td>
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<tr>
<td>13. Refined &amp; dried oil</td>
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<td>15. Hardened oil</td>
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<td>16. Finished batch</td>
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The quality control scheme now used requires that all testing is done in the laboratory using the standard analytical methods mentioned previously. There is no on-line testing by process operators. All the process units are sampled at two-hour intervals and at the time of product changes.

In the hydrogenation process, IV determination is used as the control tool rather than refractive index because of its greater accuracy. Since many of the hardened oils require specific melting curves, these are held in the vessel while the percent solids is determined. A shortened version of the proposed I.S.O. percent solids (pNMR) method is applied, that is, 30 minutes of tempering is used rather than one hour. The loss in accuracy has been found negligible for our purposes. A test program previously has shown that in some cases tempering times of as little as 20 minutes can be applied; however, palm-based blends were found to give unreliable results at this short of a tempering time. Retaining oil in the hydrogenator for such long tests does reduce utilization. However, the process changes that have been implemented combined with less testing earlier in the hardening program have led to a net gain in utilization.

Blend control as previously described is now carried out more confidently against standard formulations. The laboratory exerts maximum control by having a computer terminal in the laboratory with the facility for securing the movement of blends either still under test or about which they have some doubt.

**Contamination risks**

Experience with the plant now has shown those parts of the process that give the greatest risk of deleterious cross-contamination. The refining plant offers virtually no risk since the product hold-up is small and the problem is further minimized by programming and in-place cleaning. In contrast, the bleachers have a considerable hold-up of oil in the plant. Again, programming minimizes the problem and these first runnings of mixed oil are directed to compatible hydrogenated blends.

Common lines in the storage and blending system have been held to a minimum in order to prevent contamination. The semi-continuous deodorizer provides the final risk of contamination. Using IV checks, it has been found that contamination can be held to 0.1–0.2% in oil blend runs. The impact of this level of contamination can be mitigated by judicious program planning.

**Special oils**

The handling of special oils and/or blends gives no problems in the processing or quality control system in that virtually all the oils and blends handled are treated as "specials" in processing terms, though from a quality control point of view they may require the introduction of some alternative tests. An example of this is where a customer requires a blend with specified maximums of linoleic and linolenic acids in the hydrogenated soybean oil used in the blend. These features are controlled by applying GC of the fatty acid methyl esters at the hydrogenation end-point and the same test on the finished blend.
The requirement for sharp melting or slow melting characteristics in hardened oils is monitored as necessary in the hydrogenator based on previous knowledge of catalyst performance, in particular conditions of gas pressure, temperature and agitation by pulsed NMR and iodine value determination.

Laboratory operation
The basic operation of the laboratory is unchanged, although the receipt of samples is now predictable and the ability to control the quality of the finished oils greater.

The major analytical tests used are simple and rapid with acceptable levels of repeatability. For example, percent free fatty acid at 0.05% is repeatable to 0.005, and at 1.0% it is repeatable to 0.03%; peroxide value at 1.0 Eq/kg is repeatable to 0.1, at 6.0 m Eq/kg to 0.2; IV at 137.0 is repeatable to less than 1.0; and Lovibond color at 3.0R is repeatable to less than 1.0.

Tests such as slip melting point are carried out only if placed in the customer's specification as the test reliability is much lower than the percent solids by pNMR and provides less information on the melting characteristics of the fat being analyzed.

There is now a greater opportunity to test the final product more rigorously, for example, carrying out trace metal determinations, Rancimat test, residual phosphorus, etc. The ancillary tests mentioned earlier have been retained in part, where they can contribute to the efficiency of the refining process.

Future developments
In the continuing need for improving quality standards, and the availability of automated techniques that can speed up analyses and be applied on-line, there are opportunities to be exploited in applying these techniques to color, acidity and IV determination which will offer savings in labor time while increasing the level of process quality control. These areas are being investigated and will be implemented.

The establishment of BS 5750 (ISO 9000) accreditation among suppliers means there is a declining need for the checking of process chemicals which will further ease the burden of routine analysis on the quality control department.

The assessment and the handling of data not discussed here is becoming an issue of greater importance, and the increasing ease of gathering data will lead to evaluation trends observed in the data available in order to check process performance with a greater frequency.

References
1. B.S. 684 of the B.S.I., London.