Monitoring Peroxide Value in Fatliquor Manufacture by Fourier Transform Infrared Spectroscopy

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ABSTRACT: A Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflectance (ATR) sample handling accessory was used to rapidly monitor the peroxide value (PV) of oils undergoing catalytic oxidation to produce sulfonated fatliquors used in the leather industry. PV quantitation was based on the stoichiometric reaction of triphenylphosphine (TPP) with hydroperoxides to produce triphenylphosphine oxide (TPPO). By using a germanium ATR accessory that has a very short effective pathlength, the spectral contributions of the base oil could be subtracted out, eliminating any oil-dependent interferences as well as providing a facile means of observing the spectral changes associated with the TPP/TPPO reaction. A calibration was devised by adding a constant amount of TPP-saturated chloroform to oils containing varying amounts of *tert*-butyl hydroperoxide (TBHP) to produce TPPO that had a measurable band at 1118 cm^{-1}. This band was linearly related to TBHP concentration, and the calibration devised had an SD of ~3.4 PV over the range of 0–250 PV. The ATR–PV method was standardized and the spectrometer programmed using Visual Basic to automate the analysis. The automated FTIR–ATR method was found to be a convenient means of tracking PV of oils undergoing oxidation, and the results correlated well with the PV values obtained using the AOAC iodometric method (r = 0.94). The FTIR–ATR PV methodology provides a simple means of monitoring the PV of oils undergoing rapid oxidation and could serve as a quality-control tool in the production of sulfonated oils for the leather industry.

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KEY WORDS: Attenuated total reflectance (ATR), fatliquor, Fourier transform infrared spectroscopy (FTIR), lipid oxidation, oil analysis, peroxide value (PV), *tert*-butyl hydroperoxide, triphenylphosphine (TPP), triphenylphosphine oxide (TPPO).

Asia and particularly China have become important centers of leather manufacturing to meet world demand for high-quality leather goods. As a result there has been substantial regional growth in the production of leather chemicals such as fatliquors, an essential constituent in producing leathers. Fatliquoring agents are emulsifying mixtures used to obtain high-quality leather products by bringing oil into the leather-fiber network (1–4). Considering only fatliquors made from triacylglycerols, 80% of these products are anionic sulfate and sulfonate oils. Sulfate oils are produced by reacting sulfuric acid with highly unsaturated oils; however, the sulfate moiety is readily hydrolyzed under acidic conditions (5). This limitation can be overcome by producing sulfonated fatliquors having a more resilient C-S bond rather than a C-O-S bond. A common means of producing sulfonated fatliquors is to react highly unsaturated oils with air to produce high levels of hydroperoxides, which are subsequently reacted with sodium thiosulfate. This approach to sulfonation, however, has several disadvantages in that (i) only highly unsaturated vegetable or fish oils can be used as substrates, (ii) the oxidation process is slow, and (iii) unreacted hydroperoxides may further decompose in the leather, making it rancid.

Recently, Li *et al.* (6) developed a modification of the sulfonation reaction, speeding up the initial oxidation step prior to sulfonation as well as permitting the use of oils having only a moderate degree of unsaturation. Their modification speeds up the overall process, allows for a wider range of raw materials to be used, and also reduces the possibility of leather rancidity. As the sulfonation efficiency of this process is closely related to the extent of oil oxidation, accurate and timely hydroperoxide monitoring is a necessity. Conventionally, oxidation is monitored by following the peroxide value (PV) of the oils using the AOCS iodometric method (7) and is expressed as milliequivalents of hydroperoxide per kilogram of fat (meq/kg). Although relatively reliable, this method is time-consuming and problematic from the standpoint of ease of use and disposal of hazardous reagents. For monitoring purposes, a more rapid instrumental analytical method was deemed to be desirable so as to more effectively determine the oxidation endpoint of the process.

The McGill IR group has substantial expertise in the development of a variety of rapid Fourier transform infrared (FTIR) spectroscopic methods related to oil analysis, including PV methods. One successful approach has been the stoichiometric reaction (Scheme 1) of hydroperoxides with triphenylphosphine (TPP) to produce triphenylphosphine oxide (TPPO) (8):

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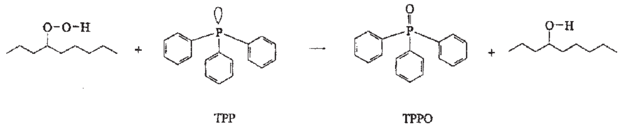

SCHEME 1

In the IR portion of the spectrum, the transformation of TPP to TPPO results in distinct spectral changes that have been used to quantitate PV in oils by both mid- and near-IR spectroscopy. Several methods have been developed using a variety of sample handling techniques, including a flow cell (8), a polymeric IR card (9), and glass vials (10,11). These analytical methods were designed for the analysis of freshly refined oils having PV values <10 and are not suited to the analysis of high PV oils (600–1200) commonly employed in sulfonated fatliquor production. The development and performance of a mid-FTIR spectroscopic method specifically suited to monitoring oils developing high PV are described.

EXPERIMENTAL PROCEDURES

Materials and methods. Reagent-grade TPP, >99%, TPPO, >99%, chloroform, and 5.0–6.0 M *tert*-butyl hydroperoxide (TBHP) in decane were obtained from Aldrich Chemicals (Milwaukee, WI). The TBHP was analyzed in triplicate for its PV by an AOCS official method (7). A saturated TPP/chloroform (sTPP/$CHCl_3$) solution was prepared in a 30-mL drop-dispenser bottle obtained from VWR Canlab (Mississauga, Ontario, Canada) and determined to be 66% w/w by evaporation on an analytical balance. Refined base oils were obtained locally and crude oils supplied by the Tingjiang Chemical Plant (Sichuan, China). Selected oils were catalytically oxidized according to the process developed by Li (6), routinely used for fatliquor production at the Tingjiang plant. Laboratory-scale oxidations were carried out in a 1-L glass reactor containing oil and catalyst, maintained at 80°C, and sparged with air so as to attain an oxidation rate of ~200 PV/h after induction. Samples taken as the reaction proceeded were analyzed for PV either by the AOCS iodometric method, by the FTIR method, or by both methods.

IR analysis. All IR spectra were collected using a Nicolet (Madison, WI) Magna 560 FTIR spectrometer, interfaced to a Pentium PC operated under Windows-based Nicolet Omnic ESP software. The optical system and sample compartment were purged with dry air using a Balston dryer (Balston, Lexington, MA) to minimize water vapor and CO_2 interferences. For spectral data acquisition, the samples were pipetted onto the surface of a Spectratech (Stamford, CT), 45° germanium (Ge) attenuated total reflectance (ATR) crystal designed for 12 reflections. The absorption spectra were obtained by collecting a single-beam spectrum by co-adding 32 scans at a resolution of 4 cm^{-1} and ratioing it against a 32-scan single-beam spectrum of the clean, bare crystal. Differential spectra were subsequently obtained by subtracting the absorption spectrum of the unoxidized base oil from the spectra of the oxidized oils, thereby allowing only spectral changes associated with oxidation to be monitored.

Calibration/validation. Calibration standards were prepared by adding known amounts of TBHP to a zero PV base oil to produce oils having PV values ranging from 0–250. To 1.0 g of each of the standards, 0.05 g of sTPP/$CHCl_3$, representing ~375 PV equivalents, was added and the sample was shaken to mix the reagent with the oil. Upon addition of sTPP/$CHCl_3$, a portion of the TPP is stoichiometrically converted to TPPO in proportion to the hydroperoxide content. Absorbance spectra of the TBHP-free base oil (PV = 0) and of the calibration standards containing TBHP were recorded. The spectrum of the base oil was then subtracted from the spectrum of each of the TBHP-spiked standards to produce a series of differential spectra. From each of these spectra the peak height at 1118 cm^{-1} relative to a baseline at 1300 cm^{-1} was measured. The TPPO PV-peak height data were plotted against the PV of the standards calculated from their TBHP concentrations to produce the standard curve. Linear regression was used to derive a calibration equation from which PV could be calculated. Validation samples consisted of oils taken from the laboratory reactor at various times during the course of three oxidation runs. A sample of the base oil was collected from the reactor prior to each oxidation run. Immediately after being collected, 0.05 g of sTPP/$CHCl_3$ was added to 1.0 g of oil, shaken, and a spectrum recorded. The spectrum of the base oil was then subtracted from each of the spectra of the samples subsequently collected during the oxidation run. Based on the final standardized version of the analytical protocol developed, the spectrometer was programmed using Visual Basic to automate spectral data acquisition as well as calculating and presenting PV values for unknowns (9–12). Both refined and crude oils were oxidized in the reactor and tracked using the chemical PV and automated ATR–FTIR PV method to correlate the results obtained by two methods.

RESULTS AND DISCUSSION

Oxidation perspective. Figure 1 presents typical PV time courses for three different oils undergoing oxidation at the Tingjiang chemical plant. The progress of the reaction for each oil type differs substantially; however, all attain high PV values (600–1000) with the PV either leveling off or then decreasing. In order to attain high sulfonation efficiency, it is important to initiate the sulfonation reaction when the PV plateaus or maximizes.

The iodometric PV method is considered to be too slow by plant management to provide "real time" data to monitor the new catalytic oxidation process now used. TPP/TPPO-PV-based IR methods present a possible alternative, but those developed to date are not suitable for analyzing high-PV samples unless the samples are diluted extensively. Beyond the dilution issue, convenience, speed, and ease of sample handling are also important factors. From the perspective of sample handling in particular, ATR is recognized to be an especially convenient technique for the analysis of oils (13–15).

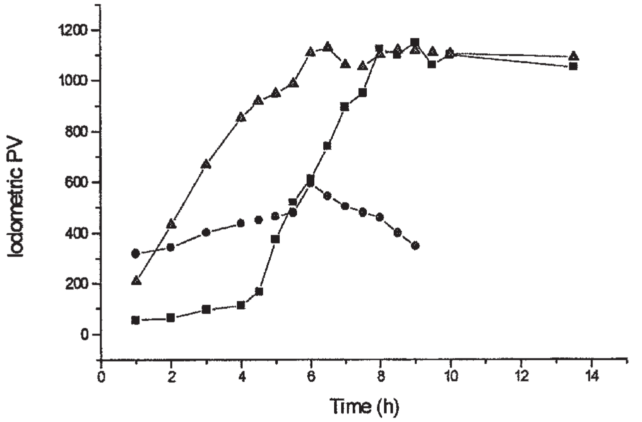

FIG. 1. Typical peroxide value (PV) profiles of fish (●), rapeseed (▲), and soybean (■) oils undergoing catalytic oxidation.

ATR analysis. Figure 2 illustrates an IR beam undergoing multiple internal reflection as it travels through the ATR crystal from the source to the detector. The interaction of the IR beam with the sample on the surface of the crystal at each point of contact results in attenuation of the beam yielding the absorption spectrum of the sample (16). The effective pathlength of an ATR crystal is a function of wavelength, the chemical makeup of the crystal, its refractive index, the angle of incidence of the IR beam, and the number of reflections within the crystal (17). The effective pathlength is usually very short, and for the Ge ATR used in this study, it ranges from 0.6–4 μm over the range of 4000–650 cm^{-1} (17). Such short pathlengths tend to be limiting from the standpoint of quantitative analyses if one is looking for the spectral signature of an analyte in solution rather than the spectral signature of the bulk. On the other hand, with such short pathlengths, even the strongest absorption bands of oils are on scale (<1.5 A) and can be accurately subtracted out. The ability to subtract allows the oxidative changes to be monitored without interference from the spectral contributions of the base oil; however, the short effective pathlength of the ATR technique limits sensitivity such that only more substantive changes are measurable (14).

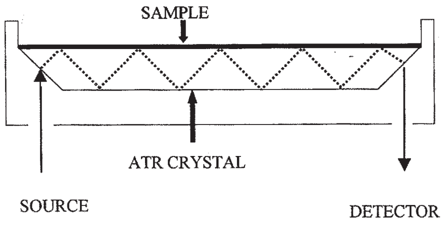

FIG. 2. Schematic representation of an infrared beam traversing an attenuated total reflectance (ATR) crystal with an oil sample applied onto its surface.

For general PV analysis ATR was not considered for two reasons: the lack of sensitivity and that the TPPO bands previously used for quantitation were close to or beyond the cutoff of Ge and ZnSe ATR crystals. For this particular application, where PV values can reach 1200, a lack of sensitivity is not necessarily an issue. However, the mid-IR bands commonly used for TPPO quantitation are not readily measurable by the ATR technique. In our TPP/TPPO method for refined oils, TPPO was quantitated on its absorption at 540 cm^{-1}, which, in

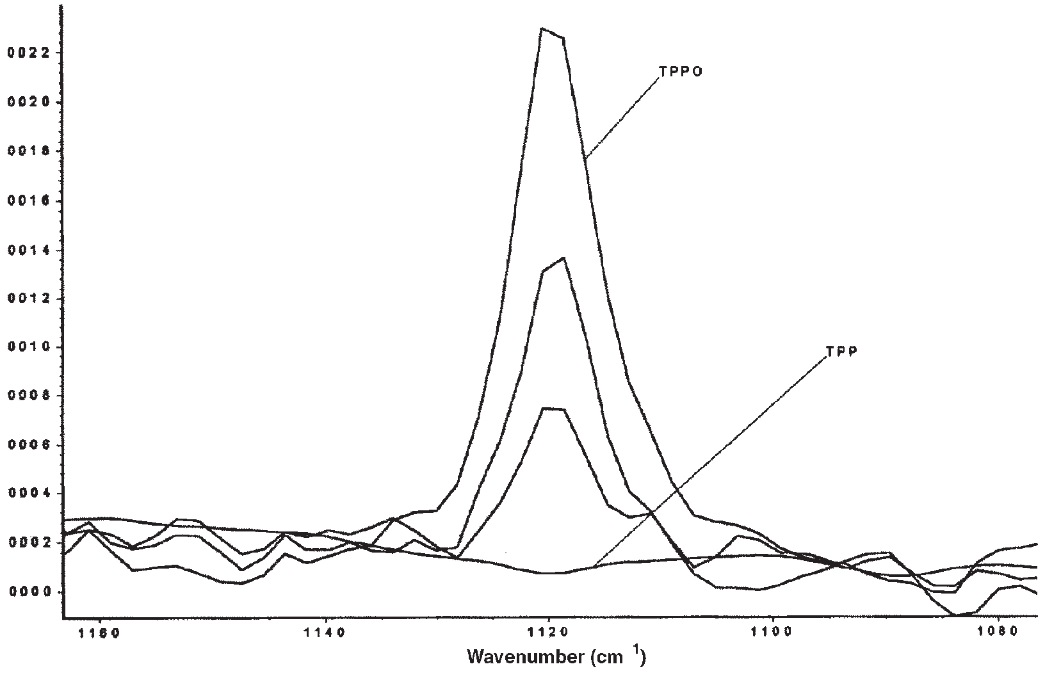

FIG. 3. Superimposed differential spectra of three concentrations of triphenylphosphine oxide (TPPO) relative to the absorption profile of triphenylphosphine (TPP) in the same spectral region.

the case of ATR, cannot be measured as it is beyond the transmission cutoff of the common ATR materials (e.g., Ge and ZnSe). However, an alternative TPPO band at 1118 cm^{-1} (18), not measurable in longer-pathlength cells because of off-scale oil absorptions, becomes available when an ATR accessory is used. Figure 3 illustrates differential spectra on a Ge ATR crystal of TPP and increasing levels of TPPO dissolved in oil after the oil contributions have been subtracted out.

TPPO has a well-defined band at 1118 cm^{-1}, while TPP has no significant absorption at this frequency. These spectra imply that TPPO formed from hydroperoxides reacting with TPP should be quantifiable using the band at 1118 cm^{-1}. The use of $CHCl_3$ as a carrier for TPP was found to be a practical means of incorporating TPP into an oil (10); however, the evaporation of $CHCl_3$ due to the open architecture of the ATR accessory requires consideration. This was assessed by placing the ATR accessory on a four-place analytical balance and loading it with varying amounts (100–500 μL) of oil spiked with a constant amount of sTPP/$CHCl_3$ and monitoring the change in weight over time. A stable constant weight was achieved within 90 s for the highest loading (500 μL), with the lowest loading stabilizing within 40 s. Beyond the volatility issue, development of a direct calibration based on dissolving TPPO in oil was found to be problematic, as its solubility was limited to PV equivalents of 40–50. On the other hand, TPPO PV equivalents of up to 250 PV could be attained if TPP was converted to TPPO through the use of TBHP. This increased TPPO solubility appears to be facilitated by the production of *tert*-butyl alcohol produced from the breakdown of TBHP, increasing the polarity of the oil. Hence a set of calibration standards was prepared by gravimetrically spiking known amounts of TBHP into zero PV oil. A calibration equation relating the peak height at 1118 cm^{-1} to the PV expressed as milliequivalents of TBHP per kilo of oil was derived by following the procedure described in the materials and methods section. The calibration plot is presented in Figure 4, and the calibration regression equation for the calibration is:

$$PV = 5.660 + 8720.4 \text{ Abs @1118 cm}^{-1} \qquad R = 0.998 \qquad SD = 3.415 \qquad [1]$$

The coefficient of variation is ~3% and is adequate for tracking the substantial changes occurring in PV as the oxidation reaction required for sulfonation proceeds. A standardized protocol was devised to facilitate the routine analysis of oil samples, consisting of the following basic steps: (i) adding 1.0 g of oil *via* a precalibrated repipette into a 5-mL test tube; (ii) adding ~0.05 g (5 drops) of sTPP/$CHCl_3$ from a drop-dispenser bottle; (iii) mixing for 30 s on a vortex mixer to facilitate the ROOH-TPP reaction; (iv) applying 100 μL of the reacted oil by repipette onto ATR crystal; let stand for 1 min; and (v) collecting spectrum/predict PV.

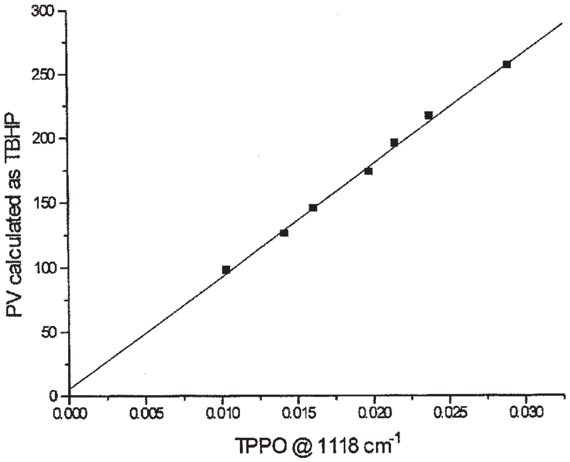

FIG. 4. Calibration curve obtained by measuring the TPPO absorption peak height at 1118 cm^{-1} based on the conversion of TPP to TPPO using *tert*-butyl hydroperoxide (TBHP). See Figure 3 for abbreviations.

By using this protocol, a reference spectrum is first obtained for the unoxidized base oil containing only sTPP/$CHCl_3$. Subsequently, samples undergoing oxidation are subjected to the same protocol to obtain a sample spectrum. By subtracting the stored reference spectrum from the sample spectrum, the absorbance of the TPPO band at 1118 cm^{-1} in the resulting differential spectrum is measured, being proportional to the hydroperoxide content or PV. Figure 5 illustrates a time course of a catalytic oxidation reaction tracked by the ATR method developed. As the oxidation proceeds, however, PV values go well beyond the calibration range of 250 PV. Thus, oil samples collected in the later stages of the oxidation need to be diluted with base oil kept on hand to ensure one works within the range of the calibration.

To facilitate the automation of the ATR PV method, spectroscopic and data manipulation aspects of the method were programmed in Visual Basic. This included a spectral time delay to allow for $CHCl_3$ evaporation, taking reference and sample spectra, carrying out spectral subtraction, measurement of peak height, and calculation of PV. This interactive analyti-

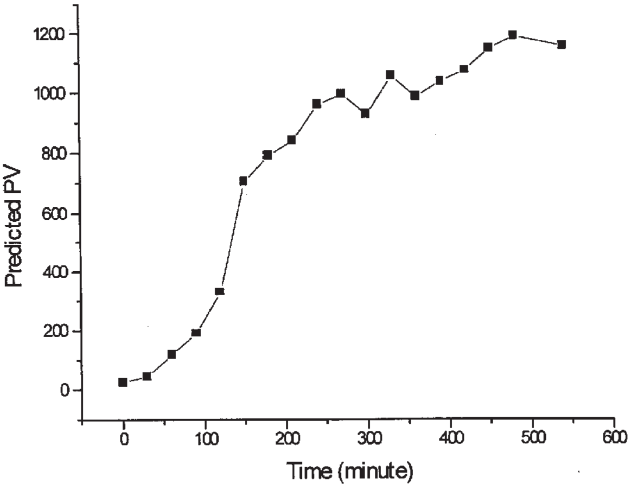

FIG. 5. Example of a PV oxidation profile obtained using the Fourier transform infrared–ATR PV method. See Figures 1 and 2 for other abbreviations.

cal system allows one to obtain PV values rapidly (~3 min/sample) from oil samples undergoing oxidation in a reactor. Various oils were tracked by both the AOCS and FTIR–ATR TPP/TPPO PV methods and were shown to correlate well (r = 0.94). Only a reasonable match between the methods is required so as to provide an indication of the relative changes in PV to initiate sulfonation. Based on plant experience, it is important to have a rapid tracking method as the progress of the oxidation reaction can be quite variable given the numerous variables which affect the process (temperature, air flow, oil variability, catalyst, etc.). The ATR-based FTIR PV method provides the capability of obtaining “real-time” data so that better control is obtained over the oxidation process, and this method could be useful for monitoring other lipid oxidation processes.

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