Automated Refractive Index Measurement of Catalyst-laden Edible Oils Undergoing Partial Hydrogenation

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A planar optical waveguide, excited by monochromatic light, becomes a sensor for measuring the refractive index (RI) of edible oils. RI is commonly used to determine iodine value (IV). This process sensor operates in the presence of nickel catalyst and diatomaceous earth (DE) powders. An on-line refractometer system, incorporating this sensor, demonstrates an accuracy of ±0.0001 RI units (RIU). Resolution is 0.00001 RIU. The waveguide refractometer is based on a loss in light transmission due to a temperature-induced matching of waveguide and oil RIs. An algorithm adjusts the RI to conform to the temperature and wavelength as specified in AOCS Method Cc 7-25 (*Official Methods and Recommended Practices of the American Oil Chemists' Society*, edited by D. Firestone, American Oil Chemists' Society, Champaign, 1989), the accepted procedure for RI measurement with an Abbé refractometer. The theory, construction and performance characteristics of a prototype waveguide refractometer are described. Samples of partially hydrogenated soybean oils (IV ranges = 106–75) are first examined with the Abbé refractometer, then tested in the prototype waveguide refractometer. Catalyst and DE are subsequently added to each sample, and RI data are taken again with the waveguide refractometer. Results confirm the instrument's ±0.0001 RIU accuracy and its immunity to interference from catalyst and DE. Real-time operation holds promise for automatic control, improved production efficiency, and better batch-to-batch consistency of the hydrogenation process.

KEY WORDS: Automated hydrogenation measurement, edible oils, on-line refractometer, refractive index measurement.

The degree of unsaturation for partially hydrogenated edible oils is normally expressed in terms of iodine value (IV) as measured by AOCS Official Method Cd 1-25 (Wijs method) (1). During the hydrogenation process, the accepted unsaturation test is AOCS Official Method Cc 7-25 (1) because it is easier and quicker to perform. It measures the oil's refractive index (RI) with an Abbé refractometer. Correlation of RI to IV is accomplished through Bailey's equation (2) (Equation 1):

$$\mathrm{IV} = \frac{n_D^{50} - 1.4441}{1.171(10^{-4})} \qquad [1]$$

where n_D^{50} is the oil's RI measured at 50 ± 0.1°C and referenced to sodium D-line light wavelength (λ = 589.3 nm). Abbé instrument accuracy is typically ±0.0001 RI units (RIU) (3), equivalent to ±0.85 IV units.

The Abbé refractometer, a manual analog device, is subject to operator interpretation. The test is performed off-line, and the hydrogenation process must be halted during this time, which introduces inefficiencies and product inconsistencies. The test sample must be pre-filtered of the nickel catalyst and diatomaceous earth (DE) present in the hydrogenating oil. Otherwise, these particles diffuse light that must pass through the oil, thereby degrading refractometer resolution. The particles also mar the refractometer optical surfaces, essential for accurate readings, and require frequent instrument repairs.

This paper describes a planar wavelength refractometer (PWGR) that measures oil RI in real-time and in the presence of catalyst and DE. The operation of the PWGR is based on transmitting light power (Pt) at wavelength λ_{meas} through an optical, planar waveguide, immersed in a stream of hydrogenating oil. The waveguide, designed with highly accurate RI characteristics, functions as the RI reference. The oil temperature is systematically varied until a minimum power transmission (Pt_{min}) is detected, indicating that RIs of the oil (n_o) and waveguide (n_s) are matched. Concurrently, the oil temperature (T_{min}) is measured. The oil RI is then calculated for a reference temperature (T_R) and wavelength (λ_R) using the oil's known RI temperature coefficient ($\partial n_o/\partial T$) and dispersion coefficient ($\partial n_o/\partial \lambda$) according to Equation 2:

$$n_o(T_R,\lambda_R) = n_S(T_{min},\lambda_{\mathrm{meas}}) + \int_{T_{min}}^{T_R} \frac{\partial n_o}{\partial T}\, dT + \int_{\lambda_{meas}}^{\lambda_R} \frac{\partial n_o}{\partial \lambda}\, d\lambda = n_{\lambda_R}^{T_R} \qquad [2]$$

Such a device could improve the efficiency of the hydrogenation process; eliminate hydrogenation "overshoot," enhance product consistency and provide control signals to automate convertor operation.

EXPERIMENTAL PROCEDURES

The laboratory configuration for the PWGR system is shown in Figure 1. A system control program senses Pt and seeks Pt_{min} by controlling oil temperatures and flow. The program records T_{min} concurrent with each Pt_{min}; modulates the temperature at $T_{min} \pm \Delta T$; and continuously calculates n_D^{50} according to Equation 2. Control is accomplished through a heater and a pump, each adjusted by silicon controller rectifiers (SCRs). Oil temperature and flow are constantly regulated to track Pt_{min} as hydrogenation progresses. All signal interfacing is accomplished through digital-to-analog (D/A) and analog-to-digital (A/D) converters.

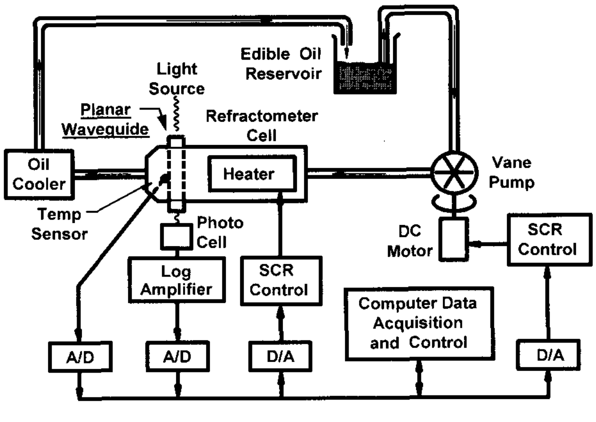

FIG. 1. Laboratory configuration for prototype planar waveguide refractometer system. A/D, analog-to-digital; D/A, digital-to-analog; SCR, silicon controlled rectifier; Temp, temperature.

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Three filtered samples of partially hydrogenated oils with IVs ranging between 105.6 and 75.0 were tested. The PWGR light source was a HeNe laser, $\lambda_{meas} = 632.8$ nm. The RI of each sample was first read with an Abbé refractometer, then placed in a reservoir and circulated through the operating PWGR system where RI readings were again taken with the PWGR. A mixture of catalyst and DE was subsequently added to the filtered sample in 0.072% concentration by weight, and further RI readings were taken with the PWGR. Finally, the IV of the test sample was reanalyzed, according to AOCS Method Cd 1-25, to confirm the sample's integrity. The PWGR system was purged and cleaned between tests.

Figure 2 shows how temperatures affect n_o of five partially hydrogenated soybean oil samples and n_S of synthetic fused silica (SiO_2) (4). For these oil samples, the average value of $\partial n_o/\partial T$ is −3.692 (10^{-4}) RIU/°C; standard deviation is 1.737 (10^{-7}) RIU/°C; the mean straight-line correlation coefficient of the data sets is −0.9999. Figure 2 demonstrated that RI matching (illustrated by Equation 3):

$$n_o(T_{min}, \lambda_{meas}) = n_S(T_{min}, \lambda_{meas}) \qquad [3]$$

will occur at some temperature, T_{min}. Provided that $n_S(T_{min}, \lambda_{meas})$ and $\partial n_S/\partial \mathrm{T}$ are known at a base temperature (T_B); then Equation 2 may be rewritten as Equation 4:

$$n_{\lambda_R}^{t_R} = [n_S(\mathrm{T}_B, \lambda_{meas}) + \int_{T_B}^{T_{min}} \frac{\partial n_S}{\partial T} \mathrm{d}T] + \int_{T_{min}}^{T_R} \frac{\partial n_O}{\partial T}\, \mathrm{d}T + \int_{\lambda_{meas}}^{\lambda_R} \frac{\partial n_O}{\partial \lambda} d\lambda \qquad [4]$$

Malitson (5) proved that n_S of typical, synthetic SiO_2 samples is consistent within ±10.5(10^{-6}) RIU at wavelengths between 214 and 3700 nm. His data established n_S (20°C, 632.82 nm) to be 1.45702. He also showed $\partial n_S/\partial T$ to be +1 (10^{-5}) RIU/°C near 50°C. Earlier research showed the RI dispersion of soybean oil ($\partial n_o/\partial \lambda$) to be approximately −4.0709(10^{-5}) RIU/nm (4). Incorporating these data and $\partial n_o/\partial T$ of soybean oils, Equation 4 may be simplified to the first-order Equation 5:

$$\begin{aligned} n_D^{50} &= 1.45702 + 1(10^{-5})(T_{min} - 20) - 3.692(10^{-4})(50 - T_{min}) \\ &\quad - 4.0709(10^{-5})(589.3 - 632.8) \\ &= 1.44013 + 3.792(10^{-4})T_{min} \end{aligned} \qquad [5]$$

Detecting T_{min} is accomplished by means of the planar waveguide configuration shown in Figure 3. The waveguide consists of a synthetic SiO_2 "core" (RI = n_S) surrounded by hydrogenated oil (RI = n_o). One end is assumed illuminated by a uniform, radially collimated, "line" light source (I w • rad^{-1} • cm^{-1}). A sensor to detect transmitted power is located at the other. Provided that the waveguide length (L), width (w) and thickness (h) ≫ 589 nm, light transmission may be analyzed by geometric optics (6). Each propagating ray follows a zig-zag trajectory and undergoes a unique number of reflections between the two parallel SiO_2/oil dielectric interfaces. The number of reflections depends on the ray's incident angle (θ_i), which remains constant, according to Fermat's principle (7). At every reflection, each ray undergoes reflectance, $0 \leqslant R \leqslant 1$, according to Snell's law and Fresnel's equations (7). Figure 4 shows the behavior of R at a planar dielectric interface as a function of ($n_o - n_S$) and θ_i in the region where $n_o \approx n_S$. For θ_i near 90°, R ≈ 1, even for small differences between n_o and n_S. R = 0 only when $n_o = n_S$.

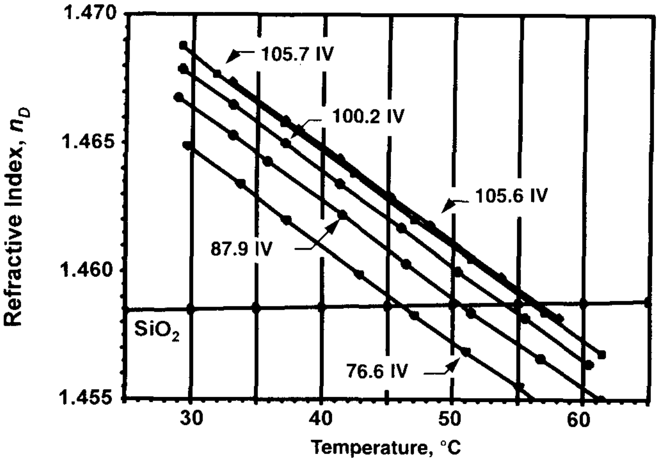

FIG. 2. Temperature influence on RI (n_o) of five various filtered soybean oils compared to SiO_2. Iodine values (IV) range from 105.6 to 76.6.

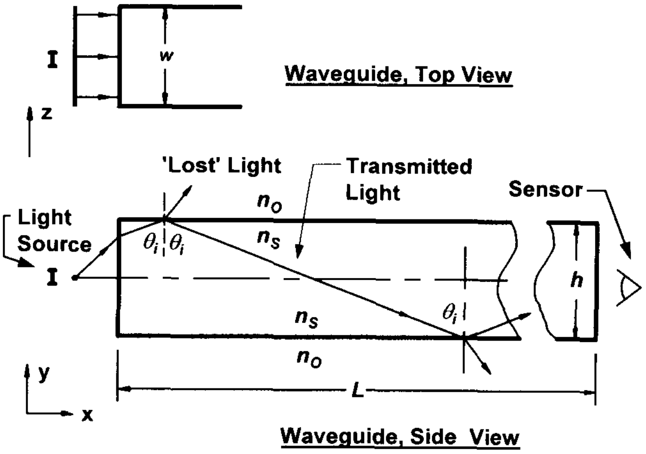

FIG. 3. Planar optical waveguide configuration used for computer modelling. L, waveguide length; w, waveguide width; h, waveguide thickness; n_o, oil refractive index; n_s, waveguide (silica) refractive index.

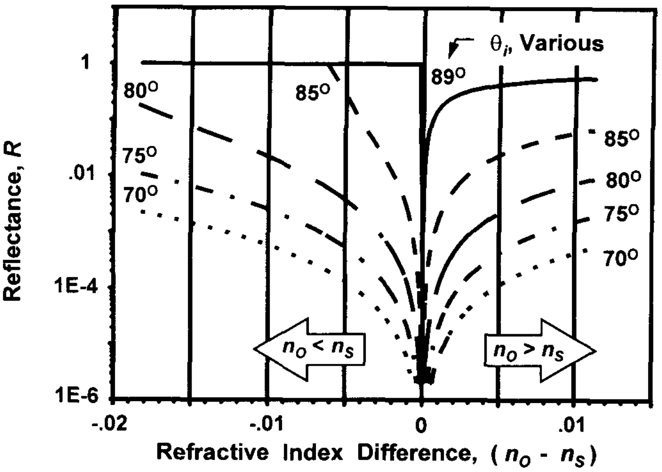

FIG. 4. Reflectance, R, at an optical dielectric interface due to Fresnel's equations. See Figure 3 for abbreviations.

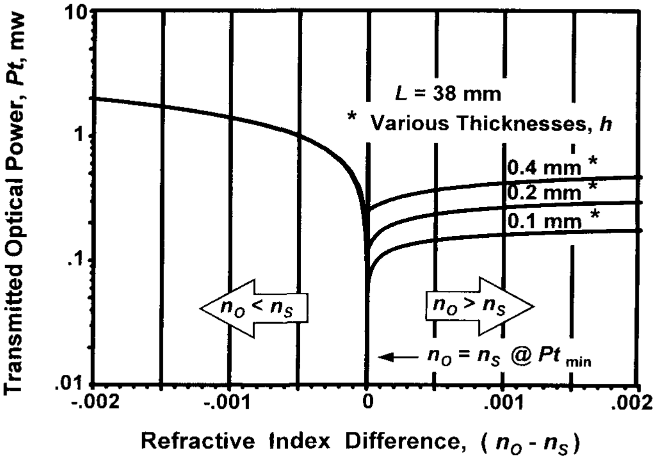

FIG. 5. Planar waveguide transmission response, computer model, Figure 3 configuration, various thicknesses (h); w = 16 mm. See Figure 3 for abbreviations.

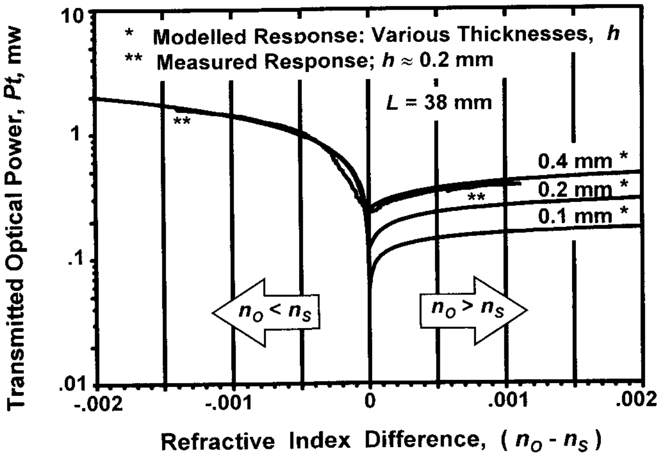

FIG. 6. Comparing theoretical and actual optical responses of the planar waveguide configuration shown in Figure 3. See Figure 3 for abbreviations.

A computer model that accounts for this optical behavior and sums all light rays transmitted through the planar waveguide as a function of ($n_o - n_S$) is shown in Figure 5 (8). Responses for three values of thickness (h) are depicted. All responses display a transmission loss, Pt_{min}, resolvable to 0.0001 RIU. Pt_{min}, induced by oil temperature modulation, always occurs at $n_o = n_S$, even though its magnitude varies with thickness (h). T_{min} may now be measured concurrent with Pt_{min} and inserted into Equation 5 to calculate n_D^{50}.

RESULTS

Figure 6 compares the response of a planar waveguide, L = 76 mm, w = 16 mm, $h \approx 0.2$ mm, with the computer model.

Data of the three partially hydrogenated soybean oil samples shown in Table 1. Figure 7 shows PWGR response under automatic control measuring sample number 1.

DISCUSSION

Figure 2 shows that $\partial n_o/\partial T$ of soybean oil is uniform from sample to sample and unaffected by degree of hydrogenation, a parameter essential for the application of Equation 5. These data also establish that oil temperature must be measured with an accuracy of ±0.1°C to maintain ±0.0001 RIU accuracy.

The waveguide response of Figure 6 validates the computer model. Because the latter shows the resolution of Pt_{min} to improve as $h/L \rightarrow 0$, the response of the actual waveguide indicates that its h/L ratio should be reduced by at least a factor of two.

Table 1 and Figure 7 confirm that the PWGR operates accurately with soybean oils that contain nickel catalyst

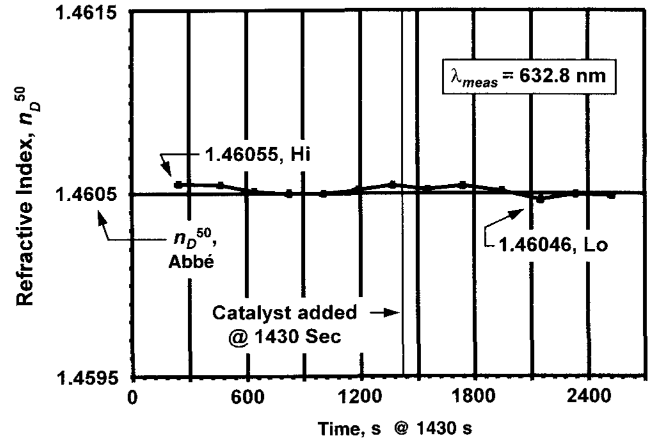

FIG. 7. Automatic refractive index measurements of soybean oil Sample #1 (Table 1) with prototype planar wavelength refractometer. Sample filtered, then with catalyst added; s, seconds.

TABLE 1

Refractive Index of Three Soybean Oil Samples, Calculated by Bailey's Equation (50°C), Measured by Abbé and PWGR refractometers[a]

		n_D^{50}				
Sample number	IV	IV	Abbé	PWGR "High" (auto)	PWGR "Low" (auto)	Period [τ (s)]
1	105.6	1.4602	1.4605	1.46055	1.46046 (Ni)	240
2	93.0	1.4587	1.4589	1.45893	1.45886	240
3	75.0	1.4566	1.4567	1.45675 (Ni)	1.45664	280

[a] (Ni) indicates nickel catalyst; τ = period between readings. PWGR, planar waveguide refractometer; IV, iodine value.

and DE powders as found in the hydrogenation process. Readings of samples agreed within ±0.0001 RI unit of the Abbé refractometer. The reason for this is that the optical interactions that produce the PWGR response take place at the dielectric interface between the oil and SiO_2. Unlike the Abbé refractometer, which measures the critical reflection angle as light passes from one optical medium to another (3), the light transmitted through the waveguide interacts with but does not pass through the unfiltered oil, in effect ignoring the suspended particles.

PWGR data agreed more closely with Abbé readings than Bailey's equation. Because the laboratory Abbé was calibrated several times against known standards as well as against a second Abbé unit, the PWGR–Abbé comparison is felt to be more valid.

Unlike operation of most on-line refractometers, PWGR operation is independent of variations in light source intensity, photosensitivity, electrical component parameters and oil turbidity. There are no moving parts. The magnitude of Pt_{min} is unimportant. Resolving Pt_{min} and T_{min} are accomplished with simple detectors. The single critical measurement required is temperature, which must be performed for any precise RI evaluation. Accuracies of ±0.1°C are easily obtained from conventional detectors. This concept can be adapted to other applications by choosing appropriate waveguide material.

The PWGR control/data acquisition program can be easily modified to present hydrogenation data in terms of either RI or IV. It can give a signal proportional to the difference between current conditions and the end-point setting, which would be useful for automatic control of the complete hydrogenation process. End-point requirements can be entered either manually or automatically; either be "batch" description or by actual value. The prototype PWGR control program gave sporadic erroneous RI values, indicating that improvement in the control algorithm is needed.

A process refractometer that dynamically measures ongoing partial hydrogenation offers significant potential to the edible oil process industry. It could (i) improve the hydrogenation process efficiency; (ii) eliminate variables introduced by sample contamination and operator interpretation, incurred during the manual refractometer test; and (iii) yield a more consistent product. As a monitor, this instrument could (i) provide RI and IV readings and/or (ii) become the feedback device now lacking for a completely automated hydrogenation process scheme. Other possible savings are (i) reduced energy costs through improved heat recovery and (ii) improved production techniques in continuous hydrogenation methods. Because hydrogenation facilities are in continuous use, any improvement in production efficiency has significant economic results.

This research holds promise for other RI measurement applications in food processing and chemical industries, whether the fluids are clear or turbid. An optical waveguide with an RI compatible with an appropriate fluid at an acceptable temperature is all that is necessary for correct operation. This refractometer, excited by various wavelengths of light, also has the potential of measuring fluid RI dispersion (9).

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