Analytical Chain to Monitor Vegetable Oil Hydrogenation[1]

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ABSTRACT

Three analyses were automated to monitor a laboratory continuous hydrogenator. Attenuated total reflectance infrared was used to follow *trans* isomer formation, refractive index for iodine value change and gas liquid chromatography for fatty acid composition. The instant response of the infrared spectrometer was confirmed by the later responses of the refractometer and gas chromatograph. All 3 operations were used to follow the progress of batch, continuous or semicontinuous hydrogenation.

INTRODUCTION

Although hydrogenation of vegetable oils is usually performed in batch process, several continuous or semicontinuous type reactors are reported (1-4). The successful development of continuous hydrogenators is dependent on effective monitoring systems. These systems must be automatic and computerized to provide almost instant measurements and control (5). As an example of instrumentation, this paper describes 3 automated analyses to monitor the progress of vegetable oil hydrogenation using infrared (IR) spectrometry, refractive index (RI), and gas liquid chromatography (GLC).

PROCEDURE AND APPARATUS

A simplified diagram of the analytical chain is shown in Figure 1. Oil for the continuous hydrogenator (6) is first mixed with 1% copper chromite catalyst and stirred constantly. The oil-catalyst slurry is then pumped through the reactor, the IR cell, and a 3-way (3W) solenoid into a collection vessel. The reactor consists of ca. 40 ft × 1/8 in. id. stainless-steel tubing in a temperature-controlled hot air oven. Pressure is controlled by a relief valve at the end of the column and is measured on a gauge at the inlet for the oil and H_2. The attenuated total reflectance (ATR) IR cell (Wilks Scientific Co., So. Norwalk, CT) is unaffected by the catalyst and permits unimpeded flow of the oil-catalyst mixture. The IR-ATR instrument is set at 10.3 μ for analysis of *trans* unsaturation formed during a hydrogenation (7, 8). Energizing the 3W solenoid diverts the desired amount of mixture to a filter for catalyst removal. Oil is pulled through the filter for both RI and GLC analyses with vacuum by a solenoid-controlled water aspirator. The RI monitor (Waters Associates, Milford, MA) is temperature-controlled with a precision water bath (Laud Co., W. Germany) at 25 C ± 0.1 C. An automated system for esterification-gas chromatographic analysis (9) is used for the GLC analysis. GLC output is recorded and interfaced with a real-time computer for calculating the fatty acid composition and iodine value (IV). Results from the IR and RI instruments are displayed on a 2-pen recorder. Omitted from Figure 1 is the electronic sequencer, which controls the sample size,timing, cleaning and purging of lines for the RI and GLC measurements.

The analytical chain was used to monitor the hydrogenation of refined-bleached soybean oil in a series of experiments in which temperature was the variable (170-205 C) and other parameters were held constant, i.e., 1% copper catalyst (0.33% copper by wt); oil flow, 2.2 mL/min; hydrogen flow, 100 mL/min; and pressure, 210 psi.

RESULTS AND DISCUSSION

The hydrogenation was monitored continuously with the IR-ATR instrument. RI and GLC monitoring were performed intermittently, depending on the time required for each analysis, i.e., 4-6 min for the RI and 10-14 min for the GLC. Samples can be taken simultaneously or separately, depending on operation of the sample solenoids. The *trans*-isomer concentration and IR transmission follow a nonlinear relationship (Fig. 2). A change in transmission of ca. 25, 33 and 47% corresponds to 5, 10 and 20% *trans*, respectively. IV decreases linearly with increasing *trans* formation as noted previously (10-13). IV can be measured by monitoring the changing RI during the reaction (Fig. 3). The "relative RI" of Figure 3 is recorder units. As measured manually, the RI changed from 1.4750 to 1.4690 during the reaction. Thus, a change of 0.00060 RI vs ca. 40 IV units produces ca. 0.00015 RI unit changes per IV unit. Although this change is nonlinear, it is sensitive enough to estimate degree of hydrogenation within the range noted.

RI measurements are extremely sensitive to temperature, pressure and flow. As already noted, an instrument with at

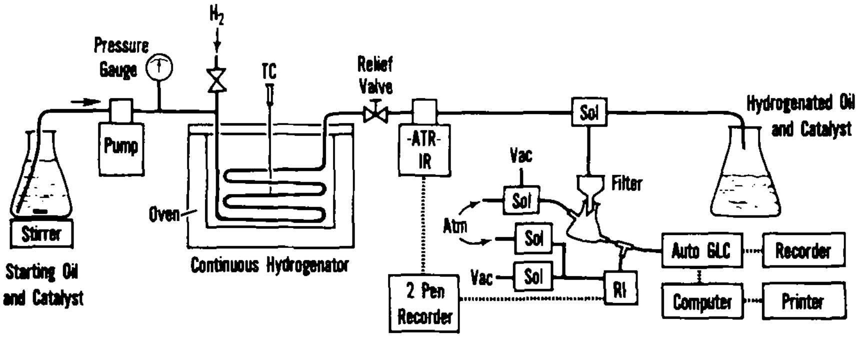

FIG. 1. Diagram of soybean oil continuous hydrogenation and automated analyses system. H_2–hydrogen; TC–thermocouple; ATR-IR–attenuated total reflectance–infrared spectrometer; SOL–solenoid; RI–refractometer; GLC–gas liquid chromatography. See text for details.

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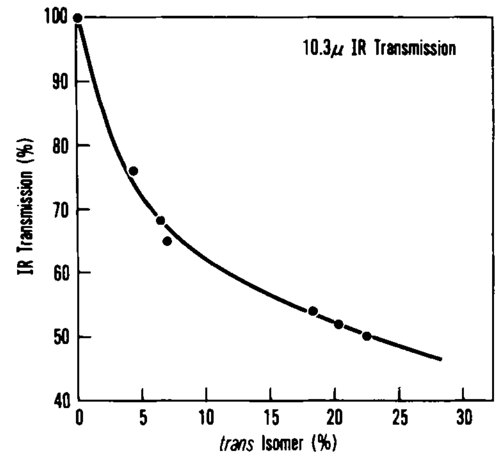

FIG. 2. *trans* Isomer formation during hydrogenation of soybean oil. IR transmission at 10.3 μ. Hydrogenation conditions: 1% copper catalyst; temperature 170 C to 205 C; oil flow, 2.2 mL/min; hydrogen flow, 200 mL/min; pressure 210 psi.

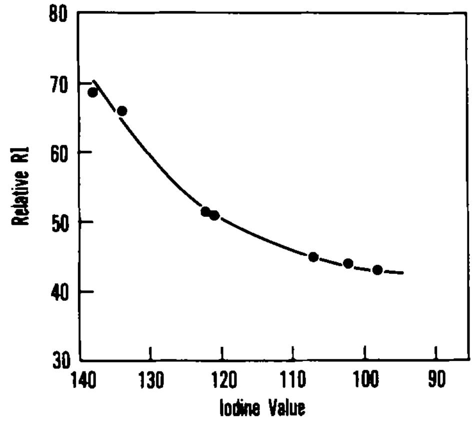

FIG. 3. Soybean oil refractive index changes during hydrogenation. RI temperature 25 C. Hydrogenation conditions: same as in Fig. 2. Relative RI in recorder units.

TABLE I

Automated GLC Analysis[a] of Soybean Oil during Continuous Hydrogenation

	Fatty acid (%)					
Sample no.	Palmitic	Stearic	Monoene	Diene	Triene	Iodine value
Starting oil	11.1	3.4	22.1	55.0	8.4	136.4
1	11.9	3.5	21.5	54.8	7.9	134.0
3	12.9	3.4	25.0	54.7	4.7	126.6
5	12.1	3.5	25.7	55.3	3.4	126.9
7	12.0	3.8	30.5	52.0	1.6	120.4

[a] Computer-calculated.

least 5-place accuracy is required. In addition, there was apparently a "shear effect" between the oil on the sides of the detector and the primary oil flow. The stop-flow technique was, therefore, used to alleviate this "shear effect" problem. Reducing viscosity by raising oil temperature or diluting with a solvent reduced shear effect but also caused additional complications for automation by requiring complex ancillary equipment, such as temperature controls, metering valves and associated circuitry.

GLC results are shown in Table I. Samples 1-6, obtained at 170 C, characterize the hydrogenation as it approaches equilibrium at an IV of 126.9. Raising the temperature to 180 C after sample 6 increases the degree of hydrogenation, as indicated by the lower IV of 120 for sample 7 taken after a return to equilibrium. The fatty acid composition follows the expected results with Cu catalyst (14). The triene and diene values decrease in concentration, the monoene increases, and the palmitic and stearic acid values remain essentially the same. The GLC results are obtained and calculated by computer and provide more complete details of hydrogenation changes than the RI measurement.

Automation is gradually overtaking control of most industrial processes, primarily to reduce costs of operation and improve reliability. The 3 automated analyses given in this article should help vegetable oil processors in converting from manual to automatic operation. A major point observed is that only the *trans* measurement with IR gives the instant response necessary for immediate control. At present, the time limit on RI and GLC restricts their use to monitoring and confirming other analyses, but this undoubtedly will improve with better instruments and techniques.

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