The Magnetic Field as an Additional Selectivity Parameter in Fat Hydrogenation

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ABSTRACT: An investigation of the influence of a magnetic field on selectivity ratios (SR) in the nickel-catalyzed hydrogenation process of fats is presented. Sesame oil and soybean oil were hydrogenated in an AC field of 300 oersted. The SR SR = K_2/K_3 and linolenic SR = K_1/K_2 obtained were higher than those without a field because the magnetization of the nickel particles reduced the concentration of hydrogen on the catalyst surface.
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KEY WORDS: Fat hardening, hydrogenation reaction rate, linoleic selectivity ratio, linolenic selectivity ratio, magnetic field, nickel catalyst G53, nickel catalyst KE-NF 20, palladium catalyst G109, sesame oil, soybean oil.

In the stepwise nickel-catalyzed hydrogenation process,

$$\text{triene} \xrightarrow{K_1} \text{diene} \xrightarrow{K_2} \text{monoene} \xrightarrow{K_3} \text{saturated acid} \qquad [1]$$

the selectivity ratios (SR) SR = K_2/K_3 and linolenic SR = K_1/K_2 will increase with increasing temperature, decreasing pressure, increasing amount of catalyst, and decreasing agitation intensity (1) owing to a lower concentration of hydrogen on the nickel surface. However, the hydrogen concentration on the nickel surface may also be influenced in another way. Absorption of molecules on the surface of a ferromagnetic solid, such as nickel, produces a change in the magnetization of the solid. If the absorption process involves appreciable electronic interaction and if the ratio of surface to volume in the adsorbent is large, as in commercial nickel-silica catalysts, the fractional change of magnetization becomes substantial (2). This means that, if the whole system is brought into a magnetic field, the magnetization and accordingly the absorption conditions will be influenced, and the concentration of hydrogen on the catalyst surface will decrease. The purpose of the present work is to demonstrate this effect experimentally.

EXPERIMENTAL PROCEDURES

Apparatus. The apparatus was home-made (Fig. 1). The reaction vessel containing the oil was a Pyrex test tube (125 × 12 mm), wound with 60 turns of a constantan heating wire (total resistance: 10 Ω), which was fastened with asbestos cement (prepared from asbestos powder and a concentrated solution of sodium silicate). A thermocouple, dipping into the oil, controlled the temperature through a relay, a transformer (220 V/22 V), and a variable resistance (10 Ω). Stirring was performed with a small spatula mounted in a laboratory stirrer (2000 rpm); hydrogen was supplied through a Teflon tube (1-mm i.d.), and surplus was allowed to escape through a hood. All experiments were performed with vigorous agitation and at atmospheric pressure. The lower part of the test tube was

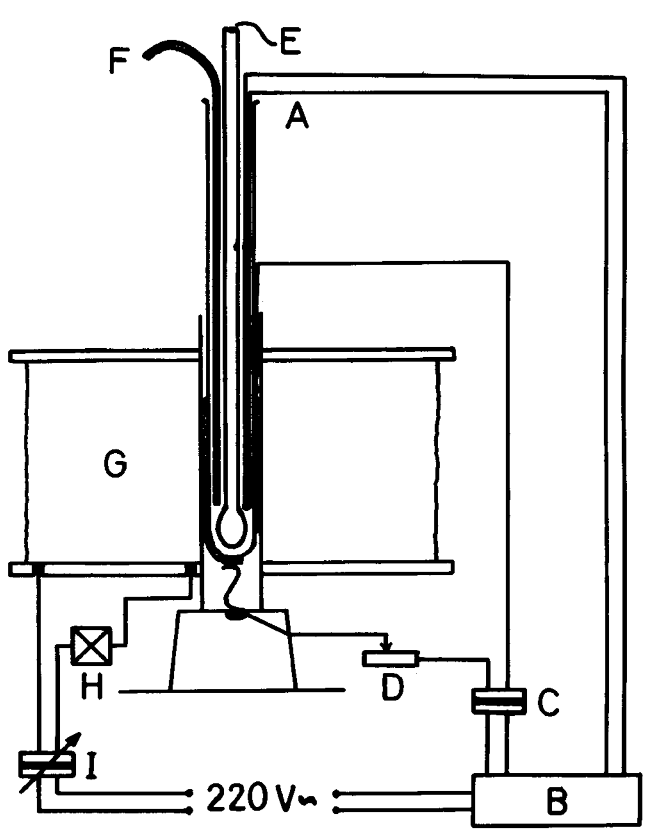

FIG. 1. Hydrogenation apparatus. A, Thermocouple; B, relay; C, transformer (220 V/22 V); D, variable resistance (10 Ω); E, spatula for stirring; F, hydrogen inlet; G, coil (1615 turns); H, lamp (275 W); I, variable transformer.

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surrounded by a coil with 1615 turns (Lübcke, Copenhagen, Denmark). By means of a variable transformer and a 275 W lamp, the AC current (50 Hz) through the coil was adjusted to 0.9 A, which corresponds to a magnetic field of 300 oersted.

Analysis. Samples were drawn from the reaction mixture by dipping a Teflon tube (0.5-mm i.d.) into the oil and transferring a small amount to a test tube. Without removing the catalyst, 1 mL of a 0.025 M sodium methylate solution (prepared from 135 mg sodium in 100 mL of dry methanol) was added, and the mixture was kept at 60°C with occasional shaking. When the solution had been clear for half an hour, 4 mL of saturated sodium chloride solution and 1.5 mL of pentane were added, and the mixture was shaken vigorously. The upper phase, which contained the methyl esters, was used directly for gas chromatography as described: chromatograph (5890 A-II; Hewlett-Packard Co., San Fernando, CA) with a 50 m × 0.25 mm × 0.20 μm CP-Sil 88 column (Chrompack, Middelburg, The Netherlands) under the following oven temperature program and conditions: 140°C for 2 min; from 140 to 220°C at 10°C/min; at 220°C for 2 min; injector temperature at 250°C; flame-ionization detector temperature at 300°C; column pressure 130 kPa; and hydrogen as carrier gas with a split ratio of 1:20. From the chromatograms, the contents of C_{18} acids were calculated in such a manner that their total amounted to 100%. From these values, the SR and linolenic SR were determined with the help of a standard computer program (3).

Hydrogenation of sesame oil. Material and conditions: 3000 mg of refined sesame oil from Aarhus Oliefabrik A/S (Aarhus, Denmark); catalyst; 0.07% Ni from KE-NF 20 (Süd-Chemie AG, Bruckmühl-Heufeld, Germany); hydrogen: 330 mL/min; temperature: 100°C. Samples were drawn every 5 min, and Figure 2 shows the content of dienoic, monoenoic, and stearic acid up to 80 min. Figure 3 shows iodine values (IV) as calculated from the samples during the two hydrogenation experiments. SR has been calculated for 20, 40, 60, and 80 min of reaction and is given in Table 1.

Hydrogenation of soybean oil. Material and conditions: 3000 mg of refined soybean oil (Aarhus Oliefabrik A/S); catalyst: 0.15% Ni from G53 (Süd-Chemie AG); hydrogen: 200 mL/min; temperature: 140°C. SR and linolenic SR have been calculated for 20 min of reaction and are given in Table 1 (averages of three experiments).

RESULTS AND DISCUSSION

The SR in Table 1 show that the conditions are better for a selective process when an AC field is applied. The original idea with these experiments was to use an AC field to get the nickel particles to oscillate, and in that way to speed up the process in a manner analogous to ultrasonic hydrogenation described recently (4). But a mechanism that involves oscillating catalyst particles and consequently better agitation was suspected to give lower SR values, contrary to the experimental results. The effect observed might be a result of both a lower hydrogen concentration on the nickel surface and a sort of oscillation phenomenon, but preliminary experiments (5) showed similar results with DC fields, and the oscillation phenomenon seems to be of no greater importance. The preliminary experiments also showed that currents above 0.6 A did not increase the effect studied because the constant magnetization level already had been reached. The magnetization effect appears in spite of agitation and AC fields; this may be due to the small particle sizes of the catalyst, which may be essentially a single magnetic domain (2) that will adjust itself according to the applied field. Additional experiments performed confirm the view (6) that the concentration of hydrogen on the nickel surface is decisive for the selectivity in the hydrogenation process. At the same time, the mag-

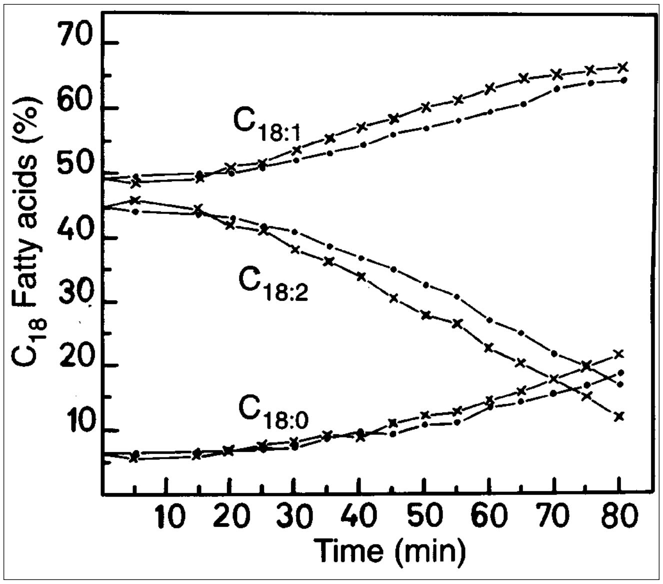

FIG. 2. The amount of individual C_{18} acids during hydrogenation of sesame oil with a magnetic field (◆—◆) and without a field (x—x).

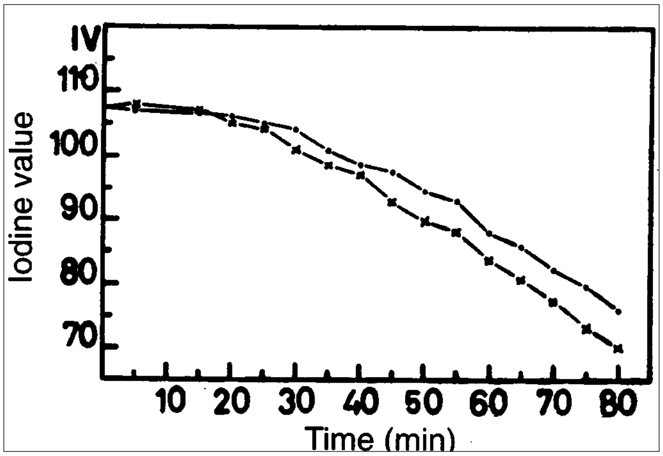

FIG. 3. Effect of an AC field of 300 oersted on the iodine value during the hydrogenation of sesame oil at 100°C; with a magnetic field (◆—◆), and without a field (x—x).

TABLE 1
Selectivity Ratios (SR) During Hydrogenation with and Without a Magnetic Field

	SR		Linolenic SR	
	No field	Field	No field	Field
Sesame oil, 100°C —20 min	3.4	5.8		
—40 min	3.2	5.6		
—60 min	4.1	4.8		
—80 min	4.7	5.3		
Soybean oil, 140°C—20 min	6.8	7.5	1.25	1.32

netic field will reduce the hydrogenation reaction rate as a result of the lower concentration of hydrogen on the catalyst surface (Fig. 3).

Experiments with a palladium catalyst (G109 from Süd-Chemie AG: 1% Pd on $\gamma\text{-A}1_20_3$) and sesame oil showed no better selectivity in the magnetic field. Although the metal resembles nickel, it also absorbs hydrogen in its interior, and the magnetic properties deviate considerably from those of nickel.

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