Continuous Hydrogenation of Vegetable Oils in Reactors Equipped with Static Mixers

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Continuous hydrogenation of industrially refined soybean oil with Harshaw Ni catalyst was achieved in a slurry column equipped with Sulzer SMV motionless mixers. The influence of the operating parameters (temperature, pressure, catalyst concentration and gas velocity) was investigated. The presumption that, in this equipment, the liquid-solid mass transfer limits the rate of the process is in good agreement with the experimental data.

KEY WORDS: **Hydrogenation, nickel catalyst, static mixers, vegetable oils.**

Hydrogenation of fatty oils is important because of both its large application (over 4 million tons/year) and the destination of the products. The complexity of the process lies in the variability of the raw materials (a consequence of climatic conditions) as well as in the requirement for specific compositions of the fatty acids in the final products: *e.g.*, high linoleic contents for some margarine types, high contents of *trans*-oleic acid in others, or low unsaturation levels for industrial greases (1).

Various catalytic systems, based on copper chromite (2,3), Ni-Cu alloys (4) or just Ni (1,5,6), were investigated by different researchers for the selective hydrogenation of fatty oils.

Only discontinuous installations are used industrially, in which the operating conditions can be modified easily to allow for fluctuation of the raw materials.

Outfitting three-phase columns with static mixers produces important intensification of mass transfer (L. Rusnac, O. Floarea and R. Vladea, submitted for publication). The wide ranges in which the operating parameters (phase velocities and temperature) can be varied without considerably affecting the gas-liquid interfacial area (which is crucial for mass transfer) provide for great flexibility in these reactors. Consequently, this equipment may be used for the continuous hydrogenation of fatty oils.

This work presents the results obtained for soybean oil hydrogenation in a column equipped with Sulzer SMV static mixers (Sulzer Brothers Ltd., Winterthur, Switzerland).

EXPERIMENTAL PROCEDURES

Both the catalyst (22% Ni on SiO_2, Harshaw Chemie BV, ZG de Meern, The Netherlands) and the oil are from commercial sources. The soybean oil had an iodine value (i.v.) of 137 and was used as such or refined by alkaline treatment and washing.

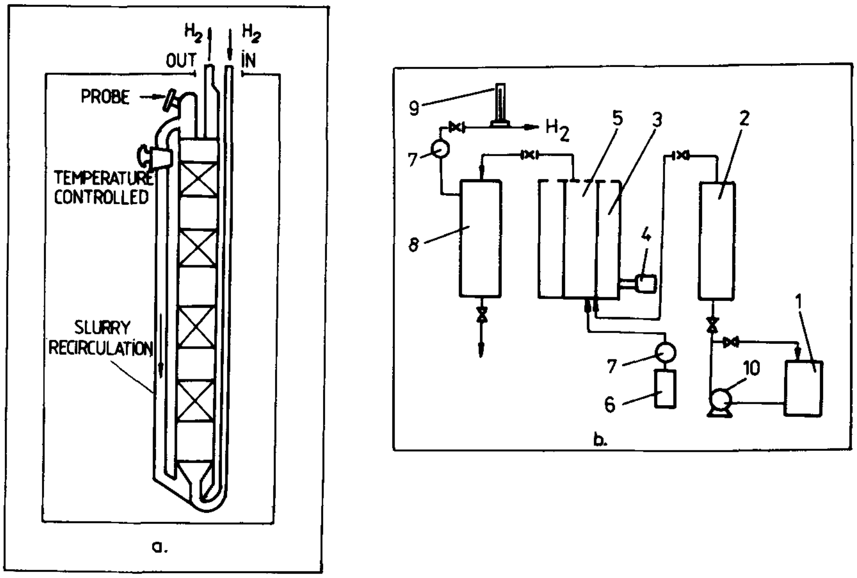

FIG. 1. Experimental setups: (a) Atmospheric pressure reactor, (b) high pressure setup: 1. slurry reservoir; 2. preheater; 3.,4. thermostated oven; 5. reactor; 6. hydrogen supply; 7. back-pressure regulator; 8. H_2 separator; 9. rotameter; 10. pump.

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For atmospheric-pressure hydrogenation, a glass reactor (Fig. 1) was used. Co-current circulation of phases and controlled recycling of the slurry were ensured in this reactor (2 cm i.d., 30 cm length, equipped with 15 Sulzer SMV mixing devices). For each run 100 mL of oil was used.

The experimental setup for the high-pressure hydrogenation (Fig. 1) included a similar steel reactor. The runs were performed with one liter of oil. The slurry crossed the reactor several times; the apparatus was cleaned after each use.

In both reactors the slurry rate was between 0.5 and 2 mm/s. To ensure the bubble flow regime (no bed pulsation), the gas linear velocity must be smaller than 35 mm/s (42 L/h). Catalyst deposition is prevented if the gas velocity is greater than 4.9 mm/s (14 L/h).

The degree of hydrogenation was followed by means of the i.v. as determined by the Hannus method after removing the catalyst by centrifugation.

The distribution of the fatty acids in the products was determined by gas chromatography, as described elsewhere (7).

Each point in the graphs represents the mean value of at least five determinations.

RESULTS AND DISCUSSION

At atmospheric pressure, the decrease of i.v. with time (Fig. 2) was more rapid at higher temperatures. For a given temperature, a linear dependence was obtained with time in the studied range.

Increasing catalyst concentration led to shortening of the reaction time necessary to reach an imposed degree of saturation (Fig. 2). It was established that the gas flow rate also affects the saturation of double bonds in the oils. An increase in the H_2 flow rate from 14.5 to 21.5 L/h led to an i.v. reduction of 30 units, and a ten-unit decrease of the i.v. was obtained by boosting the flow rate from 21.5 to 40.2 L/h (Fig. 2).

Sizeable reductions of the reaction time can be obtained with the increase of pressure (Fig. 3), but the influence of temperature is less significant (Fig. 3). The differences found between the reaction rates at atmospheric pressure for different catalyst concentrations also hold true at higher pressure, but the reaction times are greatly decreased.

According to the two-films theory, the hydrogen concentration profiles are as shown in Figure 4. The maximum H_2 concentration gradient is equal to the saturation concentration and can be achieved for high Ni content. If the gas-liquid mass transfer limits the rate of reaction, which is true in batch reactors (5,8), one can expect a limitation of the reaction rate increase with an increase in the catalyst concentration. Our experimental data disagree with this.

Figure 5 shows that the reaction rates increase continuously with catalyst concentration, but there are two fields of variation: at low catalyst content (<0.1% Ni), a fast increase of the reaction rate was observed with increasing catalyst concentration, while the slope of the curve was considerably smaller when Ni concentrations were greater than 0.1%. A similar profile was obtained for the dependence of the reaction rate on gas velocity, which is also presented in Figure 5.

The static mixers create a considerable increase of the interfacial gas-liquid area (L. Rusnac, O. Floarea and R. Vladea, submitted for publication) as a result of simultaneously decreasing the bubble mean diameter and increasing the gas holdup. Consequently, a high rate of gas-liquid mass transfer is obtained in this type of reactor. Under these circumstances, we presume that the liquid-

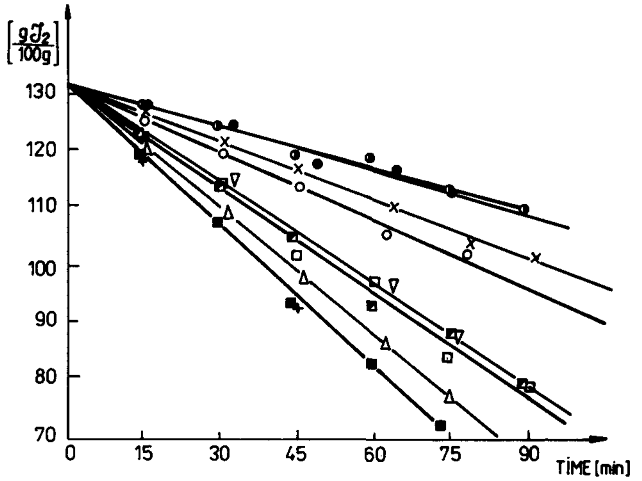

FIG. 2. The influence of temperature, catalyst concentration and gas velocity on fatty oil hydrogenation. Temperature effect (Ni concentration 0.1%; H_2 flow rate 14.5 L/h; slurry velocity 1 mm/s): X 160°C, ○ 180°C, □ 200°C, + 220°C. Catalyst concentration effect (temperature 200°C; H_2 flow rate 21.5 L/h; slurry velocity 1 mm/s): ● 0.03% Ni, ▽ 0.1% Ni, △ 1% Ni, H_2 flow rate effect (temperature 200°C; catalyst concentration 0.1% Ni; slurry velocity 1 mm/s): ◐ 14.5 L/h, ◩ 21.5 L/h, ■ 40.2 L/h.

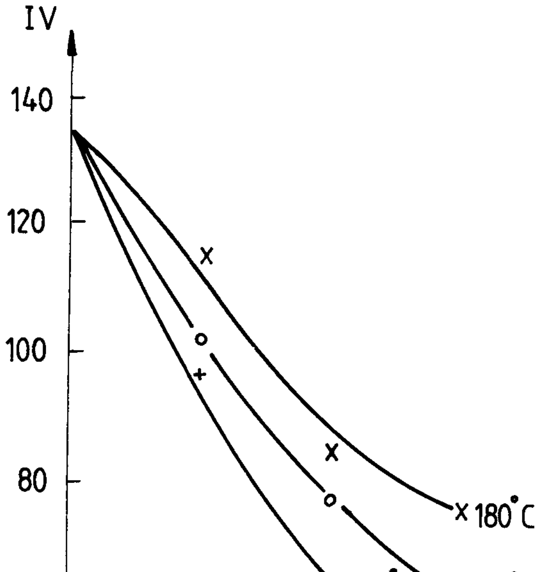

FIG. 3. Pressure influence on fatty oil hydrogenation. Catalyst concentration 0.1% Ni, slurry flow rate 0.1 mm/s, H_2 flow rate 21.5 L/h.

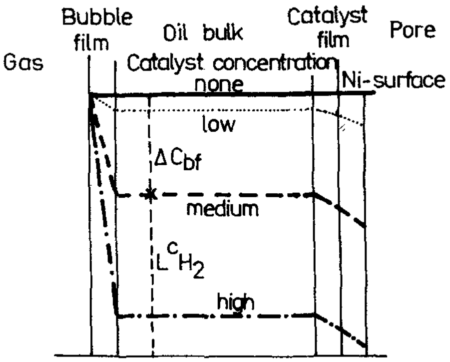

FIG. 4. H_2 **concentration profiles in oil near gas bubbles and catalyst surfaces (5).**

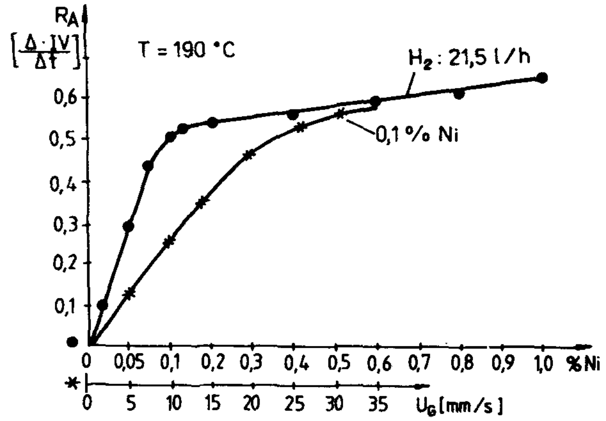

FIG. 5. Influence of catalyst concentration and gas velocity on the rate of hydrogenation of vegetable oil. Catalyst concentration 0.1% Ni, temperature 200°C, slurry flow rate 0.1 mm/s.

solid mass transfer becomes limiting for the rate of the process. The two slopes of the curves presented in Figure 5 can be explained as follows: As long as the diameter of the particle is a little less than the thickness of the laminar layer developed on the surface of the static mixer, a rotational movement of the particle takes place and this leads to a decrease of the stagnant layer around the particle. This is followed by a diminution of the resistance to mass transfer. Increasing the catalyst concentration results in an increase in the viscosity of the slurry and, consequently, in a limitation of the rotational movement. As a result, the rate of the mass transfer increases with catalyst concentration.

For gas velocities smaller than 20 mm/s, the velocity at the boundary of the laminar layer increases with the gas velocity, due to frictional forces. Consequently, the velocity of the rotational movement of the particles increases and the rate of the process increases, too. It was shown that the gas holdup increases proportionally with the gas velocity (L. Rusnac, O. Floarea and R. Vladea, submitted for publication). Simultaneously, a decrease of the frictional forces between the laminar layer and the core of liquid is induced, due to the decrease of viscosity of the core. Gas velocities greater than 20 mm/s induce such a reduction of the frictional forces that a limitation of the velocity at the boundary of the laminar layer can be assumed. As a result, the rate of the process increases only with the interfacial area.

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