❧ Hydrogenation of Soybean Oil by Nickel/Silica Catalysts in a Rotating Packed Disk Reactor

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Hydrogenation of soybean oil was carried out by nickel/silica catalysts in a newly developed rotating packed disk reactor (RPDR). The rotation of a catalyst-filled disk facilitated hydrogen transfer into the liquid phase and mixing in the reactor, resulting in an improved three-phase reaction. Performance of RPDR in a batch operation was studied by varying temperature, pressure, nickel concentration in the oil, and disk rotating speed. The overall reaction rate increased with these variables, but the selectivity of linoleic acid was high when the hydrogen transfer controlled the reaction on the catalyst.

Three-phase chemical reactions involving solid catalysts, liquid and gaseous reactants are commonly encountered in chemical and biochemical industries. Efficient gas-transfer into a liquid phase and good mixing near a catalyst particle are essential for success of the process in many cases, due to low solubility of a gaseous reactant in a liquid phase. Up to now trickle-bed and fluidized-bed generally have been used for three-phase reactions (1). However, in spite of many advantages associated with the use of these reactors, there are several defects arising from their operational features. A major disadvantage of the trickle-bed reactor is poor radial transfer of heat in a large scale operation. Flow maldistributions also are common at low liquid flow rates without incorporation of auxiliary nozzles. In fluidized-bed reactors a high degree of axial mixing often decreases the conversion, and catalyst attrition is unavoidable. Slurry reactors are used sometimes, but in this case catalyst separation from the product mixture is difficult and expensive.

Recently, Chang and coworkers (2,3) have developed a rotating packed disk reactor (RPDR) for carrying out a three-phase biochemical reaction. This reactor resembles the rotating biological contactor (RBC) widely used in wastewater treatment, but it differs from RBC in the sense that catalyst particles are packed in the disk (Fig. 1). The disks of RPDR rotate like RBC, partially submerged in a liquid. As a model reaction, we selected a glucose oxidation for RPDR, which was filled with immobilized glucose oxidase and catalase. The oxidation was enhanced with increases in the rotational speed of the packed disk, the bulk flow rate, and enzyme loading. Interestingly enough, there existed an optimal submergence of the disk, 0.4 of the disk diameter, giving a maximal conversion.

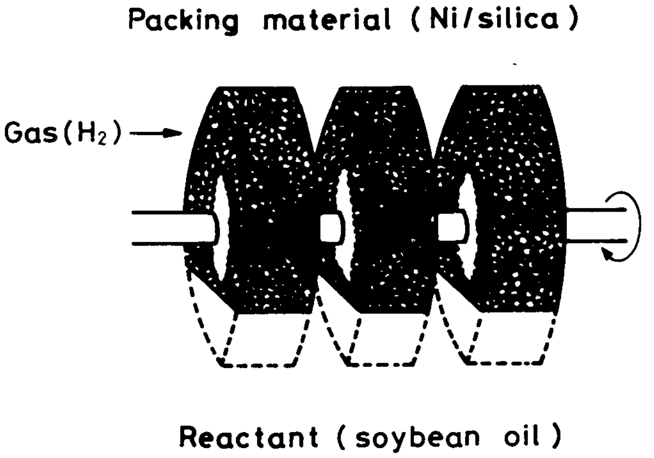

FIG. 1. Schematic diagram of a rotating packed disk reactor.

In this study we intend to test whether RPDR can be used for a three-phase catalytic hydrogenation reaction other than a biochemical reaction. Currently, the hydrogenation of soybean oil is accomplished in a dead-end reactor by bubbling hydrogen through an oil slurry containing fine catalyst particles. After the reaction is completed, the slurry is filtered and the catalyst is recovered. The process is intrinsically of a batch mode and needs improvement because of difficulties in catalyst separation and reuse. For continuous processing, Moulton and Kwolek (4) reported results with a trickle-bed reactor, Moulton et al. with a slurry ultrasonic reactor (5) and Koritala et al. with a slurry reactor (6,7). But a successful commercial reactor using these techniques has not been made as yet.

SOYBEAN OIL HYDROGENATION

Soybean oil is a mixture of triglycerides formed by condensation of three fatty acids and glycerol. Fatty acids may contain double bonds, which are apt to be oxidized upon contact with oxygen. This oxidation reaction is a major cause of oil deterioration, and proper saturation of the double bonds with hydrogen can improve oil stability. Over-saturation will reduce the fluidity of a product oil and change the melting properties.

Hydrogenation reactions were studied by Albright and many others (8–10). A model simplified by Albright et al. (8) is:

$$\text{Linolenic acid} \xrightarrow{K_a} \text{Linoleic acid} \xrightarrow{K_b} \text{Oleic acid} \xrightarrow{K_c} \text{Stearic acid} \quad [1]$$

All hydrogenation reactions are assumed to be first-order and irreversible. All isomers are considered as a group. The simplified model makes it possible to quantify the selectivity ratio by rate constants:

$$\text{LnSR} = K_a/K_b \quad [2]$$

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$$\text{LoSR} = K_b/K_c \qquad [3]$$

where LnSR and LoSR refer to the selectivities of linolenic and linoleic acids, respectively. A high LnSR means that the product oil contains little linolenic acid to guarantee a stable taste, and a high LoSR stands for a nutritious oil with a high content of linoleic acid. From an operational viewpoint, however, more attention is paid to LoSR because the removal of linolenic acid is related directly to the hydrogenation activity, but too much production of stearic acid should be avoided for appropriate oil fluidity.

As the double bonds in fatty acids also can be saturated by iodination, the overall reaction rate in oil hydrogenation is expressed in terms of the iodine value (IV) as:

$$- d(\text{IV})/dt = K \cdot (\text{IV}) \qquad [4]$$

where K indicates the overall rate constant. Thus, [Eqn. 4] can be used to measure the activity of hydrogenation reaction.

EXPERIMENTAL

Apparatus. A schematic diagram of experimental apparatus is shown in Figure 1. The reactor consists of three rotating disks partially submerged in the oil (Fig. 2). The disks' shaft was made of a stainless steel rod 1 cm in diameter. The disks were 285 cm^3, 11 cm in diameter and 3 cm wide, and they were covered by 40-mesh stainless steel screen. The disk shaft was connected to a variable speed UltraMasterflex motor (Cole-Parmer, Chicago, Illinois). The reactor vessel, 2300 cm^3, 15 cm in diameter and 13 cm long, was constructed of 2 mm stainless steel.

For operations with hydrogen, a cover was installed on the upper part of the reactor. Silicone rubber was used to seal around the shaft and the gasket between the vessel and the lid. Heating lines of 250 watts were laid at the bottom of the reactor to heat the oil. The temperature of the oil was measured by a thermocouple located in the center of the vessel. The vessel was immersed in a water bath to cool the oil when required. Hydrogen pressure in the vessel was regulated by a micro-needle valve between the cylinder and the reactor.

Materials. Soybean oil used in the present experiment was of commercial grade supplied by Cheil Sugar Co. (Inchon, Korea). Standard fatty acids for chromatography were purchased from Tokyo Kasei Co. (Tokyo, Japan). Nickel/silica catalysts were prepared by impregnation by applying an incipient wetness technique (11). Si6-5P Silica (Akzo Chemie, The Netherlands) having surface area of 180 m^2/g and porosity of 0.9 ml/g was crushed to about 12 mesh and used as a carrier. Twenty g of the silica carrier was impregnated with nickel nitrate solution made by dissolving 30.3 g $Ni(NO_3)_2 \cdot 6H_2O$ in 18 ml distilled water. The catalyst was dried at 120 C for 24 hr and then reduced under hydrogen gas stream of 80 ml/min for four hr. The catalysts were coated with stearic acid to prevent the nickel in the catalyst from being oxidized. The final concentration of nickel in the catalyst was 25%. Hydrogen and nitrogen gases used in this work were 99.99% pure.

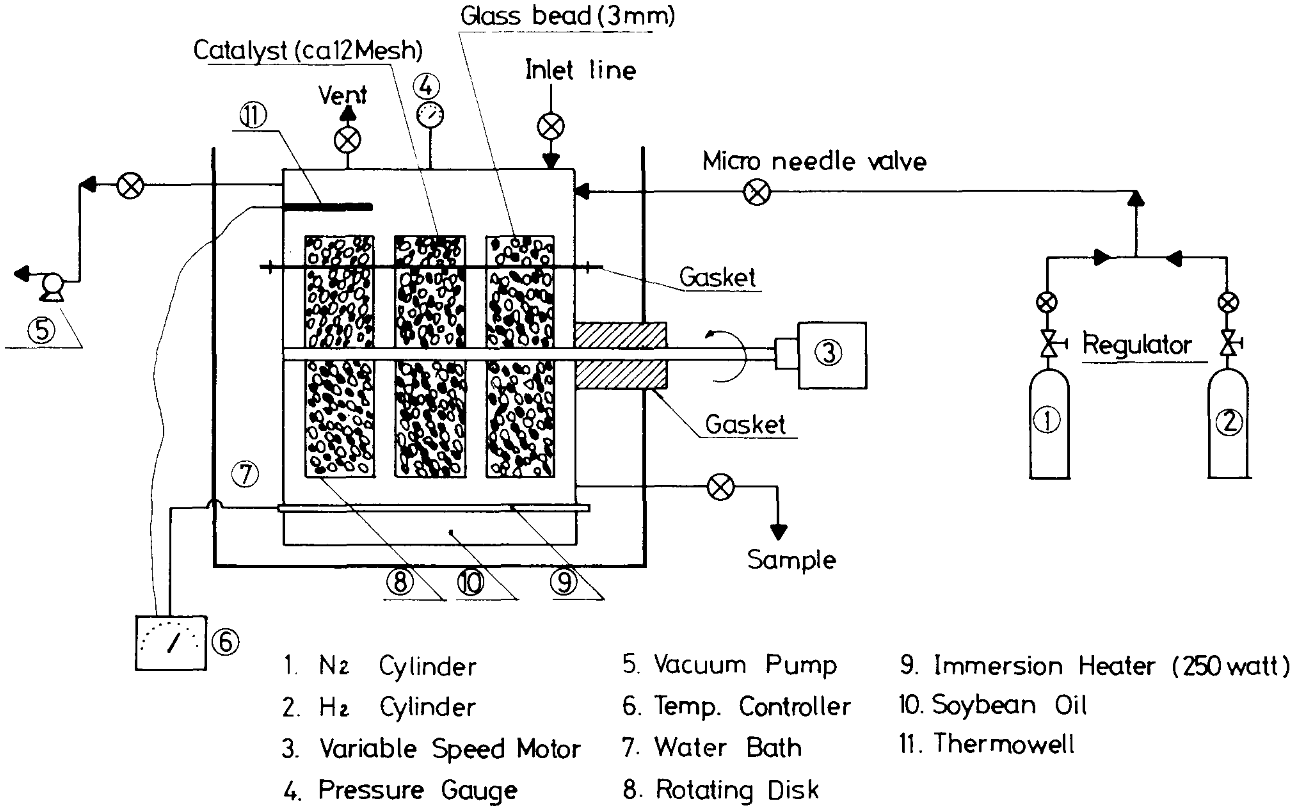

FIG. 2. Layout of experimental apparatus.

Procedure and methods. Prior to each run the empty reactor was flushed with soybean oil. The disks were charged with a given amount of catalyst and glass beads 3 mm in diameter, and the reactor was sealed. Air was removed by a vacuum pump, and soybean oil (500 ml) was introduced into the reactor through the inlet line. The reactor was purged with nitrogen gas several times to remove possible residual oxygen. When it was confirmed that no oxygen was left, nitrogen gas was used at 25 psig to fill the space above the oil. The oil was heated to a desired temperature while the disk was rotated, then nitrogen was sucked off by a vacuum pump and hydrogen was drawn in.

Periodically, a 3-ml sample was taken and filtered. Before the experiment, the refractive indices were correlated with established iodine values for partially hydrogenated oils according to the AOCS methods, Cc 7-25 for the refractive index and Cd 1-25 for the iodine value (12). Then, the iodine value of the sample was determined by its refractive index, which was measured by a Refractometer (Bausch & Lomb, Rochester, New York). The reaction was carried out to decrease the iodine value from 130 to 80. The level of submergence was maintained at 0.4 of the disk diameter, that is, at 4.4 cm.

The fresh catalyst was used for each test to exclude the possible effect of poisoning by sulfur. Experimental ranges of selected variables were 120-200 C for reaction temperature, 6-45 psig for hydrogen pressure, 0.83-3.30% Ni in the oil, and 5-100 rpm of the disk rotation. The hydrogenated oils were esterified by methanolic BF_3 reagent, and the esters were analyzed with a Gow Mac 750 gas-liquid chromatograph equipped with flame ionization detector (FID) (Bridgewater, New Jersey). The column was made of copper tube (9 ft × 1/8 in O.D.) and packed with acid washed 80-100 mesh Chromosorb W coated with 10% DEGS. Temperatures of the column oven, detector and injector were 180, 230 and 230 C, and flow rates of helium, hydrogen and air were 25, 20 and 400 ml/min, respectively.

RESULTS AND DISCUSSION

Figure 3 shows a typical result obtained under a standard condition of 180 C, 30 psig, 2.5% Ni and 60 rpm. The linoleic acid concentration decreased rapidly due to the hydrogenation, and so did the linolenic acid. The oleic acid increased with time, but finally decreased as double bonds were further saturated. Stearic acid increased steadily with some acceleration observed in the latter stage.

The solid lines in Figure 3 represent the curves according to the model of Albright et al. (5). They are in good agreement with our experimental results, indicating that the model was applicable to this RPDR system on the whole. The reaction constants calculated at iodine value of 80 were K_a = 0.0286/min, K_b = 0.0158/min, K_c = 0.0015/min, and the values of selectivity LnSR and LoSR were 1.81 and 10.5, respectively. This means that the double bonds in linolenic and linoleic acids were hydrogenated much faster than those in oleic acids.

Another important fact to be noted was that the final level of linolenic acid was below 1%. This is prerequisite for a commercial application of product oil because high contents of linolenic acid would affect flavor stability.

Effect of temperature. The effect of temperature on the hydrogenation rate and linoleate selectivity ratio (LoSR) is shown in Figure 4. As is often the case, the reaction rate increased with temperature. Several reasons can be mentioned: hydrogen is more soluble in oil at a higher temperature, and lower viscosity of oil leads to good mixing in the submerged phase and easy drain of entrained oil in the gas phase. These all facilitate the hydrogen transfer to the catalyst particles. But the most pronounced influence of temperature is exerted on the reaction constant itself, which can be confirmed by investigating the variation of selectivity.

The selectivity ratio was enhanced together with the increase in reaction rate. If sufficient hydrogen had been supplied to the catalytic surface to meet a higher rate of consumption, the portion of stearic acid in the product oil would have increased further. In spite of some increase in hydrogen transfer with temperature, it is preceded by the increase of reaction rate and the overall process would be rather limited by hydrogen transfer. A smaller amount

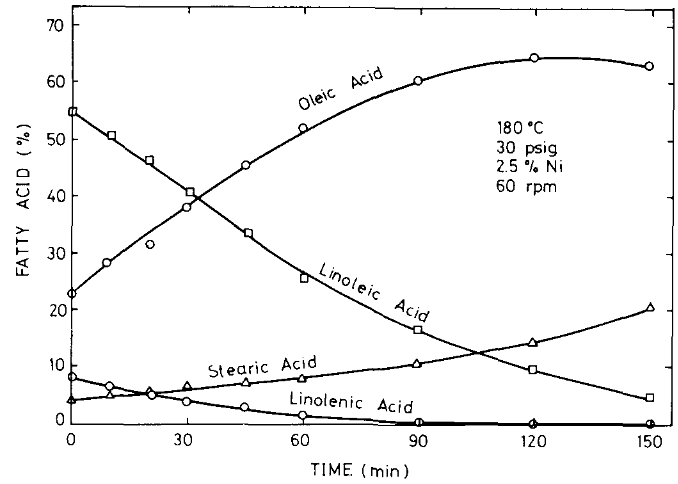

FIG. 3. Typical results of oil hydrogenation.

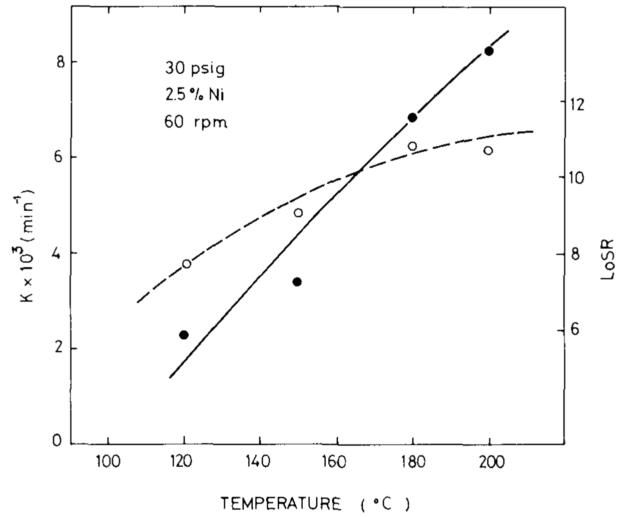

FIG. 4. Effect of temperature on the overall reaction rate (●——●) and the selectivity of linoleic acid (○– –○).

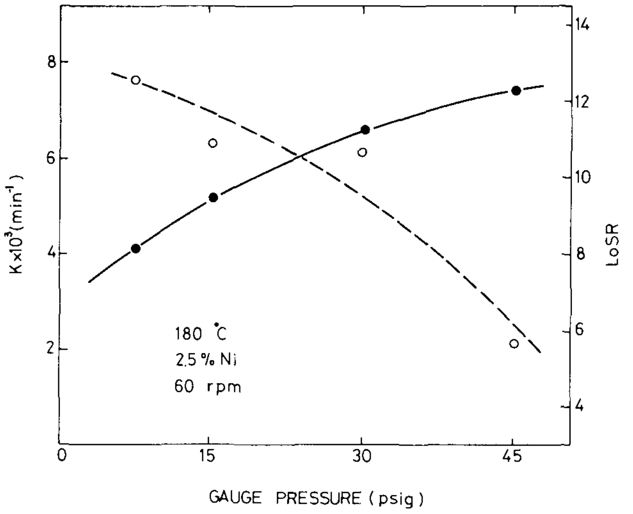

FIG. 5. Effect of pressure on the overall reaction rate (● —— ●) and the selectivity of linoleic acid (O — — O).

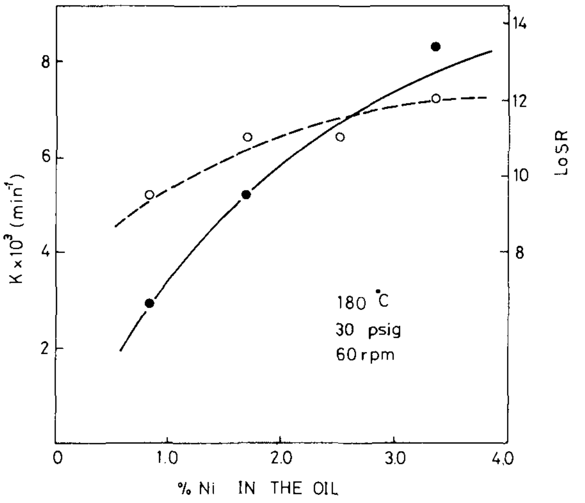

FIG. 6. Effect of nickel concentration in the oil on the overall reaction rate (● —— ●) and the selectivity of linoleic acid (O — — O).

of hydrogen is selectively consumed to hydrogenate the double bonds in linolenic and linoleic acids, due to their higher reactivities than those of oleic acids.

Effect of pressure. Figure 5 shows a similar increase of hydrogenation rate with pressure as in the case of temperature. Since the solubility of hydrogen in oil is proportional to its partial pressure, a positive effect of pressure on the reaction rate was already expected. But retardation of the increase was observed at higher pressure, indicating that the reaction was limited by a relatively small amount of unsaturated fatty acids around the catalysts. This abundance of hydrogen compared with unsaturated oil yields a random attack to double bonds regardless of their reactivities, and the selectivity decreased when hydrogen partial pressure was high.

Effect of nickel concentration. The more nickel available to the oil, the greater the catalytic activity (Fig. 6). The effect was similar to those of increasing temperature both on the reaction rate and on the selectivity ratio. However, variations are restricted to the chemical reaction not including the mass transfer. Hence, selectivity enhancement by increasing nickel to the oil is more direct than that by temperature, but increase in the reaction rate is not assisted by the mass transfer in this case.

Effect of rotating speed. One of the main advantages of RPDR is smooth transfer of hydrogen through the thin liquid film around the catalysts when the disks are exposed to the gas phase. Figure 7a clearly shows this, where an effect of disk rotation is manifested at a lower hydrogen pressure. But such effect diminishes as the hydrogen pressure increases because hydrogen becomes sufficiently available.

Figure 7b shows that the selectivity ratio increases with the rotating speed. This variation is different from that in a slurry reactor, in which the selectivity decreases with stirring due to the facilitation of hydrogen transfer to the catalytic surface. However, in RPDR reactions in the gas headspace are more important because hydrogen supply is easier than in the submerged phase. If the catalysts are exposed to the hydrogen atmosphere for a long time, more saturation will occur and the selectivity will be

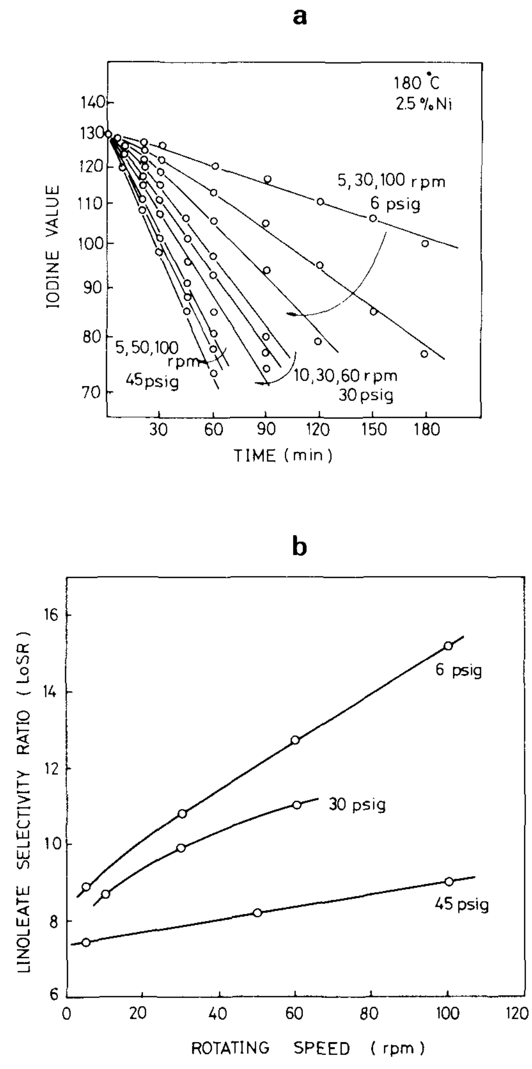

FIG. 7. Effect of rotating speed, a, on the overall reaction rate, and b, on the selectivity of linoleic acid.

TABLE 1

Comparison of Oil Hydrogenation in the Rotating Packed Disk Reactor and the Slurry Reactor

		RPDR	Slurry Reactor
Hydrogenation conditions		180 C, 30 psig 2.5% Ni 60 rpm (disk rotation)	180 C, 15 psig 0.05% Ni 1200 rpm (agitation)
Reaction	K_a	0.0286/min	0.0713/min
Rate	K_b	0.0158/min	0.0843/min
Constants	K_c	0.0015/min	0.0015/min
LoSR		10.5	58.3

reduced. But at a higher speed of rotation, relatively reactive linolenic and linoleic acids become preferentially hydrogenated during the short residence in the gas headspace. All these effects on the selectivity are distinct when the hydrogen pressure is low because disk rotation also enhances liquid mixing as with stirring in the slurry reactor and a large amount of hydrogen is also present in the liquid phase at a higher pressure of hydrogen.

Comparison with the slurry reactor. Typical operating conditions of RPDR and a slurry reactor (13) are compared in Table 1. More nickel catalyst is used in RPDR, but it does not become a weak point as RPDR can be run continuously with almost perfect retainment of catalyst. The rotational speed in RPDR is much lower than the stirring speed in a slurry reactor, which means a more economic operation of RPDR.

A major drawback of RPDR is the low value of the selectivity ratio. This may result from the use of catalyst particles in a captive range instead of fine powders in a slurry reactor. When the hydrogenation is carried out with a large particle, the greater part of reactions occur in micropores inside the particle. Oil molecules remain on the catalytic surface within the pores for a long time; this often is sufficient to become fully saturated. This is considered to be somehow inevitable if the catalyst is intended to be separated and reused easily. But the most promising aspect of applying RPDR to the oil hydrogenation process is that the selectivity ratio can be further raised if operating variables are properly adjusted.

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