

Ultrasonic vs. Nonultrasonic Hydrogenation in a Batch Reactor

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Refined and bleached soybean oil was hydrogenated with and without ultrasonic energy in a batch system. Reactions were carried out at 170°C with 0.02% nickel catalyst (Nysel, Harshaw/Filtron Partnership, Cleveland, OH) or 50 ppm nickel in the oil. Hydrogen pressure was varied from 15 to 90 psig. After 20 min, the average reaction rate was about five times faster in the presence of ultrasonic energy. Hydrogenation rate generally increased with increasing hydrogen pressure when ultrasonic energy was applied. However, the increasing rate is more sinusoidal in nature than linear.

KEY WORDS: Batch system, characteristics of ultrasonic hydrogenation, hydrogenation, increased hydrogenation rate, iodine value, nickel catalyst, soybean oil, *trans* isomers, triene content, ultrasonic energy.

In recent years many applications of ultrasonic energy have been investigated. Of particular interest is the use of high frequency sound waves to catalyze chemical reactions (1-4). The basic cause of the chemical effects of ultrasound is cavitation, resulting in a high degree of agitation with many side effects, such as electrical discharges, ionization and formation of free radicals.

Cavitation is the formation of bubbles in the liquid which can explosively collapse and generate localized pressure as high as hundreds of atmospheres. Shock waves generated at the instant of collapse are reported to be responsible for producing rapid reactions. Electrical discharges sometimes occur in these bubbles, causing ionization and formation of highly reactive free radicals. Diffusion at the boundary between a suspended solid and liquid is substantially accelerated in an ultrasonic field; the turbulent mixing resulting from using ultrasonic energy enhances heat transfer throughout the system. Physical effects of ultrasound include raising the freezing point of liquids, disintegration of materials, emulsification of substances, coagulation of aerosols, cleaning and degreasing of surfaces, and influence on crystallization processes.

Ultrasonic waves can travel through any elastic body (solid, liquid, gas) but the wave type depends on the elastic properties of the medium. Only longitudinal waves can occur in liquids and gases; however, rigid solids also can transmit shear (transverse) and torsional waves. Likewise, the speed of the wave is governed by the physical properties of the medium. The speed of ultrasonic sound in liquid and in gases is in the form of a longitudinal wave. The various types found in solids each have their own speed and are expressed in terms of the elastic constants of the solid material. When ultrasonic waves travel through a liquid and strike a solid, such as the bottom of the reactor, part of the energy passes into the solid, but part is reflected. The amount of reflected energy depends on the distance of the reflecting surface from the ultrasonic source and upon ab-

sorption occurs when part of the energy is transferred into heat, and part may be lost through irreversible chemical reactions. Viscosity and thermal conductivity influence the amount of energy absorbed. Reflected waves can combine with the source wave to form a standing wave. Nodes occur at intervals of $\lambda/2$ in a standing wave, causing a point of no motion. Halfway between nodes are the antinodes, or points of maximum motion. Amplitude at the antinodes is twice that of either traveling wave (1,5).

Moulton and co-workers (2,3) have published two papers on continuous hydrogenation of soybean oil in the presence of ultrasonic energy. They showed that ultrasonic energy greatly enhances the rate of hydrogenation and that a quality product can be produced at potentially lower cost than present methods. Preliminary investigation in our laboratory with a continuous system in a flow-through reactor showed a 30% increase in hydrogenation rate. The present work was done to study the effect of reactor geometry in a batch reactor system at various hydrogen pressures at constant temperature and catalyst concentration, and to obtain critical data to characterize the nature of ultrasonic hydrogenation.

EXPERIMENTAL PROCEDURES

The present work was done with caustic refined and bleached soybean oil from Anderson Clayton Foods (Sherman, TX). Catalyst used was standard Nysel from the Harshaw/Filtron Partnership (Cleveland, OH). Nysel is 25% nickel, 10% support and 65% stearin flakes. The reaction cell was fabricated from 316 stainless steel by G.R. Bradley (DeSoto, TX) (Fig. 1). Metal spacers in the bottom of the cell could be inserted to change the volume within the cell and to vary the distance the ultrasonic waves traveled in the soybean oil.

Ultrasonic energy was provided by a W-375 Sonicator cell disrupter (Heat Systems-Ultrasonics, Inc., Plainview, NY). Power output from the W-375 Sonicator could be varied to a maximum power output of 375 watts at a fixed frequency of 20 KHz. Hydrogen gas was industrial grade (99.5+%), supplied from Liquid Carbonics Corporation (Dallas, TX). A gas cylinder was fitted with a two-stage pressure reducer to control pressure in the reactor.

The reaction cell was submerged in an oil bath. The oil bath was set on a Corning PC-101 magnetic mixer/hot plate (Corning Glassworks, Corning, NY) to furnish oil mixing and heat to the oil bath. Temperature control in the oil bath was provided by a Model AC-503-1 controller (Blue-M Electric Company, Blue Island, IL). A 100-watt immersion heater supplied variable controlled heat. Oil bath medium was IG-2 heat transfer fluid from Multi-therm Corporation (Colwyn, PA). The seal between the ultrasonic horn and the reactor cell (Fig. 1) was a rubber O-ring. This seal was above the oil bath level and cooled with compressed air to preserve the seal.

For comparison, hydrogenation without ultrasonic energy was done in a series 4500 1-L Parr reactor. The reactor has an internal stirrer at 600 rpm and withstands pressures to 1000 psig (68 atm) and temperatures to 350°C. Original equipment was supplied by Parr Instrument Company (Moline, IL, and was modified in our lab

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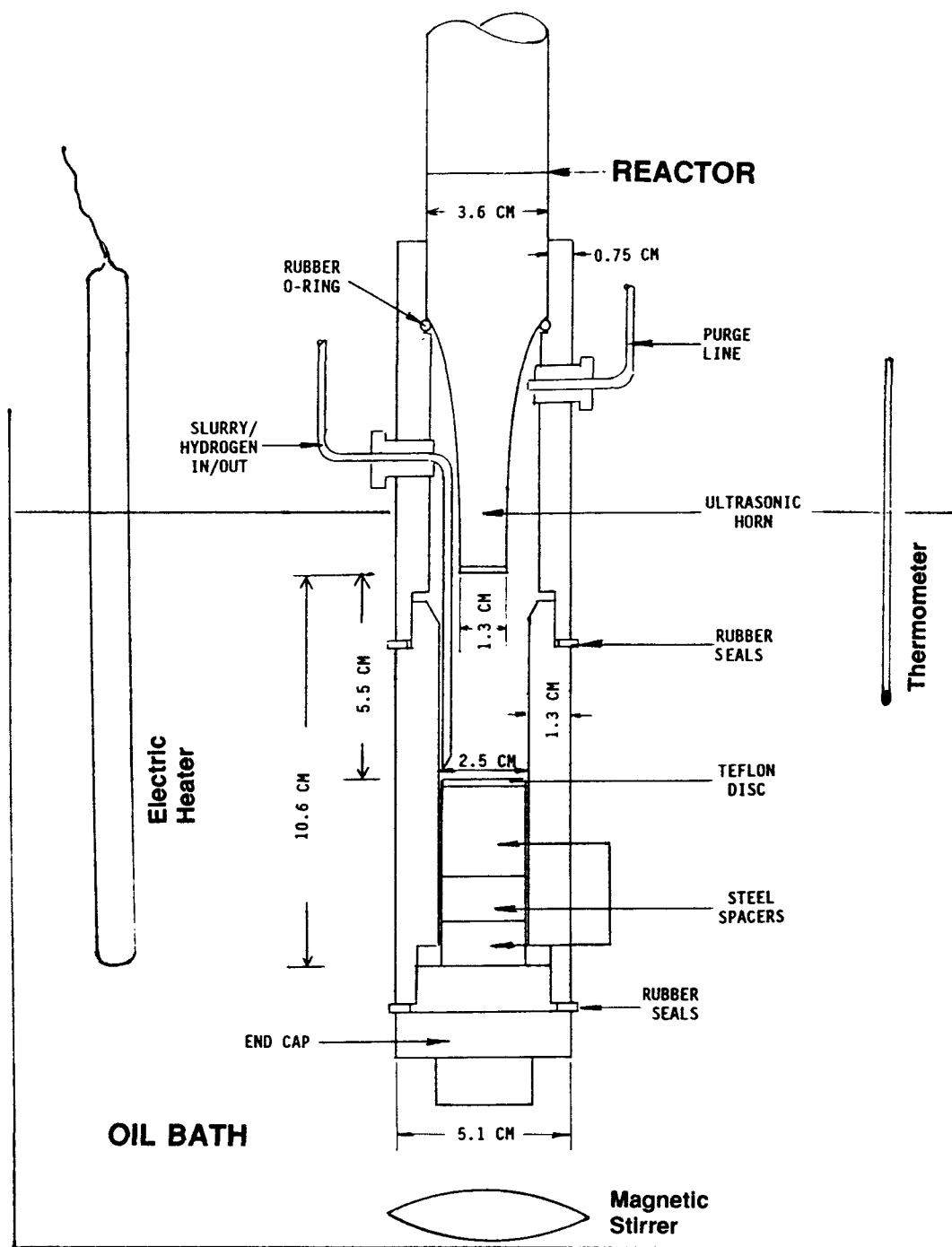


FIG. 1. Reactor (Cell A with steel spacers in place).

to accommodate total oil-bath heat control. Oil-bath temperature was controlled by a Model 149 Love Controller (Love Controls Corporation, Wheeling, IL).

Analyses of the products were carried out according to American Oil Chemists' Society (AOCS) methods (6) Ce 1-62; Cd 14-61; and recommended practice Tz 1b-79.

Two hundred grams of soybean oil was batch-hydrogenated in the Parr reactor (with no ultrasonic energy) to serve as a reference control. Soybean oil was hydrogenated at 170°C with 0.02% Nysel catalyst or 50 ppm

nickel in the oil at both 45 and 90 psig (3 and 6 atm.) hydrogen pressure. Reactions were terminated at 20 min by stopping the agitation and evacuating the hydrogen gas.

Soybean oil was batch-hydrogenated in the ultrasonic reactor with the W-375 Sonicator, a loading meter and a variable power-output control knob. The loading meter can be adjusted from 0 to 100 and indicates percentage of ultrasonic power delivered to the horn. The output control adjusts the amplitude of ultrasonic vibrations emit-

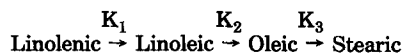
ted. Variations in hydrogen pressure applied to the system, and viscosity of the test medium can cause changes in the loading meter reading. For the first set of experiments, the power control was varied to get a fixed 100% output level on the loading meter.

RESULTS AND DISCUSSION

Initial runs were made with three metal spacers in the bottom of the reactor (Cell A). This cell had a capacity of 65 grams of soybean oil/catalyst slurry with 5.5 cm depth of oil. No additional internal agitation was used. The external temperature bath was controlled at 170°C, and 0.02% Nysel was used. Eleven runs were made at various levels of hydrogen pressure, including the 45 and 90 psig reference points. All reactions were terminated at 20 min.

Cell B, with no spacers in the bottom, held 85 grams with 10.6 cm depth of oil. Oil-bath temperature was controlled at 170°C, and 0.02% Nysel catalyst was used. Twelve runs were made at various levels of hydrogen pressure. All reactions were terminated at 20 min.

Figure 2 is a graph of the change in iodine value (ΔIV) plotted against hydrogen pressure in the presence of ultrasonic energy for Cells A and B. Both curves seem to follow a modified sinusoidal path, and Cell A is particularly distinct. The percent of *trans* isomers generated with Cell A is plotted in Figure 3 and shows a similar modified sinusoidal curve. The hydrogenation reaction follows this simplified model:



where K_1 , K_2 and K_3 are the reaction rate constants. These constants are necessary to determine the selectivity of the reaction and can be calculated from the fatty acid composition of the starting and the ending hydrogenated sample. A plot of the reaction rate constants in the presence of ultrasonic energy is shown in Figure 4.

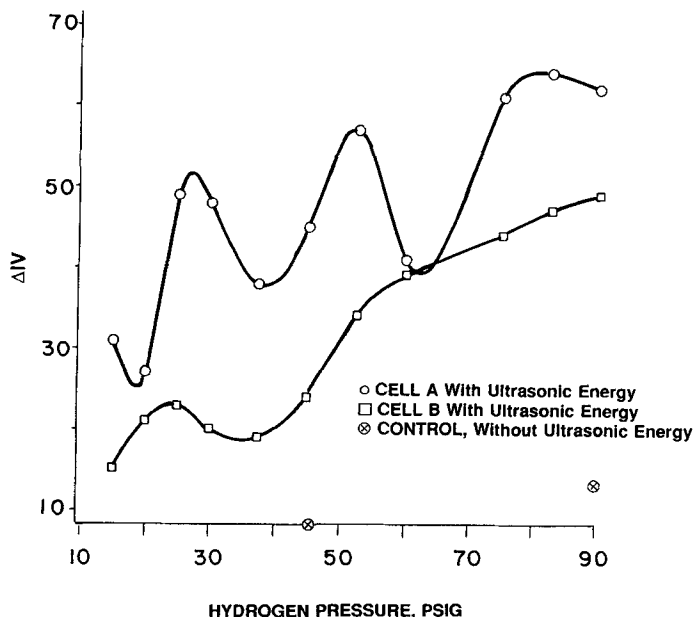


FIG. 2. Change in hydrogenation rate with increase in hydrogen pressure (psig).

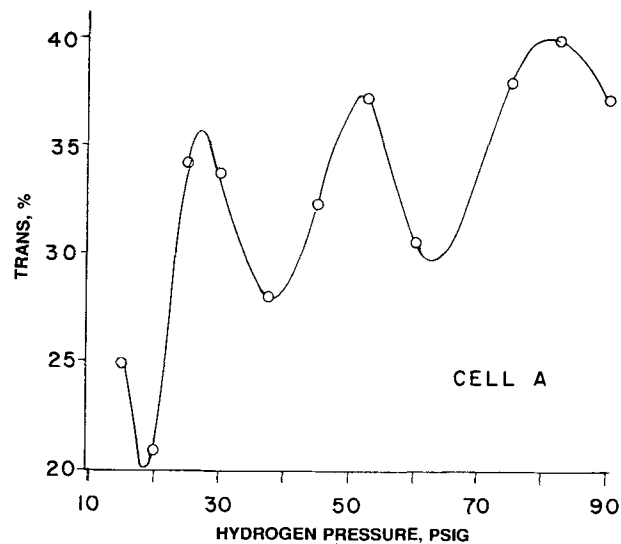


FIG. 3. *trans* Isomer formation with increase in hydrogen pressure (psig).

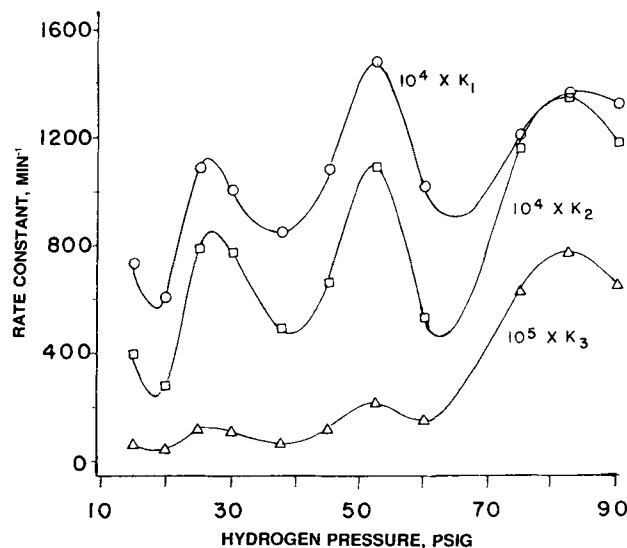


FIG. 4. Change in reaction rate constants with increase in hydrogen pressure (psig).

The sinusoidal effect is evidently the result of the gradual increase in amplitude to get a fixed output level on the loading meter or a constant power input to the reactants of the oil-catalyst-hydrogen mixture. As the hydrogenation pressure was increased the effect of ultrasonic vibrations was subdued and the reaction rate fell off. However, as the amplitude was gradually increased it eventually overcame the pressure effect and the reaction rate again increased. This varying effect became less noticeable as the path of the ultrasonic wave increased (Cell B).

The control sample hydrogenated with 45 psig hydrogen pressure dropped 8 IV units in 20 min. In Cell A, with ultrasonic energy, the drop was 45, and in Cell B, 24 units. The drop in IV was 5.6 and 3 times more for Cell A and Cell B, respectively, than for the control. The control

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TABLE 1

Comparison of Results With and without Ultrasonic Energy

	Original Soybean Oil	45 psig			90 psig		
		Control ^a	Cell A	Cell B	Control ^a	Cell A	Cell B
Fatty acid composition, (%)							
Saturates	15.1	15.8	16.8	15.8	15.8	23.0	18.0
Monoene	24.1	30.9	65.4	44.5	32.4	69.9	66.6
Diene	53.5	48.0	17.0	37.2	46.6	6.6	14.9
Triene	7.3	5.3	0.8	2.5	5.2	0.5	0.5
<i>trans</i> Isomers	3.2	7.5	32.7	19.2	8.4	37.6	33.0
Iodine value	133	125	88	109	120	71	84
ΔIV	—	8	45	24	13	62	49

^aControl experiments were carried out in a Parr reactor.

sample hydrogenated with 90 psig hydrogen pressure dropped 13 IV units in 20 min. In Cell A, with ultrasonic energy, the drop was 62, and in Cell B, 49 units. Again, this difference is 4.6 and 3.8 times faster, respectively. Table 1 shows a comparison of the fatty acid composition of the hydrogenated products between the control and Cell A and Cell B.

In all cases, the rate of *trans* isomer formation was less at high hydrogen pressure, but selectivity was better at lower pressure. Additional experiments are planned to verify this work and to evaluate other hydrogenation variables, including continuous flow through the cells in the presence of ultrasonic energy.

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