JOURNAL OF CATALYSIS 10, 47–51 (1968)

A Precision Hydrogenator*

WILLIAM K. ROHWEDDER

From the Northern Regional Research Laboratory,† Peoria, Illinois 61604

Received June 30, 1967; revised November 14, 1967

A high-speed hydrogenation apparatus has been designed and built to give highly reproducible results. The 12-cc reaction chamber has an enclosed top to prevent sample or catalyst from leaving the stirred region. The stirring paddle, which comes within 0.010 inch of the fluted walls of the reaction chamber, is driven by a motor whose speed is controlled by a tachometer from 100 to 5000 rpm. The pressure of the system is sensed by an electronic micromanometer and controlled by a stainless steel piston. An average deviation of 1.4% was found for the rate of hydrogenation of methyl oleate.

Introduction

Kinetic data for liquid-phase heterogeneous catalytic hydrogenations are difficult to reproduce. The difficulties encountered can be divided into chemical problems, such as catalyst poisons in the liquid and variations in catalyst activity, and into mechanical problems, such as temperature, pressure, stirring speed, and geometry of the reaction chamber. The hydrogenator described was designed and built to minimize as far as possible variation in kinetic rates due to these mechanical problems.

Many hydrogenators have been described in the literature. Albright, Wei, and Woods (*1*) describe a 6-liter hydrogenator with stirring speed up to 1700 rpm. Beal and Lancaster (*2*) studied the effect of agitation in hydrogenation of oil in pilot-plant equipment. Bitner and Dutton (*3*) used a 10-ml glass flask and a magnetic stirrer with gas circulation for radioactive studies. In an extensive paper on the mechanism of the selective hydrogenation of fatty oils, Coenen (*4*) used a glass apparatus capable of handling 30 g of oil and having a stirring speed of 1910 rpm. He gives curves for replicates that indicate good reproducibility. A vibration-stirred microhydrogenator was described by Low, Krishnamurthy, and Inoue (*5*) based on a glass plunger driven at 60 herz for hydrogenation of 0.2–0.5 ml samples. Riesz and Weber (*6*) used a 125-ml flat-bottom flask with indentations and a magnet bar stirrer at 1140 rpm.

Apparatus

A sectional view of the hydrogenator is shown in Fig. 1. The stainless steel reaction chamber (u) was pressed into the reaction chamber heating block (s). The wall of the chamber was fluted by drilling 16 $\frac{}{64}$-inch diameter holes on a 0.920-inch diameter circle before the chamber was bored to the 0.920-inch diameter. The $\frac{1}{8}$-inch thick square paddle (p), containing eight $\frac{11}{64}$-inch holes, mounted on a $\frac{1}{4}$-inch shaft, has a clearance of 0.010 inch with the top, bottom, and wall of the reaction chamber. These close tolerances give the sample and catalyst no place to escape and cause considerable shear while the flutes cause turbulence. The aluminum reaction-chamber heating block provides good thermal conduction between the heating wires, the reaction chamber, and the thermistor temperature sensor located at (t).

A $1\frac{3}{4}$-inch cylinder of aluminum projects

* Presented at the American Oil Chemists' Society Meeting, Cincinnati, Ohio, October 10–13, 1965.

† This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

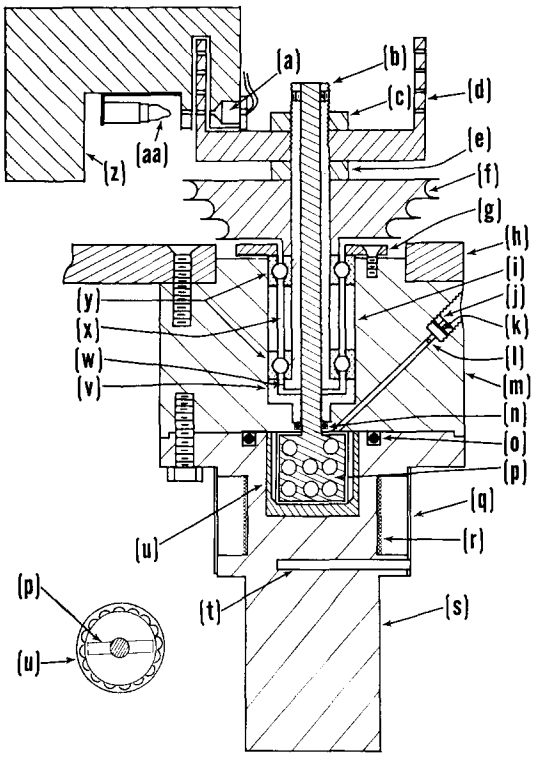

FIG. 1. Sectional view of a precision hydrogenator. (a) Phototransistor; (b) drive shaft; (c) nut; (d) optical tachometer cup; (e) spacer; (f) pulley; (g) bearing retaining plate; (h) mounting bracket; (i) bearing spacer; (j) septum nut; (k) rubber septum; (l) gas inlet tube; (m) base; (n) stirring paddle seal "O" ring; (o) reaction chamber seal "O" ring; (p) stirring paddle; (q) shield; (r) heating wire; (s) reaction-chamber heating block; (t) thermistor well; (u) stainless steel reaction chamber; (v) "O" ring support; (w) drive shaft lip; (x) bearing spacer; (y) ball bearings; (z) lamp-support block; (aa) prefocused lamp.

below the reaction-chamber heating block so that a cooling bath can be raised around it to quench a reaction quickly. The reaction-chamber block is bolted to the stainless steel base (m) of the hydrogenator with eight bolts and sealed with a Viton* "O" ring (o). The top surface of the stainless steel reaction chamber was made slightly higher than the reaction-chamber heating block by finish machining the assembly after the harder stainless chamber was pressed into the softer heating block so that the chamber fits closely to the base with little space between them to trap any part of the sample.

The stirring paddle, mounted on a ¼-inch shaft to make a sliding fit in the drive shaft (b), is fastened by two screws at the top of the drive shaft. The stirring paddle shaft is sealed with an "O" ring (n) (Precision Rubber Products Corporation, No. 6579-1588) especially compounded for high-speed turning shafts. "O" ring groove dimensions are those recommended by Precision Rubber. The reaction chamber used had a volume of approximately 12 cc (10 ½ cc with paddle), but the smooth bottom surface of the base was designed to accept reaction chambers from 2 up to 200 cc. Paddle sizes can also be changed easily without disassembling the hydrogenator.

Liquid samples are injected with a syringe through a rubber septum (k) and a hole drilled through the base to the reaction chamber. The sample hole is drilled off center so that the paddle drives the liquid away from the hole exit. After a reaction, a white pipe cleaner run through the hole comes out clean.

Since the gas inlet is connected at a right angle to the sample channel at (l), the flow of gas tends to push the liquid sample down the channel toward the reaction chamber.

The "O" ring support (v), ball bearings (y), and spacer (i) are held in place by the bearing retaining plate (g). The optical tachometer (d), pulley (f), inside bearing races, and the spacers (x and e) are fastened between a nut (c) and a lip (w) on the bottom of the drive shaft. The motor and two idler pulleys from a Unimat lathe (American Edelstaal, Inc., New York) are mounted to the hydrogenator base with an aluminum mounting bracket (h), which is also used to fasten the hydrogenator to a heavy base. The drive-shaft pulley is connected to the motor pulley and the idlers with one or more rubber "V" belts, which allow many different drive speeds.

Paddle speed is controlled by an optical tachometer that governs the drive motor

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

speed through an electronic circuit (7). The optical tachometer consists of a prefocused lamp (aa) placed so as to shine through the hole in the lamp support block (z) and through the holes in the optical tachometer cup (d) to the phototransistor (a) which measures the speed of rotation of the paddle. Stirring can be set at any speed between 100 and 5000 rpm with an accuracy of ½%.

Temperature of the reaction chamber is controlled within 0.1° with a thermistor-regulated silicon-controlled rectifier circuit (8).

The hydrogenator is connected to the rest of the apparatus, as shown in Figs. 2 and 3, with ¼-inch OD stainless steel tubing and Swagelok fittings. Pressure of the system is measured on a 6-inch dial, Wallace and Tiernan FA-160 absolute pressure indicator (Fig. 2, a) with a range of 0–800 torr and an accuracy of 0.33% of full scale. Pressure in the main system is compared with that in the reference chamber by a micromanometer (Pace Engineering Company, Model CP 51 DS ± 0.75 PSID) and the difference signal is fed to a Brown Servoamplifier which powers the piston-cylinder volume control (e) (9). A diaphragm valve (c) (Hoke, Model 411) with one leg plugged

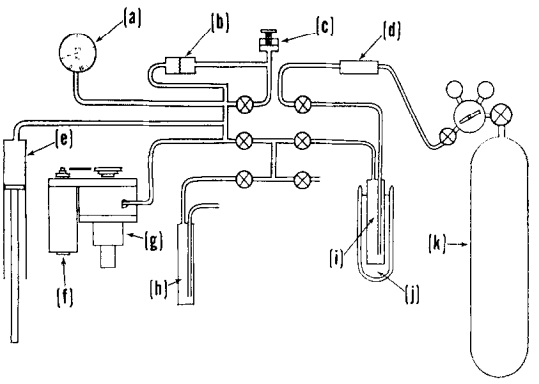

FIG. 2. Schematic of the hydrogenation apparatus. (a) Diaphragm manometer; (b) electronic micromanometer; (c) Hoke diaphragm valve; (d) Deoxo unit; (e) piston volume controller; (f) stirring motor; (g) hydrogenator; (h) molecular-sieve vacuum trap; (i) charcoal trap; (j) dry ice-acetone bath; (k) hydrogen tank.

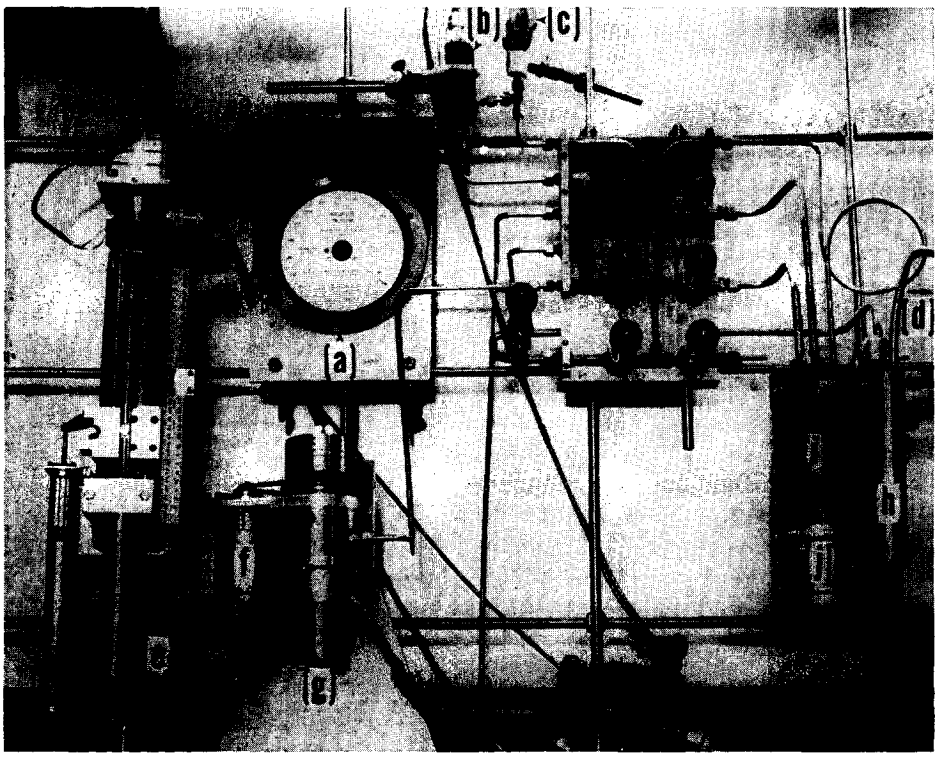

FIG. 3. Complete hydrogenation apparatus (identification same as Fig. 2).

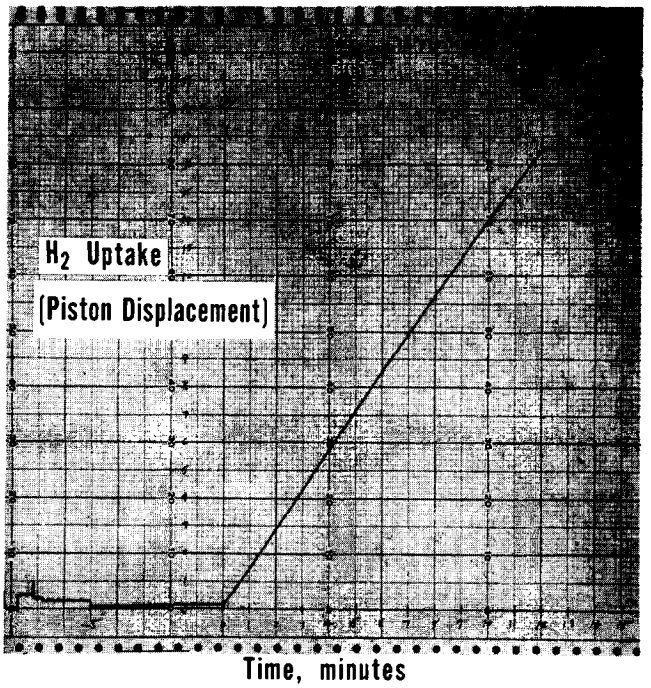

FIG. 4. Strip chart of typical hydrogenation reaction for methyl oleate.

is connected to the reference line. Turning the valve knob moves the diaphragm in or out, changing the reference volume and pressure and thus the system pressure. A Deoxo unit (d) and a Dry Ice(j)-cooled charcoal trap (i) are used to purify hydrogen from a tank (k).

OPERATION

After weighed catalyst was put in the reaction chamber, it was evacuated to better than 1 torr, and its temperature controller set for the desired level. After 15 min, hydrogen was admitted to 760 torr, the valve to the reference volume closed, and the pressure controller turned on to maintain this pressure. After another 15 min, the sample to be hydrogenated was injected into the reaction chamber through the rubber septum. Five minutes after injection the stirrer is turned on and set for the desired rpm. With unsaturated fatty esters very little reaction takes place until the stirrer is turned on. The gas pressure controller and its strip-chart recorder automatically record the hydrogen uptake and plot volume change at constant pressure against time. Five minutes after the reaction ceases the stirrer and temperature regulators are turned off, hydrogen is pumped off, the system is vented, and the reaction chamber is washed with high-purity petroleum ether.

TABLE 1
HYDROGENATOR REPRODUCIBILITY

Run No.	Hydrogen absorbed (STP volume/ sample wt.)	Hydrogenation rate (ml H_2/min g cat.)
1	74.12	238.2
2	74.31	243.2
3	74.48	250.1
4	74.53	242.8
5	74.46	245.2
6	74.79	250.4
7	74.19	244.3
8	74.10	238.1
9	74.82	248.4
Average	74.42	244.5
Average deviation	0.3%	1.43%

Performance

Reproducibility of the rate of hydrogen uptake for nine runs made over a period of several days was 1.4% as shown in Table 1. The procedure described above was used with 0.25 mg of 5% platinum-on-carbon catalyst, (Englehard Industries), 1 g of methyl oleate (Hormel Institute), and hydrogen at 760 torr, 50°C, and 2000 rpm. The plot of hydrogen uptake versus time of a typical run is given in Fig. 4.

More than 150 hydrogenations have been performed with the apparatus. This equipment is very convenient, is easy to use, and requires no supervision during a run.

Acknowledgment

Appreciation is expressed to A. E. Stauf for machining the apparatus.

References

1. Albright, L. F., Wei, C., and Woods, J. M., *J. Am. Oil Chemists' Soc.* **37**, 315 (1960).
2. Beal, R. E., and Lancaster, E. B., *J. Am. Oil Chemists' Soc.* **12**, 619 (1954).
3. Bitner, E. D., and Dutton, H. J., *J. Am. Oil Chemists' Soc.* **41**, 720 (1964).
4. Coenen, J. W. E., "The Mechanism of Heterogeneous Catalysis" (J. H. DeBoer, ed.), p. 126. Elsevier, New York, 1960.
5. Low, M. J. D., Krishnamurthy, R., and Inoue, H., *J. Am. Oil Chemists' Soc.* **41**, 433 (1964).
6. Riesz, C. H., and Weber, H. S., *J. Am. Oil Chemists' Soc.* **41**, 380 (1964).
7. Rohwedder, W. K., *Rev. Sci. Instr.* **38**, 701 (1967).
8. Scott, W. D., *Electron World* **72** (No. 5), 46 (1964).
9. Rohwedder, W. K., *Rev. Sci. Instr.* **37**, 1734 (1966).