Small-Plant-Scale Liquid-Phase Hydrogenation under High Pressure

Hydrogenation of Furfural

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HIS paper describes a small plant for the hydrogenation of furfural to furfuryl alcohol. The process uses a method described by Adkins and Connor (1), employing liquid-phase hydrogenation under high pressure in the presence of a copper chromite catalyst. In this relatively new field little information is avail-

able in the literature on the factors governing successful operation on a manufacturing scale. The experiences acquired in this particular instance are reported here in the hope that they may be of some value to those interested in similar problems.

Laboratory experiments readily confirmed the report of Adkins and Connor but made it also apparent that the process could not be transferred to plant scale without certain modifications. Three main difficulties became apparent at once: (a) The decomposition of the complex copper chromate is exothermic and self-sustaining, yet the temperature must be kept below certain limits; otherwise the product formed shows only very slight, if any, activity. This can be done fairly readily on small batches in the laboratory, but the suggested procedure must be considerably modified if it is desired to produce regularly several kilograms a day of catalyst of a uniformly high activity. (b) The hydrogenation reaction is also exothermic, and both furfural and furfuryl alcohol are somewhat sensitive to high temperature, tending to polymerize. To obtain a product of high purity, it is necessary, therefore, to employ a catalyst of sufficient activity to induce a high rate of reaction at a moderate temperature, and to remove the heat of reaction rapidly enough to prevent a substantial rise in temperature during the hydrogenation. (c) Efficiency of stirring is an important factor in liquid-gas reactions, but the method of stirring used in the laboratory (rocking autoclave) was not very adaptable to plant-scale operation, and no data were available on the relative efficiencies of different methods of stirring. Other minor problems arose as the development work progressed, and various solutions were tried until a process was finally evolved which appeared satisfactory. This final process will be described here, only passing reference being made, when relevant, to procedures which were tried and later discarded. While the plant operated smoothly and economically, the authors have no doubt that further experimentation might result in further improvements and greater economy.

As explained below, the process proved to be even more attractive than was indicated by Adkins and Connor. Under the proper conditions a catalyst was prepared which would hydrogenate furfural in less than 30 minutes instead of 2 hours, as reported by these investigators. Another advantage is that the product obtained is of high purity, being light in color and remarkably free from tetrahydrofurfuryl alcohol, methyl furane, and pentanediols, which are usually present when a nickel catalyst is used.

Furfuryl alcohol of high purity has been prepared in a small-scale plant by hydrogenation of furfural around 175° C. under 50 to 100 atmospheres pressure in the presence of a copper chromite catalyst. A detailed description is given of the delicate preparation of a highly and uniformly active catalyst, as well as of the design and operation of the hydrogenation plant. It must be remembered that practically no experience was obtained with the hydrogenation of any substance other than furfural. Some of the details of operation were no doubt made necessary by the characteristics of the two materials involved furfural and furfuryl alcohol. It seems likely, however, that in the main (and particularly in

what relates to the preparation of the catalyst and the type of autoclave used) the experience reported here is substantially directly applicable to any similar hydrogenation process.

PREPARATION OF CATALYST

BASIC COPPER AMMONIUM CHROMATE. As indicated by the amounts of materials reacting, by the yield, and by the analysis of the product, the copper chromate intermediate is precipitated in accordance with the equation:

$$\frac{2CuSO_4 + Na_2Cr_2O_7 + 4NH_3 + 3H_2O}{2Cu(OH)NH_4CrO_4 + Na_2SO_4 + (NH_4)_2SO_4}$$

In a 400-liter earthenware crock fitted with a monel stirrer, 250 gram moles of powdered commercial $CuSO_4 \cdot 5H_2O$ and 125 gram moles of commercial $Na_2Cr_2O_7 \cdot 2H_2O$ are dissolved in 300 liters of water. To this solution are then added slowly, approximately 500 gram moles of ammonia in the form of the commercial concentrated aqueous solution. The exact end point is reached when the addition of a few drops of ammonia solution to a filtered or decanted sample of the solution no longer gives any precipitate. (An excess of ammonia causes the solution to turn deep blue and results in a lower yield of precipitate.) The slurry is filtered through a filter press, and the cake is washed until the wash water is practically colorless. The cake is then dried by blowing with air, removed and dried in an air oven at 110° C. The yield is nearly theoretical, the product analyzing close to $Cu(OH)NH_4CrO_4$.

This material is fed in the form of friable lumps to a powder mixer in which it is mixed with enough water (about 10 per cent) to give a powder moist enough to cohere when squeezed in the hand without, however, becoming sticky. This is then fed to a granulator fitted with 12-mesh screen (about 5 mesh per cm.), and the granulated material is again dried in the oven. The final product contains about 80 per cent of granules and 20 per cent of fines. Material of this type is handled satisfactorily by the roaster described below, but, when the product contains enough fines to interfere with the operation of the roaster, these fines are sifted out and fed back to the powder mixer.

COPPER CHROMITE. As stated in the introduction, the decomposition of the complex chromate is induced by heat but is exothermic and self-sustaining. Assuming the formula given above to be correct, the reaction can be written:

$$2Cu(OH)NH_4CrO_4 \longrightarrow Cr_2O_2 \cdot 2CuO + N_2 + 5H_2O$$

The problem is, then, to raise the material to a temperature sufficient for the reaction to start and to keep it there while removing the heat as fast as it is evolved. The type of equipment finally adopted was a continuous rotary tube furnace, heated electrically, in which the chromate is fed from a hopper by means of a screw feed. This furnace is illustrated in Figure 1.

The granulated chromate in hopper A is fed by means of the screw feed, B, into roasting tube C. This is a copper tube 7.5 cm. in diameter and 1 meter long, fitted by means of bushings into the two stationary end assemblies. The tube is supported by two ball bearings, D, and is rotated at about 15 r. p. m. by means of the sprocket wheel, E, and a motor and reducing gear (not shown). The tube is heated by means of a resistance wire, F, wound around it on a thin coating of alundum cement, in two circuits with terminals at G, H, and I, connected to posts J, K, and L, to which the current is supplied by means of the rotating disk collector, M. Both circuits are controlled independently by means of suitable rheostats. In the first half of the tube the heating wire remains uncovered while the second half is lagged with as bestos tape T. The bearings are protected from heat radiation from the winding by the baffle plates, N. Short stem thermometers, O, of range 200° to 400° C. are inserted through seven holes along the tube in such manner that the bulbs come in contact with the granules passing through the tube. A strip of 12-mesh copper screen (5 mesh per cm.), about 1 meter long and 7.5 cm. wide, is held inside the tube by friction. This screen acts as a scoop and picks up and mixes the granules at each revolution of the tube. The progress of the granules through the tube is facilitated by the tilt of the tube. The roasted catalyst is discharged into header P and is received into a suitable container at Q. The back of the header remains open at R for inspection and sampling, and a hand-type vacuum cleaner is connected at S, drawing air through R and creating a slight suction inside the tube. This is essential to keep dust from seeping out

through the joints and also to prevent the water formed in the reaction from condensing in the cold feed and causing it to cake and clog the tube.

The heat on the two coils is so controlled that the middle thermometer reads between 320° and 340° C. With the proper adjustment of heat and lagging, the temperature along the tube rises rapidly to

 200° C. in the first 20 cm., then to $320-340^{\circ}$ in the middle, and decreases slowly to $250-220^{\circ}$ at the discharge end of the tube. Under normal operation a tube of this type will produce about 2 kg. per hour of roasted material. The product obtained is homogeneous in composition and uniform in quality as long as the temperature is controlled carefully. It has the appearance of black granules, somewhat velvety or lustrous like soot, and with a faint brownish cast. Underroasted material is decidedly brown, while overroasted granules are grayish or dull black with chrome-green specks.

The granulated material is pulverized by passing through an impact mill. The powdered catalyst is ready for use or may be stored in closed containers for several days without loss in activity. [Washing with acetic acid was found to remove some of the copper oxide without causing an increase in the activity of the material. Also, on sifting, 80 per cent of the product passed a 200-mesh screen (80 mesh per cm.), and the unsifted material was just as active as the portion which passed the screen.]

Hydrogenation

EQUIPMENT. The autoclave (Figure 2) was built by the Blaw-Knox Company of Pittsburgh. It follows the general design of a first and smaller unit, the later model embodying several improvements which suggested themselves from the experience obtained with the earlier one. This autoclave, of the vertical cylindrical type, comprises a forged steel shell, A, with bolted lid, B, and equipped with a vertical shaft, C, fitted with two turbine-type mixers comprising rotors D and G and stators E and F. The cover of the autoclave is made tight by means of a gasket of monel metal confined in a narrow groove. The autoclave is designed for normal operation at 100 atmospheres and is operated up to 120 atmospheres. The stuffing box is equipped with Garlock Chevron metal packing and is water-cooled. A 1 horsepower motor and reducing gear assembly (not shown) operates the stirrer at 325 r. p. m.

The autoclave body is approximately 40 cm. in diameter and 80 cm. deep, with a total capacity of 100 liters and a working capacity of 80 liters. The level of the top turbine is adjustable and is placed about 3 to 5 cm. below the liquid level. This creates a vortex which sucks hydrogen into the liquid and causes very efficient mixing. The cover of the autoclave is fitted with several openings: a gas outlet and a connection for the pressure gage (not shown), a liquid inlet, H, and a thermocouple tube, J. This latter is welded into the cover but is open and threaded at its bottom and is fitted with a cap. The thermocouple, similar to the one described by Dykstra and Calingaert (2), is immersed directly in the charge, thus avoiding any lag in reading the true temperature of the liquid. The hydrogen inlet, K, and the



FIGURE 1. CATALYST ROASTING TUBE

discharge opening, L, are at the bottom of the autoclave. All gas connections are fitted with Vogt high-pressure needle valves, and both liquid inlet and outlet with high-pressure Nordstrom Merco lubricated valves. In spite of the fact that the liquids handled always contained suspended solid matter, no difficulty was ever encountered in making the valves close tightly.

The autoclave is surrounded by a heating and cooling jacket, M, tested at 10 atmospheres hydrostatic pressure. The jacket contains a spiral baffle, N, welded onto the shell but without making a tight joint with the outer shell. The purpose of this baffle is to increase the efficiency of cooling by causing the cooling water to circulate at a high velocity in the spiral space. Suitable connections to the jacket permit

heating by means of steam at 7 atmospheres (175° C.) or cooling with water.



FIGURE 2. HYDROGENATION AUTOCLAVE

The auxiliary equipment comprises a hydrogen manifold with two banks, each capable of handling eight cylinders, and a preheating and feeding tank located above the autoclave. This latter is equipped with a high-speed stirrer, an immersion electric heater, and a thermocouple. While one charge was being hydrogenated, the next one was preheated to about 100° C. and was mixed with the catalyst just before charging.

MATERIALS. The furfural used was the "refined" commercial grade regularly supplied by the Quaker Oats Company. Later it was found that, if a material practically free from furoic acid is used, the result is a slightly higher rate of hydrogenation and a product which is only slightly colored. The hydrogen was electrolytic hydrogen received in standard 192-cubic-foot (5500-liter) cylinders, under 2000 pounds per square inch (137 atmospheres) pressure. The batch process used made it necessary to vent the residual hydrogen after each run so that there was no danger of accumulating oxygen if a trace of it should happen to be present in the hydrogen as received.

About 20 grams of dry slaked lime per liter of furfural were also added. F. N. Peters of the Quaker Oats Company recommended the use of magnesia to reduce acidity (3), but runs in the authors' laboratory showed the superiority of lime for that purpose. In the absence of a neutralizing agent, the rate of hydrogenation is decreased and the product is dark in color, probably because of a partial polymerization of the furfuryl alcohol.

PROCEDURE. The stirrer is started, and a charge of 80 liters of refined furfural containing 40 grams per liter of catalyst and 20 grams per liter of dry slaked lime, usually preheated to 100° C., is charged into the autoclave. The free space is flushed two or three times with hydrogen at 3 atmospheres, and the pressure is then raised to 100-120 atmospheres. Steam at 10 atmospheres is admitted into the jacket, and, when the temperature of the charge reaches 140° to 150° C., hydrogen absorption begins as evidenced by a drop in pressure. The steam is then shut off and the autoclave is maintained close to the specified operating temperature by regulating the hydrogen input and the cooling water. In 2 or 3 minutes the rate of reaction reaches a fairly constant figure, which maintains itself until the hydrogen absorbed corresponds to about 95 per cent of that calculated for the reaction. The rate then drops sharply, and the absorption stops, practically completed, with an accompanying drop in temperature, when 100 to 103 per cent of the theoretical hydrogen has been used.

The choice of a proper operating temperature is a matter of importance in this process. As mentioned before, both furfural and furfuryl alcohol are sensitive to heat, and time is an important factor in determining the maximum allowable temperature. Using a given amount of catalyst of a given activity, it was found advantageous to raise the temperature in order to decrease the time of reaction. Thus a better product (lighter in color and lower in gum) is obtained if hydrogenation is completed in 10 to 12 minutes at 180° to 190° C. than if it takes 30 to 40 minutes at 150° to 160° C. Operating around 175°, the time elapsed between the first drop in pressure and the temperature drop, which indicates completion of the reaction, varies from 11 to 30 minutes, depending on the purity of the furfural and on the activity of the catalyst, and averages usually around 18 to 22 minutes. During the run the hydrogen pressure used is lowered from an initial pressure of 100 atmospheres to a final pressure of 50 atmospheres at which the cylinders are returned to the supplier for refilling.

After hydrogenation, the charge is cooled down to 100° C., the hydrogen is vented off, and the furfuryl alcohol is discharged into a storage tank equipped with a stirrer and a cooling coil. This alcohol is filtered as soon as convenient through a closed-delivery filter press, using filter paper and Sil-O-Cel filter aid. A small Nitralloy pump, manufactured by the Northern Pump Company, was found very effective in handling this abrasive mixture. The filtered product is colored from light yellow to light brown and is practically free from furfural, furoic acid, tetrahydrofurfuryl alcohol, and gum.

The plant described above (including two catalyst roasting furnaces) was in operation for several months and functioned steadily without breakdowns, leaks, or major difficulties, turning out, whenever required, as many as eight to ten batches (a total of 800 to 1000 kg.) of hydrogenated product per 7-hour day.

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