An Improved Experimental Reactor for Applied Kinetic Studies

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A recirculation type of reactor has been designed and tested on a rapid reaction which characteristically causes difficult temperature-control problems and high diffusional resistances (hydrogenation of propylene on nickel catalyst). Descriptions of the reactor and its operation are given, together with an assessment of errors and the advantages and disadvantages of the recirculation technique. A rate equation and rate constants are determined so that the data will be more readily comparable with the work of other investigators.

Chemical-reactor design must be based on four processes—chemical reaction kinetics and the transfer of mass, heat, and momentum. For practical purposes idealized models for a given system may be selected and the approximate effects of these four processes determined simultaneously. The advent of the digital computer has made such calculations feasible.

At the present stage of development the effects of these four processes on the ultimate rate of production must often be determined experimentally. It is of primary importance, however, that these effects be studied independently, to minimize or eliminate the dependence of the data on the type and size of bench-scale or pilot plant equipment. Too often data which are assumed to represent the kinetics of a reaction have been obtained with an experimental reactor in which temperature and diffusional gradients are large. Correction by computational methods leads to data of doubtful value. The preferred procedure is to eliminate such gradients experimentally with a reactor designed for independent study of each variable. A recirculation type of reactor has been designed to meet the criteria for experimentation and has been successfully applied in the study of the kinetics of a typical rapid reaction, the catalytic hydrogenation of propylene.

RECIRCULATION TYPE OF REACTOR FOR EXPERIMENTATION

A recirculation type of differential reactor reduces some of the experimental difficulties usually encountered in determining precise reaction-rate data. This type of reactor has been mentioned by Hougen (*4*), but little work has been published describing successful applications. The outstanding feature of such a system is the recirculation of most of the reactor effluent stream, a small feed stream being continuously added and a small net-product stream continuously removed. A sketch of this arrangement is included in Figure 1.

Advantages

Perhaps the greatest advantage of this reactor is its ability to control catalyst temperatures more accurately. Recirculation rates ten to fifteen times larger than fresh feed rates, for instance, would give an adiabatic temperature rise of approximately one tenth to one fifteenth of that which would occur in an ordinary adiabatic differential reactor operating with the same over-all conversion. Hence, combining recirculation and good heat transfer to or from the catalyst bed usually provides excellent control of temperatures.

High recirculation rates also permit high gas velocities past the catalyst particles without the use of excessive

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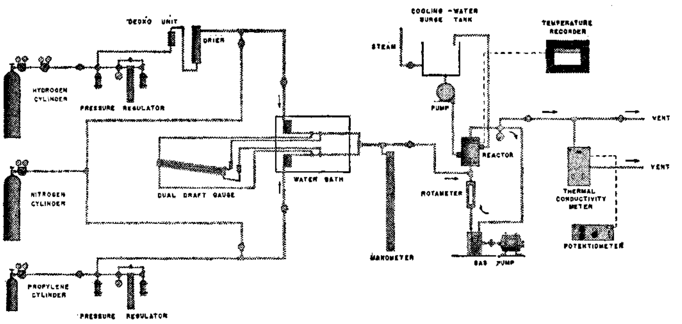

Fig. 1. Flow diagram of the experimental system.

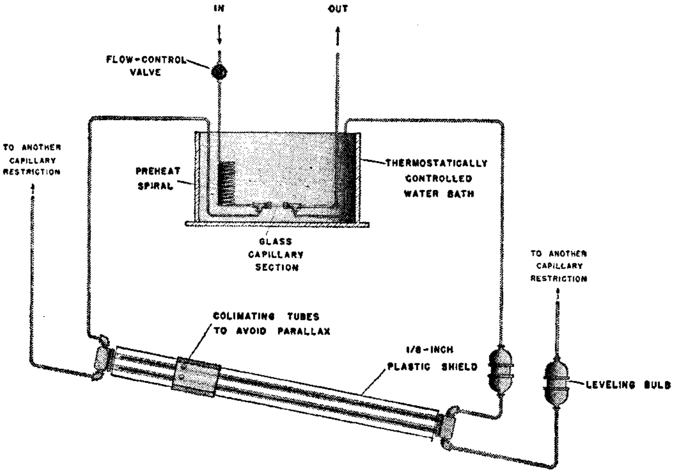

Fig. 2. Sketch of capillary flow meters.

quantities of reactants. Theoretically mass transfer could be reduced until, even for reactions occurring at a very rapid rate, the rate of mass transfer would no longer influence the over-all rate of reaction. Possibly recirculation can provide an effective experimental means of showing when mass transfer effects are absent. On the assumption that the over-all rate of reaction is being limited at low recirculation rates by the rate of mass transfer, then, as the recirculation rate is increased, the total conversion increases and approaches an asymptotic value. If there is an experimental means of varying the recirculation rate, it is necessary to show only that experimental conditions are such that a change in recirculation rate has no effect on the conversion. This method would circumvent the necessity of knowing exact activity levels of several different catalyst charges as is required when mass transfer effects are determined by the usual method (*5*) of varying catalyst weight at constant values of W/F (reciprocal space velocity).

High recirculation rates and the associated low conversions per pass also give more uniform compositions throughout the reactor. All this can be accomplished without limiting the total conversion to very low values, which would introduce errors through analysis.

Disadvantages

Although such an experimental arrangement presents these very definite advantages, there are also some disadvantages. Not every reaction can be studied in this way; in some cases various side reactions may be promoted, owing to the admixture of products to the fresh feed. Another possible difficulty is the length of time required for the recirculating portion of the system to reach steady state operation. This time can be reduced by increasing the recirculation rate and decreasing the volume of the recirculation system.

Experimental pressure drops across the reactor may be higher than those usually observed in ordinary differential beds. It is necessary to a compromise between high-pressure drop across the bed and high gas velocity past the catalyst. These can be varied independently of the total recirculation rate by varying the free area for gas flow.

Owing to the transient period after the change of any expermental variable, one must have a continuous method of analysis when using this type of reactor.

For the most part these disadvantages can be overcome by careful design of the experimental equipment. It may be concluded that a carefully designed recirculation differential-reactor system will permit precise control of experimental conditions within the catalyst bed.

EXPERIMENTAL INVESTIGATION

To investigate the merits of this type of experimental arrangement, a recirculation differential reactor system was constructed and operated to obtain reaction-rate data for the hydrogenation of propylene. Many studies (*3*, *7*, *10*) have shown that the hydrogenations of light olefins proceed in a straightforward manner, which simplifies study and analysis by the accepted kinetic theories.

Equipment was designed so that recirculation rates ten to fifteen times larger than the fresh feed rates might be attained. A brief résumé of operating characteristics follows:

1. A maximum temperature rise of 6°F. was observed. Closer control undoubtedly could have been attained by spacing the catalyst in such a manner as to give more heat transfer area between each particle.
2. Gas velocities past the catalyst particles of approximately 200 ft./sec. were achieved. Calculations and comparison with other data from these laboratories in which feed rate was varied independently of W/F show that the effects of mass transfer were negligible. Recirculation rates were not varied but were held at the maximum possible values.
3. The change in the percentage of hydrogen across the reactor was in each case less than 0.1%.
4. There was only one primary reaction, and difficulties with side reactions were not encountered.
5. Analyses of hydrogen-propylene mixtures were made by continuously measuring thermal conductivities. Conversions were calculated from the changes in percentage of hydrogen.
6. The time required for the recirculation system to reach a steady state could not be detected because it was less than the time required for the thermal conductivity meter to reach a constant reading.

EXPERIMENTAL EQUIPMENT AND MATERIALS

Feed System

Calculations of conversions from changes in percentage of hydrogen require inordinate accuracy in the gas-stream analyses. Furthermore it was necessary that compositions of the feed stream be held constant for some time. Consequently an unusually stable feed system and an accurate analytical technique were developed in addition to the reactor itself. Figure 1 shows a flow diagram of the complete system.

High-pressure hydrogen from a cylinder passed through two pressure-regulating valves, in series, where the pressure was dropped to approximately 30 lb./sq. in. gauge. It then passed through one chamber of a pressure-balancing device to control upstream pressures accurately and then through a Deoxo unit and a bed of activated alumina to remove trace quantities of oxygen and water. The hydrogen finally passed through a flow-control valve and through a glass capillary tube. The capillary-tube and draft-gauge arrangement is shown in Figure 2. After metering, the hydrogen stream was mixed with propylene from the olefin feed stream. Liquefied propylene from a 1-gal. cylinder was vaporized and passed through a similar pressure control and capillary measuring system.

The two gases entered a common back-pressure control valve where the absolute pressure on both capillary tubes was adjusted to 1,140 mm. Hg ± 0.3 mm. The combined feed stream was then fed into the recycle stream of the reactor system. A product stream was removed from the reactor and passed through the reactor-pressure control valve. The product stream was then split, a portion of it being sent to the thermal-conductivity meter for analysis and the remainder vented to the atmosphere.

Water to absorb the heat of reaction was circulated through the reactor jacket by means of a centrifugal pump. The water was maintained at the proper operating temperature by bleeding low-pressure stream into the water surge tank.

Calculations showed that for precise control of the flow rate it was necessary that the pressure upstream from the flow-control valves be held constant to within ±0.2 in. of water. A system was designed which allowed the balancing of the flowing-stream pressure against a static pressure. The equipment consisted essentially of two chambers connected by a light-oil-filled manometer with a by-pass line between the two chambers. When the system was brought on stream, the by-pass line was at first opened, and the control valve was adjusted until the gas was flowing at the desired rate and the indicated pressure on both chambers was approximately 20-lb./sq. in. gauge. When all pressures had reached constant values, the by-pass valve was closed. Any slight change in the pressure of the flowing stream was indicated rapidly by the manometer, and manual adjustment was made by the control needle valve. It was found possible to control the flowing stream pressure to within ±0.2 in. of oil (±0.17 in. of water), which was within limits that could be tolerated without a detectable change in flow rates.

Flow rates of the two reactants were determined by measuring the pressure drop across a section of 6-mm. by 1-mm. glass capillary tubing. The gas to be metered first flowed through a stainless steel needle valve, then through a preheat spiral, and finally through the capillary restriction. The capillary section and preheat spiral were immersed in a constant-temperature bath regulated to 110° ± 0.45°F.

Pressure drops across the restrictions were measured with 37-in.-long draft gauges made from heavy-wall glass tubing.

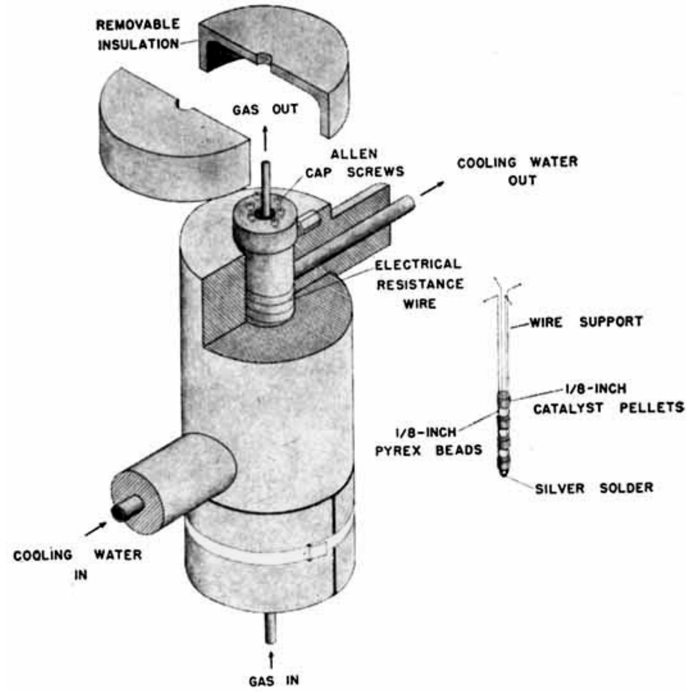

Fig. 4. The assembled reactor.

The Reactor

The reactor, Figures 3 and 4, consists of four separate tubes which can be used either individually or in parallel. For all runs reported in this work catalyst pellets were placed in only one of the tubes, and the other three were blocked with stainless steel plugs. The tubes were attached to a *floating head* at the bottom to prevent excessive stress when the reactor was raised to a high temperature during reduction of the catalyst. The outside of the water jacket was wrapped with electrical resistance wire for heating of the reactor during the reduction period. The complete reactor was surrounded with 2-in.-thick magnesia insulation.

A gas recirculation pump with a capacity of 1 to 3 cu. ft./min. was required. It was imperative that there was no leakage of the hydrogen-propylene mixture, and a low holdup of gas was desired in order that the system might reach equilibrium rapidly.

After an extensive survey of commercially available equipment and special research equipment had not uncovered a pump meeting the desired requirements, a four-cylinder diaphragm-type pump was constructed (Figure 5). Diaphragms were made from 1/32-in. fabric-reinforced neoprene. No appreciable leakage was detected, and after many hours of operation little or no wear of the diaphragms could be observed. The pump was powered by a 2-hp., 220-volt, 3-phase induction motor, with a rated operating speed of 1,730 rev./min. Two of the cylinders were exhausting at all times during operation, and the rotameter indicated no pulsation of the gas stream. Holdup in the pump was very small, as was the clearance volume, and the pump operated efficiently. Lines before and after the pump were jacketed so that the gas might be cooled with water.

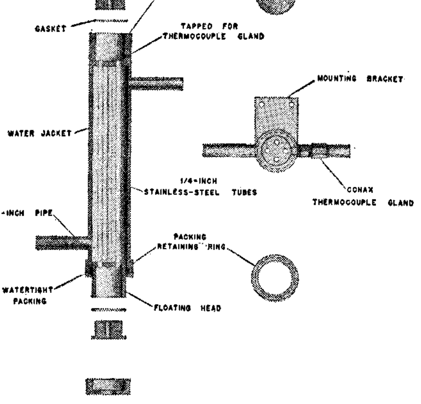

Fig. 3. The experimental reactor.

Thermal Conductivity Meter

A Leeds and Northrup model 7802-D-A9 thermal-conductivity meter with a reference cell filled with 70% hydrogen and 30% nitrogen was used for analysis. The following modifications were made to attain the desired accuracy. The heater circuit for the constant-temperature cabinet was separated from the electrical circuit for the measuring

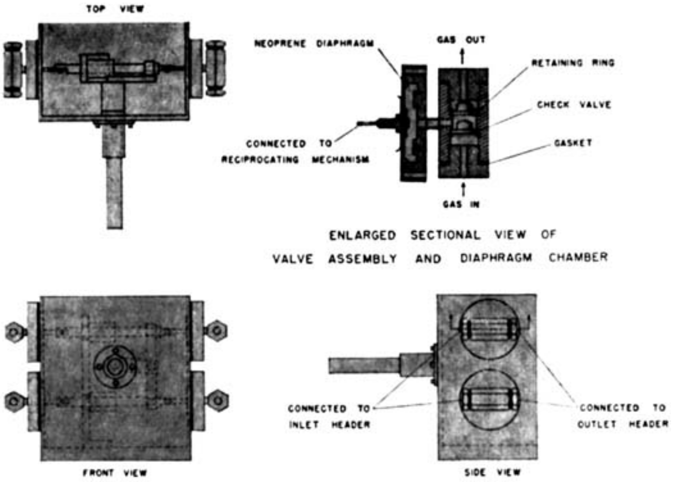

Fig. 5. The recirculation pump.

bridge. The bridge circuit was preceded by an auxiliary constant-voltage transformer. A shunt (a 50-ohm and a 10,000-ohm manganin resistor in series) was placed across the output of the selenium rectifier in order that the exact voltage to the bridge might be measured during runs. A powerstat in series with this circuit allowed precise control of the bridge voltage to an arbitrarily selected value.

The thermal-conductivity meter was calibrated by use of known compositions metered with the flow meters. The unbalance of the thermal-conductivity meter bridge is a unique function of the gas composition. As suggested by Wynkoop and Wilhelm (*10*) the data were fitted to an equation of the form

$$\log (\% H_2) = A(\text{mvr}) + B$$

Sussman and Potter (*7*) found no effect of the saturate if the hydrogen concentration was maintained above 30% (as was the case for all runs in this work).

Catalyst

To show the advantages of the recirculation type of reactor, a catalyst giving a high rate of reaction was desired. Fair (*3*) used a supported nickel catalyst and reported high rates of reaction and consequently appreciable temperature gradients in an ordinary differential reactor. The same catalyst (Harshaw Ni-0101 T 1/8) was selected for use in this investigation. A typical analysis of the unreduced catalyst, which is supplied as 1/8-in. pellets, is

	Weight %
Nickel (elemental)	44
SiO_2	16
Carbon	4
Nickel compounds	36
	100

Reactants

Electrolytic hydrogen (99.5% H_2, 0.5% O_2) "pure"-grade propylene of 99% purity (principal impurity-propane) were used.

OPERATING PROCEDURE

After the catalyst particles had been weighed they were spaced between Pyrex-glass cylinders (Figure 4). The supporting frame and catalyst were then lowered into the reactor tube, and the thermocouple was adjusted to touch the upper catalyst particle. After the reactor had been closed and the pressure tested, the system was purged with nitrogen and then with hydrogen. Pressure on the reactor was adjusted to 4 lb./sq. in gauge with hydrogen gently flowing through the reactor. The temperature of the catalyst was raised to 600°F. ± 15°F. and maintained for 6 hr. At the end of this time the reactor was again thoroughly purged with hydrogen, placed under 5 lb./sq. in. gauge hydrogen pressure, and allowed to cool.

Before rate data was taken, the activity of the catalyst was stabilized by adjustment of the temperature of the catalyst to 90° to 100°F. admission of propylene and hydrogen at low flow rates, and turning on of the recirculation pump. These conditions were held constant for several hours, when the reactor was purged with hydrogen and maintained under hydrogen pressure.

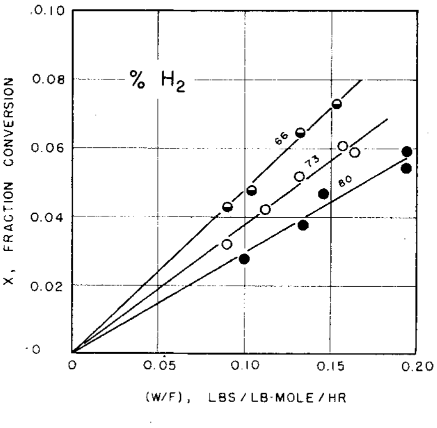

Fig. 6. Corrected conversions vs. (*W/F*), 110°F.

To ensure thermal equilibrium in the feed-metering system, the constant-temperature bath surrounding the capillary tubes was brought up to temperature and maintained for at least 1 hr. before each series of runs. At the beginning of the runs the reactor cooling water was brought up to the maximum desired temperature and circulated through the water jacket; then the cooling-water rate to the recirculation pump was adjusted. All equipment other than the reactor was purged with nitrogen. The reactor was by-passed, and the desired flow rates of gases were set. Gauge pressures on the manual pressure controllers were maintained at 20 lb./sq. in., and the back pressure on the flow meters was adjusted to 1.5 atm. abs. A check reading was taken on the thermal-conductivity meter. When all conditions had reached equilibrium, the gas stream was diverted through the reactor, and the recirculation pump was turned on. When a constant effluent analysis reading was reached on the thermal-conductivity meter, it was recorded, and the temperature of the cooling water was adjusted to a new value. Each point of data required 10 to 15 min.

After several series of runs the activity of the catalyst was checked by repeating some of the earlier runs. The activity was calculated in the manner described by Hougen and Watson (*5*).

The activity of the reactor alone was also investigated. Pyrex glass cylinders were charged in the same manner as the catalyst, and the usual reduction procedure was followed. Runs at a maximum water temperature, with and without the recirculation pump, showed no measurable conversion.

RESULTS

To complete the evaluation of this reactor, a rate equation was selected as described by Hougen and Watson (*5*) and applied by others (*6, 7, 8*). Experimental data were obtained at five temperatures in the range of 110° to 190°F. and at three hydrogen partial pressures. Complete data and plots showing a comparison of experimental and calculated conversions are available (*5a*). See Figure 6.

Examination of the complete data indicated that, within experimental accuracy and over the range investigated, the propane formed had no effect. Thus p_s terms (partial pressure of propane) were eliminated in all rate equations considered; terms involving the reverse reaction were also omitted because of the high equilibrium constant.

Preliminary graphical interpretation of all possible rate equations indicated the following as the most consistent:

Rate Equation (1)

$$R = \frac{aK_h p_u p_h}{(1 + K_h p_h)^2}$$

Rate Equation (2)

$$R = \frac{aK_h p_u p_h}{(1 + \sqrt{K_h p_h})^3}$$

Values of the constants for the two rate equations were determined by an iterative procedure on an IBM-CPC computer and are given in Table 1.

TABLE 1. CONSTANTS FOR THE RATE EQUATIONS

General equation
$\ln \text{constant} = -m/T + n$
where T = °K.

	m	n
Rate Equation (1)		
a	1,715	1.68×10^{3}
K_h	−1,381	5.25×10^{-3}
Rate Equation (2)		
a	2,003	1.27×10^{4}
K_h	−1,833	6.72×10^{-4}

Both rate equations are based on the surface reaction between adsorbed propylene and adsorbed hydrogen, molecular hydrogen in Equation (1) and atomic hydrogen in Equation (2). The average deviations for Equations (1) and (2) were ±3.3% and ±3.5%, respectively; maximum deviations were in both cases 9.1%.

Owing to the similarity of the equations and the limited range of variables investigated in this work, it is not possible to recommend one of the equations more strongly than the other, each having been reported by previous investigators for the hydrogenation of light olefins. There is much evidence in the literature indicating adsorption of both reactants, as suggested here, and some to the contrary for similar reactions on nickel films (*1*, *9*).

ASSESSMENT OF ERRORS

A careful assessment of errors was made to complete the evaluation of the reactor system, and the results are given in Table 2.

TABLE 2. TABULATION OF ERRORS

Measured variable	Maximum error
Feed composition	±0.4% H_2 at 66% H_2 ±0.02% H_2 at 80% H_2
Product composition	±0.002% H_2
Catalyst weight	Negligible
Reaction temperature	Maximum temperature rise was 6°F.
Reactor pressure	Maximum pressure drop was 1 to 2 in. Hg

The consistency of any one set of experimental points is better than the over-all accuracy owing to the order in which data were taken. For any one set of points flow rates were held constant while the temperature was varied. Hence uncertainties due to errors in flow rates were the same for each point of data in the given series. In a correlation of the various series of runs it is estimated that the maximum probable error in the calculated over-all conversion in no more than ±10%.

CONCLUSIONS

A recirculation differential reactor eliminates many of the experimental difficulties encountered in determining rate data for highly exothermic or endothermic reactions occurring at rapid rates. By proper design of the reactor, temperature gradients in the catalyst section can be maintained within acceptable limits. High gas velocities in the reactor prevent interfering mass transfer effects. Owing to the small conversion per pass, gas compositions within the reactor are more uniform than those encountered in ordinary differential reactors. All reactions, however, may not lend themselves to treatment in this type of equipment, as admixture of products to the feed may promote secondary reactions.

The free volume of the recirculation system must be small to reach steady state rapidly. Because of the transient period occurring after the change of any variable, a continuous method of analysis is desirable; measurement of the thermal conductivity has proved to be a good method of analyzing hydrogen and propylene mixtures.

The recirculation type of reactor permitted the determination of accurate initial-rate data for the vapor-phase hydrogenation of propylene over nickel-kieselguhr catalyst. It was, therefore, possible to conclude that the data can be represented equally well with two equations over a range of reaction conditions of 110° to 190° F., 1-atm. pressure, and 65 to 80% hydrogen. Both equations are based on the surface reaction as the controlling step, in one case with reaction between adsorbed propylene and adsorbed molecular hydrogen and in the other with reaction between adsorbed propylene and hydrogen adsorbed as atoms.

These conclusions can be made with some confidence because the measurements were carried out with a good degree of accuracy and with negligible temperature and differential gradients. In a nonrecirculation type of reactor the temperature and diffusional gradients for this rapid reaction would have been high and the results uncertain.

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NOTATION

a = an empirical constant which includes the over-all effectiveness factor and the reaction-velocity constant
F = feed rate, g.-moles of propylene/sec.
K = an adsorption-equilibrium constant
m = constant, °K.
mvr = millivolt reading of the potentiometer
n = constant, lb./moles/(lb. unreduced catalyst)(hr.)(atm.)^2
p = partial pressure, atm.
R = reaction rate, lb.-moles of propane produced/(hr.)(lb. of unreduced catalyst)
S = corrected scale reading on flow meters
T = absolute temperature, °K.
W = weight of catalyst, lb.
x = fraction of propylene reacted

Subscripts

h = hydrogen
u = propylene
1 = upstream conditions
2 = downstream conditions

Other

log = logarithm to base 10
ln = logarithm to base e

LITERATURE CITED

1. Beeck, Otto, *Revs. Mod. Phys.*, **17**, 61 (1945).
2. Binder, R. C., "Fluid Mechanics," 2 ed., Prentice-Hall, Inc., New York (1952).
3. Fair, J. R., Ph.D. dissertation, Univ. Texas, Austin (1955).
4. Hougen, O. A., Reaction Kinetics in Chemical Engineering, Chem. Eng. Progr. Monograph Ser., **47**, No. 1 (1951).
5. ———, and K. M. Watson, "Chemical Process Principles," Part III, John Wiley and Sons, New York (1947).

5a. Perkins, T. K., Ph.D. dissertation, Univ. Texas, Austin (1957); available from University Microfilms, Ann Arbor, Michigan, Microfilm Mic 57-4081, $2.00.

6. Potter, Charles, and Seymour Baron, *Chem. Eng. Progr.*, **47**, No. 9, 473 (1951).
7. Sussman, M. V., and Charles Potter, *Ind. Eng. Chem.*, **46**, 457 (1954).
8. Tschernitz, J. L., Sidney Bornstein, and R. B. Beckmann, *Trans. Am. Inst. Chem. Engrs.*, 42, 883 (1946).
9. Twigg, G. H., *Trans. Faraday Soc.*, **35**, 934 (1939).
10. Wynkoop, Raymond, and Richard H. Wilhelm, *Chem. Eng. Progr.*, **46**, 300 No. 6 (1950).

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