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SOLAR-CHEMICAL ENERGY CONVERSION AND STORAGE:
CYCLOHEXANE DEHYDROGENATION

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Abstract

The objective of this project is to provide research support for the cyclohexane/benzene heat pipe development program at Sandia Laboratories.

We have studied the apparent kinetics of the gas-phase catalytic dehydrogenation of cyclohexane to benzene in an internally recirculated (gradientless) reactor over the temperature range 500-800°F at 1 atm at various space velocities. We have also developed a kinetic model based on a reversible mass-action rate expression and a catalyst effectiveness factor which is able to correlate both the conversion and reaction rate data very well over the temperature range 500-750°F. The data taken at 800°F appear to be qualitatively and quantitatively different than the data taken at the lower temperatures. It is not as yet clear, whether this can be attributed to a change in kinetic mechanism or some reversible alteration of the catalyst surface at the higher temperature.

We have also studied the formation of side products in this system over the same temperature range. Both the number and amount of side product(s) formed increases with increasing temperature and residence time. Over the temperature range 500-600°F the side products produced appear to be strongly related to the presence of low molecular weight unsaturated hydrocarbon impurities in our (reagent grade) cyclohexane feed and it is possible that no side products would be formed were it not for the presence of these impurities. At temperatures above 600°F, both the number and amount of side product(s) produced increases markedly.

Finally, we have designed and partially fabricated a test loop which will enable us to study the effects of long term continuous cycling of the system on catalyst activity and side product formation. The size of the loop will also enable us to generate design data for scaleup of a benzene/cyclohexane thermochemical energy storage/recovery system and gain operating experience with closed loop chemical energy storage systems deliberately designed to run in a transient mode.

Introduction

The concept of storing excess thermal energy as chemical bond energy and the subsequent recovery of this energy on demand utilizing reversible catalytic chemical reactions shows great promise from an energy density point of view. In the temperature range 400-800°F, the cyclohexane-benzene reaction appears to be the most appropriate (Ritter, et al., 1977). While this reaction has been extensively studied in the exothermic (benzene hydrogenation) direction, little useful design data exists for the endothermic (cyclohexane decomposition) step. We have studied the apparent kinetics of the gas-phase decomposition of cyclohexane to benzene in an internally recirculated (gradientless) reactor over a commercially available naptha reforming catalyst (RD-150, Englehard Industries). A brief review of some of the reactions which have been suggested for thermo-chemical energy storage and at least partially evaluated using an energy density criterion as well as a description of the experimental system used to study the cyclohexane decomposition reaction and some experimental kinetic data in the range 400-600°F and 1 atm have been reported previously (Ritter, et al., 1977). The kinetic study produced two conclusions which have important implications for the design of reactors utilizing the cyclohexane decomposition reaction. First, in the temperature range 400-600°F and 1 atm, at low space velocities (high conversions), anywhere from zero to 0.2% of the product formed in a single pass over the catalyst were side products which may or may not be reversible. One of the side products has been clearly identified as toluene, while the other side product(s) may be intermediates or fragmentation products of the cyclohexane molecule and appear to vary both qualitatively and quantitatively with reaction conditions. A more detailed discussion of the side product issue is presented below.

Secondly, at high space velocities (high reaction rates), there are significant external mass transfer limitations on conversion.

Over the past year a major change in emphasis has occurred in the program. The original concept of utilizing reversible chemical reactions to store and recover thermal energy has been extended to include the important application in which the collection and utilization of the thermal energy take place at different locations. For example, the endothermic reaction (energy collection step) is carried out at one location (e.g., where sunshine is plentiful and regular) and the reaction products are shipped via the existing natural gas and/or petroleum pipeline distribution system to one or more users. At the utilization site, the exothermic reaction (energy recovery step) is then carried out and the products of this reaction returned to the collection site, again, via pipeline distribution systems. This is the so-called "chemical heat pipe" concept (Vakil, 1976). Support for the chemical heat pipe concept has come from the solar energy division of DOE, through Sandia Laboratories. For the past year the objective of our project has been to provide research support for the cyclohexane heat pipe development program

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at Sandia, although the funding has been through a special research support agreement from the Hydrogen/Chemical Energy Storage division of DOE through Brookhaven National Laboratories.

An economic analysis of the cyclohexane chemical heat pipe system has shown (Haaland, 1977) that it is economically advantageous to operate the cyclohexane decomposition reactor (energy collection) at 500 psig rather than at 1 atm. This essentially saves the capital investment and operating costs of hydrogen compression to pipeline pressure for transmission of the hydrogen. Since three moles of hydrogen and 1 mole of benzene are produced for every mole of cyclohexane that decomposes, the conversion and therefore the maximum amount of energy stored in a single pass at a given temperature is a strong function of pressure. The higher the pressure, the lower the conversion of cyclohexane. At 1 atm pressure the equilibrium (maximum) conversion is 96% at 600°F and 98% at 750°F. Operating at 34 atm (~500 psig) pressure, temperatures in the range 700-900°F would be required to achieve similar conversions. The higher temperature, of course, is the penalty one pays for operation at the higher pressure. Apparently the tradeoff is economically justified for the cyclohexane heat pipe application.

Although commercial reforming units operate at about 900°F and 34 atm, the thermal cracking and dehydrogenation of lower molecular weight hydrocarbons over the catalyst under these conditions lead to coke deposition and catalyst poisoning. Approximately 20% of the catalyst used must be reactivated in any 24 hour period. If we wish to operate at the higher temperatures and pressures, several questions must be answered. First, what are the relationships between conversion and reaction rate and temperature and pressure? Second, to what extent are side products formed at the higher temperatures and pressures and what effect do they have on catalyst activity? Also, what are the effects of long-term cycling on catalyst performance?

We have spent the past year preparing to answer some of these questions as well as related peripheral questions involving the design, simulation and control of chemical processes which continuously operate under transient (rather than steady-state) conditions. A discussion of our progress in each of these areas over the past year is presented below.

Cyclohexane Dehydrogenation: Batch Kinetic Data

Cyclohexane conversion data have been obtained at reactor temperatures of 750°F and 800°F, at a pressure of 2 psig. This data is shown in Figure 1, along with previously reported data (Ritter, et al., 1977) at reactor temperatures in the range of 500-600°F. As with the previous data, conversion data at each temperature and space velocity were taken at several fan speeds to eliminate external mass transfer effects.

Comparing the 800°F data in Figure 1 with the 750°F data, it can be seen that at the same space velocities, the conversions are lower at the higher temperature, except for one case where they are the same. In fact, at one space velocity (0.576 Hr^{-1}), the conversion at 800°F is lower than that at 600°F. Also, as the space velocity approaches zero, the 800°F conversion does not seem to approach the equilibrium conversion (100%) as do the conversions at all other temperatures. It was suspected that this behavior was due to a loss of catalyst activity. However, a subsequent check of catalyst activity indicated that there was no detectable activity loss at a 600°F reactor temperature. This activity check was performed using the procedure that was frequently used in the past, by duplicating a high conversion data point that was taken on fresh catalyst.

Therefore, the apparent loss of activity at 800°F must have been due to a temporary, reversible mechanism. This mechanism may be inhibition of the reaction at the catalyst surface by adsorption of a side product that acts as a temporary poison, or a change in the properties of the catalyst at the higher temperature. -----

Thus, for a reactor operating at 2 psig total pressure, it is likely that a maximum reaction rate exists in the range of 750°F to 800°F. However it may be that higher reaction rates can be obtained at higher reactor pressures.

System Modifications for High Pressure, High Temperature Operation

The reaction system has been described previously (Ritter, et al., 1977). The following modifications have been made to the batch reactor system, illustrated in Figure 2, to permit operation of the reactor at temperatures up to 1000°F and pressures up to 1000 psig.

A) The 110 volt electric furnace has been replaced with a 230 volt unit capable of surface temperatures up to 1300°F, which will permit sustained catalyst temperatures up to 1000°F.

B) The magnetic unit which drives the fan has been replaced with an Autoclave Engineers Magnedrive II. The old unit was designed for a maximum speed of 1500 RPM, while it was typically operated at speeds of 1800-2050 RPM, and a maximum temperature of 650°F. Although an external cooling coil had been added to the unit, the magnetic field that transmits the power to the drive shaft was slowly deteriorating due to the 750°F-800°F operating temperatures, and catalyst activations at 900°F. The weakening magnetic field combined with operation at high fan speeds caused the frequency of replacement of the internal graphite bearings to be excessive. The new Magnedrive II is designed to operate at speeds up to 2500 RPM, and is equipped with a cooling jacket to protect the magnets from high reactor temperatures.

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C) The Harvard infusion feed pump has been replaced by a high pressure liquid chromatography metering pump. Since the minimum flow rate which the new pump can deliver exceeds several of the rates that have been of interest in the past, further feed system modifications may be necessary.

D) To drop the pressure of the reactor effluent vapor to a level suitable for sampling by the gas chromatograph, a specially designed needle valve has been added. Also, the sampling system is protected by a safety valve that will vent vapor to the exhaust hood in the event that the pressure reaches a safe upper limit.

E) A pressure gauge with a 0-2000 psig range has been added.

F) The glass condenser has been replaced with a stainless steel shell-and-tube heat exchanger, and a stainless steel knockout drum downstream.

G) A new temperature controller has been purchased with a range of 500-1500°F to replace the 200-800°F controller presently on the system.

Catalyst Particle Size Distribution

In order to correlate the kinetic data, it was necessary to obtain data on the size distribution of the RD-150 C catalyst. The correlation method is described below.

The catalyst particles are cylindrical in shape, with a diameter of approximately 1/16 in. Although the diameter of the particles is uniform, their lengths can vary significantly. To obtain the size distribution data, approximately 100 catalyst particles were weighed individually. The density of the particles was obtained by measuring and weighing large catalyst particles. Assuming that all particles were of the same diameter and density, the length of each particle was calculated from its weight. The results of this procedure are shown in Figure 3, for data obtained on used RD-150 C catalyst.

Analysis of Kinetic Data

At this juncture, a reliable set of kinetic data has been obtained for the dehydrogenation reaction at 16.7 psig and 500°-750°F. The data at 800°F must be considered separately and will not be analyzed here. The measured rates do not necessarily represent true reaction kinetics as no experimental effort was made to eliminate intraparticle temperature and concentration gradients by, for example, obtaining measurements with decreasing particle sizes. As cyclohexane dehydrogenation is generally known to be a rapid reaction with a large, enthalpy change and was in fact selected for those reasons, the complete effectiveness of the catalyst particles cannot be presumed. To account for this analytically,

it is necessary first to select an expression for the intrinsic kinetics and then to impose with a suitable model the molecular transport restrictions that occur within the porous material for the calculation of the apparent kinetics. Such an approach, of course, folds the inadequacies of both the intrinsic rate expression and the transport model into the kinetic parameters which are adjusted to match the calculated with the experimental values of the apparent kinetics.

The intrinsic rate expression must reflect the thermodynamic limitations on conversion as the hydrogenation direction is favorable at 400°F and the dehydrogenation direction is favorable at 600°F, which is an attractive feature of the system from the applications point of view. The pertinent thermodynamic variables are summarized in Table A which were calculated without fugacity corrections at atmospheric pressure. The equilibrium conversions from Table A are included in Figure 1, from which it can be seen that the kinetic data are consistent with the thermodynamic calculations. Consequently, the simplest expression of the intrinsic kinetics is given by

$$r = \frac{k}{RT} (P_c - \frac{1}{K_p} P_b P_h^3) \quad (1)$$

Considerations of the reaction mechanisms at the catalytic surface may add significant features to equation (1) without detracting from its capability to vanish in the appropriate thermodynamic manner. As the expression is written, it is consistent with the dissociative adsorption mechanism which was proposed by Ritchie and Nixon (1968) if the desorption equilibrium constants are large and the dissociative adsorption step is rate controlling.

Equation (1) is not necessarily consistent with the work of Gland, et al. (1975) who propose that the slow step in cyclohexane dehydrogenation over single Pt crystals is the dehydrogenation of cyclohexene, an intermediate formed at the catalytic surface. Cyclohexene has also been observed over Pt - Al₂O₃ catalysts (Smith and Prater, 1967) as well as methyl cyclopentane (Barrett, et al., 1961), but at temperatures, pressures, or hydrogen/hydrocarbon ratios significantly different from the experimental conditions reported here. Other workers (Usov, et al., 1974; Bridges and Houghton, 1959) have not observed any secondary products in experiments which are more relevant to the present discussion.

It appears that the mechanism of the dehydrogenation reaction may be strongly dependent upon the operating conditions and that it is not yet possible to formulate an intrinsic rate expression on the basis of an established mechanism. The approach taken here was to fully exploit the merits of equation (1) for representing the experimental data, in conjunction with a transport model, without further reference to its mechanistic implications. Improvements in the representation would then be expected if additional degrees of freedom were made available through

the full Langmuir-Hinshelwood approach.

The effects of intraparticle gradients are normally expressed through an effectiveness factor, ϵ , which provides the appropriate correction to the intrinsic reaction rate expressed in terms of the extrapolated conditions at the exterior surface of the catalyst pellets (Satterfield, 1970).

$$r_{app} = \left[\int_0^\infty f(a) \epsilon(a) da \right] r_s \quad (2)$$

The effect of the particle size distribution has been included in equation (2) as the effectiveness factor depends upon the particle dimensions through the Thiele parameter:

$$\Lambda_p = a \sqrt{\frac{\rho_p RT_s r_s}{D_c P_{es}}} \quad (3)$$

The particle size distribution is given as a function of the cylinder length in Figure 3. The effective particle size, a , is defined as the ratio of the apparent volume of the pellet to the external surface area which for cylinders is given by

$$a = \frac{d}{4} \left[\frac{2L/d}{1 + 2L/d} \right] \quad (4)$$

This definition of the particle size permits the evaluation of the effectiveness factor in a simple semi-infinite slab geometry with a large measure of confidence (Rester and Aris, 1969). The thickness of the slab is $2a$.

The result (Petersen, 1965) is that

$$\epsilon = \frac{1}{\Lambda_p} \sqrt{2 \int_0^1 \psi(o) \psi^1 r^-(\psi) d\psi} \quad (5)$$

and

$$\Lambda_p = \psi(o) \int_0^1 [2 \int_0^\psi \psi(o) \psi^1 r^-(\xi) d\xi]^{-\frac{1}{2}} d\psi \quad (6)$$

The concentration of cyclohexane relative to its value at the exterior surface of the pellets is denoted by ψ with $\psi(o)$ being the value at the center. The temperature and the concentrations of benzene and hydrogen at the interior of the pellets are given by

$$c_b = c_{bs} + \frac{D_c}{D_b} c_{cs} (1 - \psi) \quad (7)$$

$$c_h = c_{hs} + 3 \frac{D_c}{D_h} C_{cs} (1 - \psi) \quad (8)$$

$$T = T_s - \frac{D_c \Delta H_R C_{cs}}{\lambda} (1 - \psi) \quad (9)$$

The intrinsic reaction rate given by equation (1) can then be considered a function of the single variable ψ throughout the pellet. This rate relative to the value at the exterior surface of the pellet is denoted by $r^*(\psi)$ in equations (5) and (6). Equations (5) to (9) imply that the catalyst effectiveness is a function of the concentrations and temperature at the exterior surface, the three transport parameters, and the Thiele parameter in addition to the Arrhenius parameters in the rate constant, k .

The conditions at the pellet surface are given in terms of the conversion of cyclohexane as

$$C_{cs} = \frac{P_s}{RT_s} \frac{1 - x}{1 + 3x} \quad (10)$$

$$C_{bs} = \frac{P_s}{RT_s} \frac{x}{1 + 3x} \quad (11)$$

$$C_{hs} = \frac{P_s}{RT_s} \frac{3x}{1 + 3x} \quad (12)$$

The temperature and pressure are measured directly while the conversion was computed from the chromatographic results.

The effective diffusion coefficients were evaluated with the expressions derived by Rothfeld (1963) for a single pore and the parallel pore model (Johnson and Stewart, 1965) assuming no distribution of pore sizes:

$$\frac{1}{D_i} = \frac{\tau}{\epsilon} \left[\frac{1}{D_{ik}} + \frac{P_s}{RT_s} \sum_j \frac{C_{js} - (v_i/v_j) C_{is}}{D_{ij}} \right] \quad (13)$$

$i, j = c, b, h$

The evaluation was made at the exterior surface of the pellets.

The binary diffusion coefficients were calculated as functions of the surface temperature with the Chapman-Enskog equation and the Lennard-Jones potential (Bird, et al., 1960). This equation was used to scale available diffusion data (Satterfield, 1970; Sherwood, et al., 1975) to 500°F. Thereafter the 3/2 power of temperature was used. In the case

of the binary hydrocarbon system, the binary diffusion coefficient was calculated at 500°F with the Chapman-Enskog equation which was in full agreement with the reported data for the remaining binary systems. The Knudsen diffusion coefficients were calculated as functions of temperature with an average pore radius. The thermal conductivity of the pellet was taken as 5.3×10^{-4} cal/(sec cm °K) on the basis of the data reported in Satterfield (1970) for a Pt reforming catalyst.

The catalyst properties were taken to be those reported by Korbach and Stewart (1964) for the RD-150 catalyst. The average pore radius was estimated to be 22.4 Å from the reported values of surface area, 500 m²/g, and total pore volume, 0.56 cc/g. The apparent density was measured to be 1.34 g/cc in the course of obtaining the particle size distribution the porosity, ϵ , was taken as 0.40.

The tortuosity factor, τ , may vary over a wide range of values (Satterfield, 1970). A value of 3.0 was used which is what would be expected if the pore system were isotropic (Johnson and Stewart, 1965).

Provided that values of the pre-exponential factor and the activation energy are specified, the catalyst effectiveness may be evaluated with equations (2) to (6) for each particle size at each of the measured values of temperature and conversion. The corresponding calculated value of the apparent kinetics may then be evaluated with equation (2) and compared with the experimental value. Such calculations were carried out until no better agreement between the calculated and experimental rates could be obtained with further adjustments in A and E. The method of evaluating the effectiveness factor is summarized in the Appendix and the comparison of the calculated with the experimental results is given in Figure 4.

Because of the sensitivity of the measured conversions to the agitation rate, it was necessary to use the model as a guide for extrapolating the data in several cases. An example of the range of sensitivity is illustrated in Figure 2 of a previous report (Ritter, et al., 1977). A slight adjustment of the extrapolated conversion was seen to have a marked effect on the calculated reaction rate. The data in Figure 4 are slightly different from those reported earlier (Ritter, et al., 1977).

In addition, there were three cases where the extrapolated conversions were beyond the calculated equilibrium conversion. These data points occurred at 500°F and low reaction rates when the thermodynamic limit is important. The cause is believed to be primarily in the experimental error although it may be necessary to make more accurate equilibrium calculations under these conditions. These data were not included in the analysis.

In all cases, the effectiveness of the catalyst was found to be a pronounced function of the particle size. The effectiveness factor was

evaluated in each range of particle sizes at the average value for the range. An example of the behavior is given by the calculated results in Table B.

The value of the activation energy which is given in Figure 4 is in close agreement with the range of apparent activation energies that were reported by Bridges and Houghton (1959), $21,000 \pm 2,000$ cal/g mole, if one assumes that the effectiveness of their Pt-Al₂O₃ catalyst was in the diffusion limited regime. Their catalyst was in the form of 0.16 cm beads. In the diffusion limited case, their range of true activation energies becomes $10,500 \pm 1,000$ cal/g mole. These data were obtained in a rising temperature tubular converter over the range 300-550°F, at approximately atmospheric pressure, and with stoichiometric reaction conditions. The properties of their catalyst were not reported nor is it clear that their data are free of external heat and mass transfer effects.

The calculated value of the activation energy is also close to the value of 11,000 cal/g mole that was obtained by Usov, et al., (1974) in the temperature range of 572-662°F with small (0.25-0.50 mm) particles and low stoichiometric reaction rates. The assumption of complete effectiveness of the catalyst particles under these conditions appears justified.

The root mean square error between the calculated and measured reaction rates for the data reported here is 8.97×10^{-8} g mole/sec g while the relative value for this measure of error is 0.268. The error was considered acceptable in view of the sensitivity of the calculated rates to the extrapolated values of conversion and to the fact that the most significant errors are conservative. The calculated rates are considered satisfactory for design calculations but the basis of stoichiometric reaction conditions and atmospheric pressure must be borne in mind. If the data are extrapolated to other conditions, e.g. higher pressure, the effect on catalyst effectiveness must be considered in conjunction with the effect on the reaction kinetics. More extensive data will be obtained at higher temperatures and pressures and more sophisticated intrinsic rate expressions will be evaluated.

Intermediates and Side Products

There is no question that the primary reaction with which we are dealing is the dehydrogenation of cyclohexane to benzene. However, the possibility of simultaneous or consecutive reactions appears in our results as well as in other investigations. The whole question of the effects of these side products which may or may not be reversible and which may cause catalyst deactivation and a loss in net thermal storage capacity is being investigated. It should be noted that the existence of chemical species other than the primary participants is not necessarily troublesome since these may be transient intermediates or themselves

may be participants in reversible side reactions which may not result in a deterioration of the thermo-chemical cycle. Moreover, in the closed systems which are being proposed it is always possible to include periodic catalyst regeneration or replacement and chemical purification steps. These will, of course, incur economic penalties in the form of higher capital and operating costs. Since modern reforming units operate in this mode any limitations on the application of this system to thermo-chemical energy storage would be economic rather than technical.

Our information on side product formation has been generated in an internal recirculation reactor. The distribution of residence times in such a reactor is much broader than those encountered in the non-recirculating tubular reactors which have been proposed for the thermo-chemical energy storage-recovery cycle. The distribution of residence times in the internal recirculating reactor is such that some of the reactant (and product) molecules spend a much longer time in the vicinity of the catalyst surface than the average, thereby allowing the formation of side products whose kinetics require long catalyst contact times. On the other hand, in packed tubular reactors, under approximately plug flow conditions, the distribution of residence times is relatively narrow around the mean. This means that any side products whose kinetics require long intimate contact with the catalyst surface would be attenuated.

With these points in mind, we can now consider a summary of our side product information to date and our plans for the future concerning the evaluation of side product formation.

Table C is a summary of the indication of minor products in the kinetic data. The data are not necessarily free of interphase mass transfer effects and area percents less than 0.01 are reported as 0.01. The conversion ranges were selected on the basis that the reported area percents are indicative of the behavior over the range of conversions. The influence of the distribution of residence times discussed above on the appearance of extraneous products was particularly evident in those instances where the reactor was "bottled up" in order to speed the approach to higher conversions. In these cases side products were produced during the no-flow period of operation that were gradually washed out of the reactor before the new steady state was reached and are not reported in Table C.

Referring to Table C, we observe that at temperatures less than 700°F, two extra peaks appeared on the chromatograph, although not consistently. However in all cases these extra products constituted less than 0.05% of the total area that was integrated. At 700°F a significant change took place. Two peaks were present up to 800°F but their percent of the total area increased and their relative retention times changed in both magnitude and uniformity. In the 800°F data, three and four extra peaks were present on several occasions with further changes

in magnitude and uniformity.

The data beyond 600°F cannot be compared in every respect with the data at the lower temperatures as the relative retention times are, to some extent, a function of concentration (area percent) and in these runs the chromatographic columns may have (inadvertently) experienced temperatures beyond its design limit. This caused a gradual deterioration in its performance which necessitated individual calibrations for all of the kinetic data points. However, the increase in the area percents and the number of extraneous peaks are considered to be indicative of side products produced in the reactor rather than artifacts of the chromatographic column. The extra peaks in these data all appeared before benzene, which appears in all cases after the cyclohexane peak. Finally, there is more chromatographic evidence that even lighter materials are present in the products. However, the combination of chromatographic column and attenuation setting necessary to produce good benzene-cyclohexane kinetic data was not also capable of adequately resolving these low molecular weight peaks. The chromatographic column used for these studies was 1/4" D x 6 ft. stainless steel column packed with 15% carbowax 1540 on 60/80 mesh chromasorb p and supplied by Beckman Instruments Corporation. This has recently been replaced by a similar column purchased from Alltech Associates.. The only difference is that non-acid washed chromasorb p was specified. The new column appears to give sharper resolution of some of the lighter fraction peaks.

The reagent grade cyclohexane feed is supplied by Fisher Scientific Company and a chromatogram supplied by the manufacturer as well as our own chromatographic studies reveal that it usually contains one or more impurities. The presence of these impurities in the feed has a pronounced effect on the chromatographic results given in Table C and in fact are crucial to the explanation of the side products present at temperatures below 700°F. A possible mechanism for side product formation at the lower temperatures (<700°F) is given below.

A mass spectrometric analysis of a gas sample taken from the reactor operating at 600°F and 92% conversion is given in Table D. The N₂, O₂, Ar and CO₂ constituents are not significant. The presence of butene and either butane or methyl pentane in the sample was puzzling at first since it could only be explained by the existence of an hydrogenolysis reaction with subsequent dehydrogenation. However, the hydrogenolysis activity of Pt is nonselective (Sinfelt, 1973) so that one would expect a spectrum of products from methane through pentane if this were the case. A series of chromatographic and side product identification runs made over the temperature range 500-600°F at very low attenuation allow at least a partial interpretation of the chromatographic and mass spectrometer observations. First, there were two impurities present in the reagent grade cyclohexane. On our chromatographic column these had retention times of -0.14 and -0.18 minutes relative to (before) cyclohexane. Both 1-butene and cis-trans-2-butene were added to the cyclo-

hexane feed and appeared as a single peak with a relative retention time of -0.14 minutes, thus establishing the presence of butene as an impurity in the feed. Methylpentane was separately added to the cyclohexane feed and exhibited a retention time of -0.07 minutes relative to cyclohexane at low attenuations. This means that at our usual attenuation any methylpentane produced over the catalyst or introduced in the feed would be masked by the cyclohexane peak. The identification of the lighter impurity (RT = -0.18) was not established. This cyclohexane feed was then introduced into the reactor over the catalyst in the temperature range 500-600°F and several changes were observed in the chromatographic records produced (at low attenuations). Initially, as the temperature was increased from 500-600°F, the two peaks remained at -0.14 and -0.18 minutes, but the total area of the butene peak (-0.14) diminished and the total area of the lighter fraction (RT = 0.18) increased proportionately. At higher temperatures, two additional, even lighter peaks appeared at RT = -0.56 and RT = -0.64, plus a longer RT peak appeared at RT = +3.32. The peak at RT = +3.32 was previously identified as toluene. This allows us to at least offer a partial explanation for the side products formed in our system at temperatures between 500 and 600°F. The butenes are impurities entering with the cyclohexane feed. At the higher temperatures, they may be preferentially cracked (rather than being hydrogenated) at the catalyst surface. The methyl fragments produced can combine with the plethora of benzene also being produced at the surface to form toluene. This would explain the observed decrease in the butene area and the simultaneous appearance of toluene and increase in the number and area percent of the lighter fragments. In fact, in the limit, one butene molecule can theoretically provide methyl fragments for the production of 4 toluene molecules. Finally, the presence of butane in the mass spectrometer data would be explained by a straightforward hydrogenation of the butene impurity on the catalyst surface.

Possibilities from the Literature

Hydrocracking may take place on the Pt/Al₂O₃ catalyst (Meyers, et al., 1958) from which one would also expect a variety of products. Ritchie (1968) observed cracked products at temperatures near 1000°F and 10 atm pressure. The production of toluene in the reactor is difficult to rationalize if one does not postulate low molecular weight impurities in the feed. However, similar increases in the carbon number of cycloalkanes have been observed at higher temperatures and pressures (Shuikin, 1958). The mechanism proposed involves the reaction of the adsorbed species with a CH₂ residue resulting from fragmentation of the parent molecule. These reactions are apparently not well understood (Anderson, 1973).

The possibility of methylpentane can be rationalized as resulting from the dehydrocyclization of methylcyclopentane on the acid centers. The occurrence of methylcyclopentane could arise from the isomerization

CATALYST TEST LOOP

Process Description

The catalyst cycling test loop which is shown schematically in Figure 5, consists of four major subsystems: the collector, the boiler, the hydrogen storage and the steam generating systems. While there are many opportunities for improving the thermal efficiency of the process (e.g., by using the hotter streams to preheat the inlet stream), for simplicity the reactor feed streams are all preheated electrically. All streams will be mixtures of two or more components, but to keep the flow diagram uncluttered only the major component is shown on each stream line in Figure 5.

Starting with the collector subsystem, cyclohexane, containing a small amount of benzene, is fed to an electrically heated vaporizer by a diaphragm pump before being preheated to the reacting temperature by a second electrical heater. In the collector reactor, the thermal energy source, which may be solar, is simulated by electrical heating. A special furnace was designed containing five heaters, each of which can be heated independently of the others. Thus, some degree of variation in the axial heat input may be attained. The collector reactor is a one inch diameter stainless steel tube packed with catalyst pellets of the same type used in the batch kinetic studies. A sheathed thermocouple enters from the top of the bed and allows the measurement of temperature at one fixed point along the bed length. Obtaining several axial bed temperatures would be more desirable, but this would complicate the design considerably. The reactor assembly, consisting of the reactor and furnace, can be rotated from its vertical position to facilitate catalyst removal and addition without disturbing the inlet and outlet piping. Also, on the off center position the catalyst may be loaded by sliding the catalyst down the tube wall thus minimizing catalyst fragmentation.

In the reactor, cyclohexane is converted to benzene and hydrogen with the absorption of ~52 Kcal of thermal energy per mole of cyclohexane converted. After exiting from the reactor, the reaction products are cooled to a safe temperature by a heat exchanger to protect both a pressure control valve and the condenser located after the cooler. After condensation the benzene and unreacted cyclohexane are separated from the hydrogen in the storage vessel. The hydrogen is then compressed and stored.

With the exception of the reactor, the boiler subsystem is identical to the collector subsystem. The boiler reactor consists of several tubes in parallel packed with catalyst pellets. In the boiler reactor hydrogen is reacted with benzene producing cyclohexane and releasing ~52 Kcal of thermal energy per mole of cyclohexane produced. The energy is removed by boiling water to produce steam which is condensed and recycled. The steam pressure will be controlled by a control valve located before

the condenser.

Unreacted hydrogen from the boiler reactor is combined with the hydrogen from the collector reactor. Before compression the small amounts of cyclohexane and benzene in the hydrogen stream are removed in the refrigerated cooler to prevent condensation within the compressor. The condensed vapors, which contain mostly benzene, are mixed with the boiler reactor feed. The system was initially designed to be operated without a compressor by purchasing high pressure tanks of hydrogen for the boiler reactor and venting the hydrogen produced in the collector. Besides the nuisance of continually replacing the hydrogen, this procedure is technically questionable because the vented hydrogen is in effect a purge. Since the major purpose of the test loop is to study the behavior of the catalyst over many cycles and one of the unknown factors is the possible buildup of unwanted side products, leading to poisoning of the catalyst, a vented hydrogen stream could prevent the detection of these effects.

The system is designed with considerable flexibility. It can be operated with hydrogen purchased from a supplier and eventually with recycled hydrogen using a compressor. The collector reactor can be operated independently of the boiler reactor by venting the hydrogen. The boiler reactor can also be operated independently of the collector reactor using purchased hydrogen. Although the system has been designed to test the effects of side product accumulation on the dehydrogenation catalyst, its size is sufficiently large so that it can also be used to develop performance data for designing a full scale system.

The existence of this facility, which should be fully operational within the next year, has some major implications for DOE's Chemical Energy Storage program. Not only is the cyclohexane/benzene system a major candidate for use in the full scale application of solar-chemical energy storage, but equally as important, an operational test loop of this size based on the cyclohexane/benzene system can be used as a model for comparison of the performance of other solar-chemical energy storage systems, regardless of whether or not the cyclohexane/benzene system is eventually chosen for full scale development. Also, the test loop can be used to develop operational technology (control, startup, shutdown) and gain practical experience with operating closed cycle chemical energy storage systems in a transient mode.

Instrumentation and Control

An instrumentation and control system for the catalyst test loop is shown in Figure 6. For economic reasons the number of instruments and controls had to be kept to a minimum. The only variable that is under automatic control in all the subsystems is pressure. Thus the system will have to be kept in balance by an operator. Once operating experience has been gained with the system in this mode, it will be easier to design a more sophisticated control system.

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Temperature, pressure, liquid level and composition will be measured at various points in the system as shown in Figure 6. The flows into each reactor and water flow into the shell side of the reactor will not be measured, but will be determined by calibration of the settings of the metering pumps. Eventually, flow meters will be installed in the feed lines. Compositions of the streams entering and leaving each reactor will be sampled and analyzed by the Hewlett-Packard Chromatograph used in the catalyst kinetic studies.

Several electrical engineering undergraduates have undertaken the design of a data acquisition and control system for the test loop as their senior design project. They are developing the software and interfacing hardware for an LSI-11 microprocessor based data acquisition and control system. The inputs to the LSI-11 computer will be the thermocouple, pressure and level indicator analog signals. The analog signals will then go through multiplexed A/D converters and either displayed or stored on some mass storage device (e.g., Disk, magnetic tape). Eventually the data collected will be used as inputs to a control algorithm which will compute the state of the process at any instant of time, compare it to some desired state and, if necessary, return one or more control signals to change flow, pressure and/or heating rates at one or more points in the process.

Project Status

Activation of the test loop is proceeding in several stages. In the first stage the collector subsystem is being constructed and tested at atmospheric pressure. After this phase is completed the collector reactor will be brought up to 1000 psi and 1000°F, the design pressure and temperature. Following this the boiler and steam generating systems will be constructed and tested. Next the hydrogen storage subsystem will be designed, constructed and tested. Finally, all systems will be integrated and operated simultaneously.

The funds currently allocated to the project are not sufficient to complete the entire test loop. Since the operation of the collector reactor is more technically uncertain the initial effort has focused on this part of the test loop. The design of the collector subsystem has been completed, a major part of the equipment has been received and construction has begun. Although an effort was made to purchase standard equipment to save time and expense, the reactor with the furnace, the preheater and the storage vessel all required special designs. Arrangements have been made for welding all the components. Because of the large consumption of power for the reactor, preheater and vaporizer, the electrical power supplied to the laboratory will have to be increased. No automatic controls have been included in the design of this system but will be added as experimental information on the system behavior is obtained and funds become available.

Since the hydrogenation of benzene is a commercial process, more information was available for the design of this subsystem and a proven catalyst supplied by the Harshaw Chemical Company is being used. The major parts of the boiler reactor subsystem have been designed, purchased and constructed. Although these components will be installed, the boiler reactor itself cannot become operational until additional funds become available. To complete this part of the test loop the preheater and vaporizer must be purchased along with piping, fittings and valves to connect the various components and instrumentation.

The hydrogen storage system was not included in the original design, but because of the technical considerations discussed earlier it was decided that a storage system would be necessary. For preliminary testing, however, the hydrogen supply will be from pressureized tanks. Fortunately, a used compressor was donated by the Central Operating Company of West Virginia Power and Lighting, New Haven, WV. Overhaul of the compressor and replacement of used and missing parts will cost \$2600. This is approximately 10% of the price of a new compressor alone. To complete the hydrogen storage system a storage vessel, instrumentation and controls, and the necessary piping, mounting pad and electrical outlets will be required.

Future Plans

Our plans over the next year are the continuation of our research support for the benzene/cyclohexane heat pipe development program at Sandia. However, the studies which we expect to carry out on the benzene/cyclohexane system and its catalysts are not only applicable to the particular application (e.g., chemical heat pipe) but are sufficiently general so that they would provide research support for the use of this system in a straight energy storage mode as well. Moreover, the size of the catalyst cycling test loop we have developed is such that it is capable of providing design data for scaleup of a benzene/cyclohexane solar-chemical energy storage system as well as operational experience with closed cycle chemical energy storage processes deliberately run in a transient mode, regardless of the particular reaction system being used.

In particular, an analysis will be made of the catalyst deactivation problem with the objective of defining, measuring, and understanding the rates and mechanisms of catalyst deactivation. Also, the transient behavior of gas-phase catalytic reactors typically used in closed loop chemical heat pipe or chemical energy storage systems will be modelled and potential problems associated with their dynamic behavior will be identified. Several different tasks have been defined and are briefly described below.

Catalyst Characterization

The objective of this task will be to measure the activity of the

RD-150 naphtha reforming catalyst and correlate its activity with operating conditions (temperature, pressure, long-term cycling).

An apparatus has been designed for the measurement of both hydrogen adsorption and nitrogen adsorption, the former taking place at approximately 250°C and the latter at -196°C. A schematic of the apparatus is provided in Figure 7 which is based to a large extent on the apparatus utilized by Harkins and Jura (1944) for nitrogen adsorption. Hydrogen adsorption isotherms on Pt catalysts can be carried out by well known methods (Spenadel and Boudart, 1960) on the same apparatus.

In addition to total area, the nitrogen adsorption isotherms will provide the distribution of surface area versus pore size, as well as the pore size distribution (Cranston and Inkley, 1957). The pore size distribution can be used for the estimation of effective diffusion coefficients in the catalyst (Johnson and Stewart, 1965).

The sensitivity of the active area, the total area, and the pore size distribution to the time on stream of the catalyst will be of interest with respect to deactivation phenomena. In addition, it will be possible to characterize new catalysts with the system which is relevant to the undesirable features of the acidic sites on the RD-150 catalyst. The importance of diffusion in the catalysts is very important to design calculations as the analysis of the data reported here indicates.

Long Term Cycling Studies

We have designed and partially fabricated a catalyst cycling test loop which, when completed, will allow us to study the effects of (condensable) side product buildup on catalyst activity under long term cycling of the benzene/cyclohexane system at temperatures up to 1000°F and pressures up to 1000 psig at various space velocities.

The objectives of this task are to measure the quantity and number of side products produced in the cyclohexane decomposition (collector) reactor as a function of temperature, pressure and space velocity in the temperature range 600-1000°F, and pressure range 0-1000 psig and to measure the effects of temperature, pressure and side product formation on catalyst activity.

In order to accomplish this task we will first have to complete the test loop by purchasing some remaining components in both the collector and boiler reactor subsystems. At that time the test loop can be run on an interim basis using bottled hydrogen for the boiler reactor and venting the hydrogen produced by the collector reactor. This will not allow us to measure the effects of noncondensable side products on catalyst activity nor the effects of their buildup on overall system performance. However, the gas phase will be sampled periodically and analyzed by gas chromatograph and mass spectrometer for the noncondensable products pro-

duced in a single pass.

However, because of the cost and logistics involved in using 6 bottles of hydrogen for every 24 hour run (much of the bottled hydrogen will not be useable at the higher pressures) we propose to add a hydrogen storage subsystem. A hydrogen compressor has been donated to us and can be reconditioned for approximately 10% of the cost of a new compressor. This now makes the addition of a hydrogen storage subsystem feasible within the level of funding contemplated. After installation of the hydrogen storage subsystem, side product buildup and catalyst activity data can be taken on the closed loop.

Batch Reactor Studies and Side Product Identification

These studies will focus on the identification of the side products produced in the cyclohexane decomposition reaction as a function of temperature, pressure and space velocity in the region 6-0-1000°F and 1-1000 psig. Specifically, the quantitative changes that take place with respect to both the number and amount of side products produced will be studied.

Additional kinetic models for the intrinsic reaction rate will be postulated and an attempt will be made to generate a better fit of the experimental reaction rate data in terms of the postulated model(s) and a catalyst effectiveness factor over the temperature and pressure range studied.

Finally, the effects of temperature, pressure and side product production on catalyst activity will be studied and catalyst samples will be supplied for measurements of catalyst adsorption isotherms, pore size distribution and surface studies as proposed above. If time permits, kinetic and catalyst deactivation studies can be performed on catalysts other than RD-150.

Model Development and Simulation Studies

These studies will continue the development of a mathematical model to simulate the behavior of both the collector and boiler reactors to startup, shutdown, and transient changes in feed composition, temperature and heat flux.

An early version of the transient model has been reported previously (Ritter, et al., 1976). This model has been reformulated to include heat and mass transfer effects which were previously not included and which may be significant. The kinetic model presented previously will be used as input to the transient reactor model.

We expect to program the transient model for the Stevens PDP-10 computer and conduct dynamic simulation studies for the collector and

boiler reactor subsystem over the next year.

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Appendix

The method of calculating the apparent reaction rates expressed by equation (2) consisted of a series of trial and error calculations each of which were carried out to within 1% convergence error. At each data point representing conversion and temperature in the reactor, a value of the Thiele parameter was calculated with equation (3) for each particle size. Regarding the center concentrations as parameters, equation (6) was solved as the center concentration, $\psi(0)$, was progressively varied from unity to the equilibrium value, ψ_e , corresponding to the prescribed conditions at the exterior surface. When the calculated value of the Thiele parameter was reached, the associated center concentration was used to evaluate the effectiveness factor with equation (5).

The integral in equation (6) was evaluated with the following first order approximation:

$$\Lambda_p = \left(\frac{\delta}{2}\right)^{\frac{1}{2}} \sum_{n=0}^{N-1} \left\{ \sum_{j=0}^{n-1} [r^-(\psi(0) + (j + \frac{1}{2}) \delta) + \frac{1}{2} r^-(\psi(0) + (n + \frac{1}{2}) \delta)] \right\}^{-\frac{1}{2}}$$

where the step size is given by

$$\delta = \frac{1 - \psi(0)}{N}$$

and N is the number of increments. The number of increments was progressively doubled until convergence within 1% error was obtained. A similar approach was used to evaluate the integral in equation (5).

If at any point it was found that the center concentration satisfied

$$\psi(0) < \alpha + \frac{0.01}{r^-(\psi(0))} \int_{\psi_\alpha}^1 r^-(\xi) d\xi$$

then the asymptotic form was employed:

$$\epsilon_\infty = \frac{1}{\Lambda_p} \sqrt{2 \int_{\psi_e}^1 r^-(\xi) d\xi}$$

TABLE A

Thermodynamic Resultsp = 1 atm: Pure C₆H₁₂ Feed

T(°F)	$\Delta H^{\circ}R$ (cal/g mole)	$\Delta G^{\circ}R$ (cal/g mole)	$\Delta S^{\circ}R$ (cal/g mole °K)	K_p (atm ³)	x_{eq}
400	51457	7193	92.60	0.514×10^{-3}	0.076
500	51918	2073	93.52	0.141×10^0	0.437
540	52084	-81	93.82	0.108×10^1	0.762
575	52210	-1866	94.04	0.512×10^1	0.928
600	52296	-3183	94.19	0.152×10^2	0.974
625	52554	-7810	94.61	0.473×10^3	0.999
750	52812	-14394	95.00	0.280×10^5	1.000

$$\Delta H^{\circ}R (298^{\circ}K) = 49,250 \text{ cal/g mole}$$

$$\Delta S^{\circ}R (298^{\circ}K) = 86.69 \text{ cal/g mole}$$

$$C_p = a + bT + cT^2$$

TABLE B

Catalyst Effectiveness and Reaction
Rate Distribution

T = 750°F, Conversion = 0.91

a_{min}	a_{max}	$f\Delta a$	ϵ	Δ	$r_{app} \times 10^8$
0.0070	0.0158	0.031	0.984	0.314	0.603
0.0158	0.0208	0.076	0.940	0.489	1.458
0.0208	0.0239	0.188	0.911	0.588	3.494
0.0239	0.0260	0.269	0.889	0.654	4.882
0.0260	0.0275	0.201	0.873	0.701	3.582
0.0275	0.0287	0.144	0.862	0.735	2.534
0.0287	0.0293	0.091	0.857	0.758	1.591

$$\text{Experimental } r_{app} = 1.749 \times 10^{-7}$$

$$\text{Calculated } r_{app} = 1.814 \times 10^{-7}$$

TABLE C

Minor Product*

T(°F)	Conversion Range	t (min)	A (%)	t (min)	A (%)
500	0.40-0.45	-0.21	0.01	1.33	0.04
540	0.45-0.65	--	--	1.32	0.03
540	0.65-0.75	-0.21	0.01	1.32	0.04
575	0.40-0.60	--	--	--	--
	0.65-0.70	-0.21	0.01	1.33	0.02
	0.75-0.85	-0.21	0.05	1.33	0.05
600	0.35-0.40	--	--	--	--
	0.40-0.45	-0.20	0.01	--	--
	0.45-0.55	--	--	--	--
	0.55-0.65	-0.20	0.01	1.33	0.02
	0.70-0.75	-0.20	0.02	1.34	0.03
	0.80-0.85	-0.22	0.05	1.38	0.05
700	0.45-0.95	-0.17	0.80	0.91	0.14
750	0.55-0.60	-0.77	0.01	-0.26	0.12
	0.65-0.70	-0.28	0.19	--	--
	0.75-0.80	-0.21	0.09	-0.33	0.35
	0.90-0.95	-0.46	0.86	-0.94	0.01
800	0.45-0.50	-0.27	0.20	--	--
	0.60-0.65	-0.29	0.34	-0.88, -0.78, -0.14	0.01
	0.75-0.80	-0.32	0.51	-0.16	0.01
	0.85-0.90	-0.36	1.12	--	--
	0.90-0.95	-0.42	1.83	-0.99, -0.89	0.01

* retention time relative to C_6H_{12} = t
 area percent from chromatogram = A

TABLE D

Mass Spectrometric Analysis of Gas Product (Gollob, 1977)

(Conversion = 84%, temperature = 600°F)

<u>Constituent</u>	<u>Volume Percent</u>
Nitrogen	1.8
Oxygen	0.10
Argon	0.009
Carbon Dioxide	0.008
Butene	0.16
Cyclohexane	0.23
Benzene	0.26
Toluene	0.0005
Unknown*	0.10
Hydrogen	balance

* An aliphatic hydrocarbon, possibly butane or methylpentane

FIGURE 1: CYCLOHEXANE CONVERSION VS WHSV

FIGURE 2: EXPERIMENTAL FLOW SYSTEM FOR BATCH KINETIC STUDIES OF GAS-PHASE CATALYTIC REACTIONS

LEGEND

- (M) BALL VALVE
- (N) NEEDLE VALVE
- (LP) LOW PRESSURE GAUGE
- (HP) HIGH PRESSURE GAUGE
- (T) THERMOCOUPLE

FIGURE 3: DISTRIBUTION OF PARTICLE SIZES

FIGURE 4: COMPARISON OF CALCULATED WITH EXPERIMENTAL
REACTION RATES

FIGURE 5: CATALYST TEST LOOP

FIGURE 6: CATALYST TEST LOOP: INSTRUMENTATION AND CONTROL DIAGRAM

FIGURE 7: HYDROGEN AND NITROGEN ADSORPTION APPARATUS

25 cm = 1 in
 — = capillary tubing