1966

Hydroisomerization of Normal Pentane Over a Zeolite Catalyst.

Philip Auburn Bryant

Louisiana State University and Agricultural & Mechanical College

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HYDROISOMERIZATION OF NORMAL PENTANE
OVER A ZEOLITE CATALYST

A Dissertation

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Doctor of Philosophy

in

The Department of Chemical Engineering

by

Philip Auburn Bryant
B.S., Louisiana State University, 1959
M.S., Louisiana State University, 1961
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ABSTRACT

A screening study of various zeolite catalysts has shown the unusually high hydroisomerization activity of synthetic mordenite. The isomerizing properties of this unique crystalline material have been investigated, using n-pentane as a reactant. For these studies, crystalline particles, 1-5 microns in diameter, were impregnated with a noble metal, pillared and crushed to approximately 0.60 mm. diameter. Typical hydroisomerization conditions were 550°F., 450 psig, 3.4 moles of hydrogen per mole of pentane, and a liquid hourly space velocity of 8 grams/hr. per gram of catalyst.

Experiments with superficial gas velocities ranging from 0.35 to 2.0 cm/sec have shown that fluid-to-particle mass transfer is not a limiting factor in the overall conversion process. The effect of temperature on the overall conversion rate, however, was substantial. The activation energy, of the order of 30 Kcal/gm-mole, compares favorably with values reported for this reaction on conventional large-pore catalysts. A series of experiments with compressed particle sizes ranging from 0.1 to 1.1 mm. have shown that diffusion inside the macropores is not a rate-limiting mechanism. Micropore diffusion inside the crystal structure was not investigated in a systematic way due to the unavailability of mordenite crystals with different particle size ranges.

The overall conversion rate was found to be independent of the concentration of the dispersed noble metal, indicating that the hydrogenation-dehydrogenation functions of the catalyst were not rate-controlling. The overall conversion rate was significantly influenced by the acidity of the cations in the crystalline lattice, indicating that the isomerization reactions taking place on these sites were rate-limiting.

The data from this study were correlated with a simplified model which assumed that the reaction mechanism could be described as a first order, reversible reaction between n-pentane and isopentane. The effects of increasing partial pressures of the three principal components, n-pentane, isopentane and hydrogen, were found to be compatible with the assumption of a "dual-site" catalytic mechanism. The integral-reactor data, taken over wide ranges of partial pressures, showed no significant differences between the dynamic "adsorption constants" of the three components, resulting in an apparent effect of total system pressure on the overall rate of reaction.

This study shows that chemical reaction rates inside such small-pore systems ($4-7\text{\AA}$) can be successfully correlated by conventional approaches to heterogeneous catalytic systems. However, the actual mechanisms taking place inside the "pores" are obviously very different from those taking place in conventional catalyst particles which can be characterized by a dynamic equilibrium between

gas-phase reactants and molecules adsorbed on "active sites,"
and in which the diffusion mechanisms are well-characterized by
bulk or Knudsen equations.

CHAPTER I

INTRODUCTION

The interest shown during the past two decades in the subject of pentane isomerization is evidenced by the large number of research programs, both industrial and academic, that have concentrated upon fundamental studies of the detailed mechanisms involved in this seemingly simple chemical reaction. This research, given impetus by the obvious commercial importance of higher-octane paraffin isomers, as opposed to the large quantities of lower-octane normal-paraffins normally found in refinery gasoline streams, has led to many advances in the areas of catalysis, both homogeneous and heterogeneous.

For a general study of the mechanisms of isomerization reactions, the pentane system holds many advantages, among them being the ease of handling the liquid feed and the fact that only two isomers are normally found in the reaction product. The latter leads to simplified analytical techniques and relatively simple mathematical methods of data analyses.

Isomerization reactions have recently been carried out through the use of solid "dual-function" catalysts, which have been prepared to accelerate the rates of two separate types of chemical reactions: dehydrogenation-hydrogenation reactions of paraffins, and olefinic isomerization reactions. The development of these catalysts for use in paraffin isomerization reactions has evolved

hand-in-hand with a better understanding of the reaction mechanisms, now generally considered to consist of three steps: dehydrogenation of a normal paraffin, isomerization of the resulting olefin, and a subsequent hydrogenation of the iso-olefin to an iso-paraffin.

Recently, the recognition of the catalytic activity of certain types of crystalline aluminosilicate materials led to important discoveries concerning the nature of zeolites, their three-dimensional structures, and the nature of the lattice bonding. Methods have been developed to prepare artificial zeolites having properties of symmetry and crystalline regularity unrivaled by their counterparts found in nature.

This dissertation consists of a study of the newly-discovered isomerization properties of solid catalysts made from the artificial crystalline aluminosilicate, mordenite. This zeolite has been found⁽¹⁾ to be about eight times as active, under normal process conditions, as the most active zeolite isomerization catalyst available at this time. This study has shed light on some of the controlling factors in the use of this new catalyst, has shown that the overall isomerization rate can be described by simplified equations of the type conventionally employed in heterogeneous catalysis, and has pointed out specific areas in these fields wherein our understanding of nature's mechanisms is in but a very early stage of development.

(1) During the course of this project research and also independently by research workers of The Shell Oil Company (U.S. Patent 3,190,939.)

CHAPTER II
LITERATURE REVIEW

A. Normal Pentane Isomerization

1. Introduction

The industrial importance of paraffin isomerization is primarily due to the fact that branched paraffin isomers perform more satisfactorily in internal combustion engines, as is evidenced by the octane numbers tabulated below. (67)

<u>Carbon Number</u>	<u>Component</u>	<u>Motor Octane Number</u>	<u>Research Octane Number</u>
4	n-Butane	89.1	94.0
	iso-Butane	97.0	102.1
5	n-Pentane	61.8	63.2
	iso-Pentane	89.7	93.0
6	n-Hexane	26.0	24.8
	iso-Hexanes	73.3-94.2	73.4-104.3
7	n-Heptane	0.0	0.0
	iso-Heptanes	46.4-101.3	42.4-112.1

For this reason, there has been a large incentive to convert the normal paraffins found in refinery streams to the corresponding isomers. This has prompted considerable research in the areas of paraffin isomerization, both with regard to catalysts and to mechanism studies of isomerization reactions. In order to simplify the systems under study, most exploratory work has been done with pure compounds, generally selected from the lighter paraffins. This particular research was carried out with normal

pentane, as it led to a relatively simple isomeric system, was easy to handle, and yielded products that could be analyzed with a minimum of difficulty.

2. Pentane Equilibrium Data

There are but three isomeric pentanes: normal pentane, boiling at 97.0°F; isopentane (2-methylbutane), boiling at 82.2°F; and neopentane (2,2-dimethylpropane), boiling at 49.1°F. The latter, the most symmetrical of the three, is not normally found in nature, and has not been observed as an isomerization product of either of the other two. The thermodynamic equilibria, as calculated from API Project 44 free energy data⁽⁷¹⁾, are shown below:

For uncatalyzed mixtures of the pentanes, the rate of isomerization is immeasurably slow. For example, "pure grade" samples of pentane isomers have been left standing for years with no perceptible change. As will be brought out later, certain catalysts will accelerate the isomerization reactions to such an extent that equilibrium yields can be approached quite easily in the chemical industry. However, even with the "most active" isomerization catalysts known, no neopentane has ever been produced from normal pentane, nor from isopentane. This was also the case in this study. Theories advanced for this will be discussed in section 3 of this chapter. For this reason, the isomerization equilibria were analyzed on a neopentane-free basis in this dissertation, as has been done in previous pentane isomerization studies.

The equilibrium curves for the isomeric pentane system presented above were calculated from API Project 44 free energy data.⁽⁷¹⁾ Although this system would appear to be relatively simple, especially on a neopentane-free basis, some discrepancy has been noted in published experimental data. Figure 2 (page 6), similar to one presented by Block⁽⁸⁾, summarizes the reported results to date.

The upper curve represents the equilibrium relationship, as calculated from API Project 44 free energy data, covering the range from 100°F to 900°F. Early low temperature data from Schuit, et al.⁽⁷³⁾ and Van Voorthuijsen⁽⁸⁷⁾ are shown, as are early data by Pines, et al.⁽⁶¹⁾ Data by Evering and d'Ouville⁽²⁵⁾ are indicated in the 200-400°F temperature range.

Figure 2. Experimental Equilibrium Data for Neopentane-Free System

Experimental equilibrium values at 850°F by Belden, et al.⁽³⁾ and from the National Bureau of Standards⁽⁷⁰⁾ are almost 8% below the curve calculated from API Project 44 free energy data. A more recent data point by Hutchins⁽³⁷⁾ is also significantly below the calculated Project 44 curve. The data of Rabo, et al.⁽⁶⁵⁾ are shown at 662°F. The lower curve, extending from 100 to 900°F, is a calculated curve by Asselin of Universal Oil Products Company⁽¹⁸⁾. This curve was forced through the indicated data point at 716°F, and extrapolated by API Project 44 enthalpy and heat capacity data.

The experimentally-determined equilibrium compositions are considered to be more accurate, in that they were determined directly, under precisely-controlled conditions, usually by approaching the equilibrium composition from both sides. The equilibrium compositions calculated from the free energy data result from calculations involving small differences between large numbers, and therefore are subject to relatively large percentage errors. The relationship used in the analysis of the data from this dissertation research is given by the solid curve drawn through the most recent data. As will be discussed later, this curve was represented by a simple empirical equation in the relatively narrow temperature range under investigation (500-650°F.)

3. Isomerization Process Studies

a. Aluminum Halide Catalysts

Although the isomeric forms of pentane have been known for many years, the first reported data on the preparation of isopentane from normal pentane did not appear until 1936, in a paper by Glasebrook, et al.⁽²⁹⁾ They reported both liquid and vapor-phase experiments in which aluminum chloride and aluminum bromide were used as catalysts.

This type of catalyst system was used extensively for about fifteen years. During this time, it was found that hydrogen could be used effectively to suppress coking and unwanted side reactions.^(26,40,73) These studies indicated that coking was severe at low hydrogen partial pressures, while above a critical hydrogen partial pressure, the presence of hydrogen retarded the isomerization.

The effects of slight traces of impurities⁽⁵⁰⁾, particularly benzene, led to increased speculation concerning the mechanisms involved in the isomerization process. Various details were proposed, but most investigators accepted the postulate that the reaction proceeded stepwise, requiring the existence of C_5 carbonium ions as intermediates.

During the war years, isomerization was used extensively to upgrade gasoline, with several major refining companies involved in this effort. All the production facilities were based on variations of the aluminum halide process, which could be operated at

relatively low temperatures (80-250°F), thus taking advantage of favorable equilibrium conditions. This process, however, had three serious disadvantages: (1) the catalyst system was extremely corrosive in the presence of even minute amounts of water, (2) it was non-recoverable after being deactivated, and (3) a sludging complex, which led to process problems, was generally formed by the mixture of aluminum chloride and hydrocarbons.

The sludging problem was later obviated by the introduction of catalytic systems composed of solid hydrogenation catalysts which were impregnated with aluminum chloride. This combination led to a packed-bed process that was somewhat less active than the "sludge" process, due to the smaller amounts of aluminum chloride used. Typical operating temperatures ranged from 250-375°F.

b. Supported Noble Metal Catalysts

(1) Early Solid Supports

The combination of a cracking component (silica-alumina base) with a hydrogenation component (dispersed metal) was used as a "dual-function" catalyst in petroleum cracking processes. Ciapetta and Hunter⁽¹⁷⁾ used this catalyst system for the isomerization of saturated hydrocarbons. These initial vapor-phase studies were made with nickel on silica-alumina catalysts, which proved to be quite active at 24 atmospheres in the range of 590-770°F. In order to suppress coking, hydrogen was used at a 4/1 molar ratio. The results of these experiments indicated that a carbonium-ion mechanism was involved in the pentane isomerization

process, and the controlling step was postulated to be the dissociation of a C-H bond on a metal (hydrogenation) site. As was the case in earlier investigations, no neopentane was observed in the products. No alkylation was observed, as opposed to the aluminum-halide processes, where significant amounts of high molecular weight products were obtained.

Published simultaneously with the above work was an article by Mills, et al.⁽⁵⁶⁾, which suggested that the isomerization process consisted of three steps on these dual-function catalysts. They postulated the existence of two independent types of sites. They inferred that the reactant was first dehydrogenated to an olefin at a "dehydrogenation" site and the olefin isomerized at an "isomerization" site, yielding the isomerized, saturated product. The same type of site would, of course, serve for both hydrogenation and dehydrogenation.

This theory was tested by Weisz and Swegler⁽⁹⁵⁾ who prepared a "dual-function" catalyst by mechanically mixing particles of silica-alumina (isomerizing component) with particles composed of platinum (dehydrogenation component) supported on an inert base. Provided the particles were small enough (less than 1 micron), this mixture was as active as were catalysts prepared with both catalytic functions on the same particle. The individual types of particles showed essentially no activity when tested alone. Hindin, et al.⁽³³⁾ used mechanical mixtures of such "single-function" catalysts for the dehydroisomerization of methylcyclopentane to benzene. These experiments demonstrated that the two types of

sites act independently, and that the reaction intermediates are able to diffuse, through the gas phase, from one type of catalytic site to another.

Sinfelt, et al.⁽⁷⁶⁾ presented data on the hydroisomerization of n-pentane over platinum on alumina catalyst which supported the postulated 3-step mechanism by which paraffin isomerization proceeds via an olefin intermediate. This stepwise mechanism, as discussed above, was represented by the equilibrium relationships below:

The isomerization of an olefin via a carbonium ion mechanism is itself considered⁽⁴²⁾ to be a complex mechanism, also consisting of three steps:

In an extensive study made by Clark, et al.⁽¹⁹⁾, molybdena-impregnated silica alumina catalysts were used to isomerize n-pentane at relatively low hydrogen/pentane ratios. These runs, made at relatively high temperatures (860°F) showed significant effects of both hydrogen partial pressure and total pressure on the overall isomerization rate. Runs were also made with pure molybdena and with pure alumina, yielding very low conversion in both cases. The combination of the two produced a catalyst yielding a high conversion with a high ultimate yield of isopentane, supporting the step-wise mechanism that had been proposed.

Hutchins⁽³⁷⁾ investigated the hydroisomerization of pentane on a platinum-alumina catalyst. Significant results of this study were:

1. n-Pentane isomerizes more readily than isopentane.
2. Isomerization rates decrease steadily with total pressure.
3. Isomerization rates decrease as hydrogen partial pressure is increased.
4. Isomerization rates increase and level out as pentane partial pressure is increased.
5. Rapid catalyst deactivation was noted at low hydrogen partial pressures.

6. The initial isomerization rates were correlated by an equation compatible with the assumption that the rate controlling step was the structural rearrangement of a weakly adsorbed olefin on the alumina sites of the catalyst.

An alumina base, impregnated with platinum, was also used by Lyster, et al.⁽⁴⁸⁾ to study the isomerization of n-pentane. These data were successfully correlated by a rate equation consistent with the assumption that the isomerization rate controlled the overall process, and that the isomerization reaction took place via a "dual-site" mechanism on the catalyst surface. The results of this study are also compatible with the "three-step" mechanism. Presumably, the first and third steps (dehydrogenation of the paraffin and hydrogenation of the olefin) occurred on the impregnated metal sites; and the second step (isomerization of the olefin) occurred on the acidic sites of the catalyst base.

More recent studies by Owen, et al.⁽⁸⁴⁾ with a hydrogen chloride-activated dual-function catalyst have also indicated that the same three-step mechanism was involved in the overall isomerization process. These studies were carried out with 0-0.6% platinum on $B_2O_3-Al_2O_3$ mixtures. The use of this platinum impregnated silica-boria mixture, when activated by hydrogen chloride, led to a catalytic system that was somewhat more active than were previous "dual-function" catalysts in that relatively high conversions could be attained at slightly lower temperatures, e.g., 600°F.

(2) Zeolite Supported Catalysts

The unique properties of certain crystalline aluminosilicates known as "zeolites," have been shown to be conducive to a remarkable degree of catalytic activity. Their regular crystalline structure, which occurs in various forms and which can be impregnated by "foreign" catalytic components, allows them to be used as selective catalysts for various chemical reactions, among which is the isomerization of saturated hydrocarbons. The next section of this dissertation will be devoted to a discussion of the structural properties of zeolites.

In an early publication in this field⁽⁶⁵⁾, Rabo and co-workers of the Linde Company described the use of a palladium-impregnated zeolite for the isomerization of n-pentane and n-hexane. As this publication represented an innovation in catalytic isomerization processes, no specific data were given as to the type of zeolite used in these studies. The temperatures required were intermediate between those required for the "high temperature" (700-850°F) catalysts (supported precious metals), and those required for conventional "low temperature" (200-250°F) catalytic systems (e.g., those using AlCl_3 as the key component). The studies with the zeolite catalyst were carried out between 650 and 700°F with a hydrogen/pentane ratio of 3/1 and a liquid pentane space velocity of 2. Operations were reported only at 450 psig.

As was noted in the above-mentioned publication, the zeolite catalyst was seen to be relatively insensitive to water.

It was coke-resistant, with good sulfur tolerance and showed a long life. It required no "catalyst activator."

In a more recent paper, Rabo and Schomaker⁽⁶⁶⁾ reported on a catalyst composed of a "Y-zeolite" upon which platinum had been cation-exchanged, rendering a true atomic dispersion within the crystal structure. This catalyst was used for the isomerization of n-hexane, and was shown to be much more resistant to sulfur poisoning than a conventional palladium-impregnated Y-zeolite.

This type of catalyst system, which required no acids and formed no sludge, had a considerable advantage over the aluminum halide processes in that corrosion and sludging problems were obviated. It was an improvement over previous dual-function catalytic systems in that its higher activity allowed operation at a lower temperature. However, even up to the present time, the goal of a catalyst with the desirable process features of the solid, dual-function system and the high activity of the aluminum-halide system has not been attained.

The use of the crystalline zeolite, mordenite, as described in this dissertation, represents a significant improvement in isomerization catalysis, and a step toward the above goal. As part of this research, the exceptionally high isomerization activity of mordenite-based catalysts was discovered. As will be discussed below in more detail, this catalyst system is approximately eight times as active as the best commercially-available zeolite catalyst.

B. Crystalline Zeolites

1. Introduction

The zeolites compose a family of over 40 different crystalline minerals consisting chiefly of silicon, aluminum, and oxygen. These minerals generally contain 10-20% entrapped water, together with sodium and calcium ions. They occur most commonly in cavities and veins in basic igneous rocks such as basalt and less frequently in acid rocks such as granite. Natural zeolites have been observed in many colors, from colorless (even transparent or translucent) to pink, red, green, gray and brown. They have relatively low densities, usually 2.0 to 2.4, and are relatively soft (hardness ranging from 3.5 to 5.5 on the Mohs scale).

Most zeolites decompose rapidly upon treatment with acid, yielding a gelatinous mass. This decomposition is accompanied by a generation of heat, and is responsible for the general name of this group of minerals. The name "Zeolite," is derived from two Greek words, "to boil" and "a stone." Although initially used for pigments, and later for "ion-exchange" applications such as water-softening, the unique properties of these minerals have allowed them to be successfully used in adsorption applications, and more recently as catalysts in the promotion of various chemical reactions.

2. General Structural Properties of Zeolites

a. General

Zeolites have been divided into three classes as described by Wells⁽⁹⁷⁾. In the first, $(\text{SiAl})\text{O}_4$, tetrahedra are linked into relatively open three-dimensional frameworks consisting primarily of interlocked 4- and 6-membered rings. In the second group, there is evidence of parallel sheets of tetrahedra. The third group consists of "cross-linked" chains of tetrahedra and are called "fibrous zeolites." This dissertation will be concerned primarily with representatives of the first group.

b. Faujasite

Faujasite, an important member of the first group, will be used as an example in describing a typical structural pattern. As shown in Figure 3 (page 18), basic 6-membered rings of Si or Al atoms are interconnected to form a regular three-dimensional structure. In the figure, each vertex represents a silicon or aluminum atom. These atoms are not directly connected together, but are linked by relatively large "bridging" oxygen atoms, as in Figure 4. Schematically, each "edge" in Figure 3 can be thought of as representing an oxygen atom. These three-dimensional structures are called "sodalite units."

If four of the hexagonal planar faces of the polyhedra described above are connected together (by the "bridging" oxygen atoms), each polyhedron will be in contact with four others, forming a three-dimensional structure as sketched in Figure 5. This

same pattern, extended in all directions, results in an open, "cage-like" network such as the one sketched in Figure 6. In this sketch, the "nodes" represent sodalite units connected together by the set of six oxygen atoms.

In the natural state, the interstices of these three-dimensional structures are normally occupied by water molecules and by positive ions such as sodium or calcium. These latter ions are necessary to balance the electrical charge, since the framework, as described above, would have one unit of negative charge for each aluminum atom. In most catalytic applications, the original ions are replaced by other positive ions, and the water is driven out of the structure by a calcination operation.

c. Other Zeolites

Although members of the zeolite family are similar in many respects, they can differ individually in the relative amounts of silicon, aluminum and oxygen atoms, in the spatial arrangement of the atoms, and in the metal cations present within the structure. A general structural formula,

can be applied to the members of the family⁽¹²⁾. "Me" is a metal cation, whose positive charge is "N." "M" represents the number of molecules of water that are associated with one unit cell in the zeolite structure. This number can vary over a wide range. Breck,

in an excellent report on crystalline zeolites⁽¹²⁾, gives examples of zeolites with M ranging from 15 to 264. The table on page 21, abridged from the above reference, tabulates the properties of some of the more important zeolites in catalytic applications.

d. Synthetic Zeolites

The natural zeolites, while in many cases plentiful, normally suffer from impurities and "stacking faults" in their crystalline lattices, which render them unsuitable for many chemical applications. The search for methods of synthesizing these minerals was given impetus by the potential industrial applications of the new family of minerals. Research workers at Linde and Norton have succeeded in producing commercial quantities of synthetic zeolites having a high degree of uniformity and purity. The aluminosilicate crystals, generally 1-5 microns in diameter, are crystallized from "gels"--typically prepared from aqueous solutions of sodium aluminate, sodium silicate, and sodium hydroxide.

e. Zeolites as Catalytic Materials

The unique structural properties of zeolite crystals have enabled chemical researchers to take giant strides toward "selective catalysis," on catalytic processes which can be designed for certain types of reactions while eliminating or greatly reducing unwanted side reactions. For example, zeolite-based catalysts have found many applications in petroleum refining⁽⁵¹⁾, including applications in catalytic cracking, isomerization, naphtha reforming, alkylation, hydrogenation, hydrodesulfurization, and hydrodenitrogenation.

TABLE I
PROPERTIES OF SEVERAL IMPORTANT ZEOLITES

Name	Source	Composition	Density (a) gm/cc	Void Volume (b) cc/gm	Aperture Size, Å
Faujasite	Germany	$(\text{Na}_2, \text{C}_2\text{M}_8)_{60} \left[(\text{AlO}_2)_{60} (\text{SiO}_2)_{132} \right] \cdot 260 \text{ H}_2\text{O}$	1.31	0.35	8
Zeolite A	Synthetic	$\text{Na}_{12} \left[(\text{AlO}_2)_{12} (\text{SiO}_2)_{12} \right] \cdot 27 \text{ H}_2\text{O}$	1.33	0.30	4.2
Zeolite X	Synthetic	$\text{Na}_{86} \left[(\text{AlO}_2)_{86} (\text{SiO}_2)_{106} \right] \cdot 264 \text{ H}_2\text{O}$	1.29	0.36	8
Zeolite Y	Synthetic	$\text{Na}_{56} \left[(\text{AlO}_2)_{56} (\text{SiO}_2)_{136} \right] \cdot 264 \text{ H}_2\text{O}$	1.30	0.35	8
Mordenite	Idaho	$\text{Na}_8 \left[(\text{AlO}_2)_8 (\text{SiO}_2)_{40} \right] \cdot 24 \text{ H}_2\text{O}$	1.72	0.14	6.6
Mordenite	Synthetic	$\text{Na}_8 \left[(\text{AlO}_2)_8 (\text{SiO}_2)_{40} \right] \cdot 24 \text{ H}_2\text{O}$	1.72	0.14	6.6
Erionite	Oregon Nevada	$(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_{4.5} \left[(\text{AlO}_2)_9 (\text{SiO}_2) \right] \cdot 27 \text{ H}_2\text{O}$	1.50	0.21	3.6 x 5.2

(a) Calculated for dehydrated zeolite.

(b) Based on water contained per gram of dehydrated crystal.

The "cage," or "sieve-like" structures of these materials have been briefly described above. As can be noted from Table I (page 21), the openings into the three-dimensional structures and the interconnected voids within them are of the same order of magnitude as "normal" molecules. Thus, for a given type of crystal, there is an important "critical" molecular size. Molecules below this size (determined by the cage openings) can enter into the interstices of the crystal structure and can move about at random in an environment characterized by unusually strong electrostatic fields that tend to strain and distort "guest" molecules. These fields are more than sufficient to polarize the C-H bonds in hydrocarbon molecules, giving them a high degree of reactivity. Molecules larger than this "critical size," of course, cannot enter the crystalline lattice, and will not come in contact with the highly reactive "sites" inside. These "sieve-like" properties are responsible for the general term "molecular sieves."

These "active sites" within the structure can take several different forms, depending on the charge distributions in the neighborhood of the various structural atoms. The types of "sites" or their relative strengths can be modified, for example, by exchanging the original cations for other positive cations, such as magnesium ions, or even positive hydrogen ions. Thus, the basic "molecular sieve" offers a powerful catalytic tool, one which is just beginning to be understood and exploited.

3. Properties of Mordenite

a. Natural Mordenite

Mordenite is one of the more dense crystalline zeolites, having a specific gravity of 1.72 in the dehydrated form. Its composition, given by the general formula $\text{Na}_8(\text{AlO}_2)_8(\text{SiO}_2)_{40} \cdot 24 \text{H}_2\text{O}$, shows a high Si/Al ratio (5/1) and a correspondingly low cation content. In its natural state, mordenite has been reported in Nova Scotia⁽²⁰⁾, Italy⁽²⁰⁾, Idaho⁽¹²⁾, Wyoming⁽²⁰⁾, and in the southern part of the Soviet Union⁽⁴⁶⁾. Recently, mordenite has been found in Nevada⁽⁵⁷⁾ in a deposit estimated to be of the Early Pliocene Age (2,000,000–8,000,000 years old).

b. Synthetic Mordenite

As noted in a recent patent*, synthetic mordenite has been prepared by the Norton Company by heating 240 parts of amorphous SiO_2 , 500 parts of 28% sodium silicate solution, and 100 parts of sodium aluminate at 150°C for 24 hours. This synthetic material has a much higher purity and crystalline uniformity than does the natural material. The mordenite used in this research was obtained as 1–5 micron particles from Norton and subsequently pilled at Esso Research Laboratories in Baton Rouge, Louisiana.

c. Crystalline Structure of Mordenite

The crystal structure of mordenite is somewhat different from that of the "typical" zeolite (faujasite) discussed earlier in this chapter. This particular crystalline pattern is sketched in

* Brit. 983,756

Figure 7 (page 25). The figure shows a cross-section view, with the points of intersection representing silicon or aluminum atoms and the lines oxygen atoms. This arrangement, essentially planar, is repeated at regular intervals, forming a dense three-dimensional structure (Figure 8, page 25) characterized by the presence of parallel "tunnels." These elliptical "tunnels," with major diameter of $6.95\text{\AA}$ and minor diameters of $5.81\text{\AA}$, traverse the entire crystal. They are interconnected by small openings, also approximately elliptical with major and minor diameters of 4.72 and $3.87\text{\AA}$, respectively.

The catalytic cracking activity of synthetic mordenite has been the subject of several research programs during the past five years.⁽¹⁾ The extremely high cracking activity and unusual selectivity properties of various cation-exchanged forms, especially the hydrogen form, have served to stimulate more detailed programs in this area and also to suggest that this material may have potential applications in other types of conversion processes.

d. Catalytic Properties of Mordenite

Very recently (in 1965, during the course of this research), a patent* was issued which reported the use of mordenite-based catalysts in a hydrocracking process. In hydrocracking, "dual-function" catalysts have been required, since the overall operation consists of a complex series of cracking and hydrogenation reactions requiring two types of sites.⁽⁵⁾ These sites have been described as (1) "acidic sites" which are required for cracking reactions, and

* Belg. 660,897

(2), "metallic sites," which are required for the hydrogenation of the olefinic products of the cracking reactions. The preparation of these catalytically active mordenite-based dual-function catalysts has been described as follows.*

The synthetic mordenite crystals are ion-exchanged with a solution of NH_4OH or NH_4Cl to replace the sodium cations with NH_4^+ cations. This exchange operation is followed by an "impregnation" step in which the crystals are soaked in a solution of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, allowing the palladium and chloride ions to penetrate into the sieve structure. The water is dried off, leaving the palladium complexes inside the sieve structure. A subsequent calcination operation in air drives off H_2O , NH_3 , NH_4Cl and HCl , leaving simpler palladium compounds (presumably palladium chloride or oxide) inside the sieve. Actually, the subsequent process conditions of normal hydrocracking operations are such that the palladium compounds are rapidly reduced to palladium metal with the evolution of HCl and H_2O . The final catalyst, therefore, consists of dehydrated H-mordenite crystals with finely-dispersed aggregates of palladium (perhaps even dispersed palladium atoms).

* Brit. 983,756

CHAPTER III

EXPERIMENTAL APPARATUS

A. General

The experimental equipment used in this project was, for the most part, constructed at the Esso Research Laboratories in Baton Rouge, Louisiana, and transported to Louisiana State University.* The reactor system was mounted on a steel frame, three feet wide, three feet deep, and six feet high, as sketched in Figure 9 (page 28). This "palletized" unit was placed under a steel walk-in hood, as sketched in Figure 10 (page 29). Details of the process system are given below.

B. Flow Diagram of System

Figure 11 (page 30) is a simplified diagram of the entire system. The catalyst was contained in a vertical, packed bed reactor which was heated in a fluidized sand bath. Typical process conditions were 550°F and 450 psig. In most cases, 15 cc catalyst charges were used.

Feed streams consisted of liquid n-pentane and hydrogen gas. These streams were mixed and introduced into a preheat coil in which the pentane was vaporized and the mixed gases brought to

* During the period of time that the apparatus was being constructed, the author was an employee of Esso Research Laboratories, and was responsible for coordinating the design and construction of this equipment.

Figure 11. Flow Diagram of Experimental System

reactor temperature. A calibrated positive displacement feed pump was used for the pentane, while the hydrogen flow was adjusted by a rotameter and held constant with a differential-pressure regulator. As is shown in Figure 11, a nitrogen supply was also available. This was used to purge the system before each run.

The gas-phase reactor product was passed through a cooling coil which served to reduce the temperature of the stream in order to protect the back-pressure regulator. The temperature drop due to the sudden expansion across the pressure regulator quite often caused a portion of the pentanes to condense. A heating coil was provided to vaporize this condensate and bring the product gases up to room temperature. The gases were then passed through a water saturator and a wet-test meter. In the event that the product composition was such that condensate would still be present at room temperature, an ice-bath was available to condense a large portion of the pentane and reduce the dew point of the off-gas stream to well below room temperature.

Product samples could be taken of the off-gases, which were measured in the wet-test meter during the "material balance" period. A liquid accumulator was available to contain the condensed product during the material balance.

C. Details of Reactor

The reactor itself was constructed of Inconel, and held up to 40 cc of catalyst. Figure 12 (page 32) is a simplified sketch of the reactor system.

Figure 12. Details of Reactor System

The reactor body was constructed of 1/2" schedule 80 Inconel pipe. Micro-metallic frits were placed above and below the catalyst particles. A temperature-compensated coupling was provided to allow the reactor to be opened for catalyst loading and discharge. A pressure-tight seal was made with a steel O-ring which was replaced after every run.

Three thermocouples were placed inside the catalyst bed for precise temperature control. These were passed through the reactor wall through Conax fittings. The thermocouple tips were 1/16" diameter, and protruded 1/4" into the catalyst bed.

The feed line, as indicated by the sketch, entered through the top after making several turns around the reactor. This additional length of line was provided to insure that the feed would enter the catalyst bed as a vapor at the proper temperature.

The reactor was constructed such that it could be easily connected into the system after being charged with catalyst. One-quarter inch stainless steel "Quick-Connects" were used for this purpose.

D. Details of Reactor Heating System

In order to control the temperature as precisely as possible, the reactor was immersed in a bed of fluidized sand.* This fluidized bed was heated by electrical strip heaters placed

* Actually silica-alumina particles ($\sim .05$ mm diameter).

on the outside of the walls, beneath two inches of insulation. The bed itself was 4-1/2" in diameter and 21" high. Metered air was introduced through a porous frit across the bottom. A 4" disengaging zone was provided above the sand level. The air was discharged through a cyclone separator, which returned the fine particles to the fluidized bed.

The strip heaters were controlled by two electrical circuits. Six 500-watt heater elements were placed around the bed, three on each circuit. One circuit was controlled manually by a rheostat. This was adjusted to provide most of the required heat input. The maximum input of the second set could also be controlled by a rheostat. The electrical input to this second set was controlled by a temperature-indicator-controller which sensed the reaction temperature. This unit was used to control the temperature precisely at a given point ($\pm 2^{\circ}\text{F}$). The actual temperature data were taken by a Leeds & Northrup temperature-indicator.

E. Feed Systems

1. n-Pentane

Liquid n-pentane (stored over 13X sieve particles to remove impurities) was fed by a precision, high-pressure Ruska pump. Liquid was forced from a 250 cc reservoir by a piston which was driven by a synchronous motor through an adjustable gear train. Flow rates of pentane were selected by manually inserting the appropriate reduction gears. Twenty-four different flow rates, ranging from 2 to 240 cc/hr, were available and were reproducible to within 0.15%.

Figure 13 (page 36) shows a simplified diagram of the liquid feed system. The pump reservoir was loaded from a glass buret, after which the air was driven out of the vent by manually advancing the piston. Liquid leaving the pump passed through an 0.018" i.d. capillary tube into the mixing tee, through which it was introduced into the reactor. The capillary tube actually extended six inches below the sand level in order to allow the pentane to be sprayed into hot flowing hydrogen, thus assuring that vaporization would take place well downstream of the cool feed lines, preventing any condensate from forming and backing up in the hydrogen line.

2. Hydrogen

Dry, electrolytic hydrogen was fed from a cylinder and adjusted by a Fischer-Porter rotameter. Before each run, the flow rate of hydrogen was calibrated by a wet-test meter. This was done after pressure-testing the system, and before liquid pentane was introduced. The flow rate of hydrogen was stabilized by a differential pressure regulator which maintained a constant pressure drop across the regulating valve.

By the use of two downstream regulators, the pressure in the hydrogen feed system was reduced from cylinder pressure (maximum 2300 psig) to the desired pressure at the rotameter. This rotameter pressure was normally maintained at 30-50 psi above the operating reactor pressure. A safety valve, set at 500 psig, prevented the hydrogen pressure from exceeding the published maximum allowable rotameter pressure.

In order to remove any traces of oxygen or water, the hydrogen was passed first through a bed of platinum-on-alumina particles, followed by a bed of indicating Drierite. Periodic inspection of the Drierite showed no visible traces of moisture.

F. Product Recovery and Sampling Systems

The reactor products were passed through a water-cooled heat exchanger and then through a Grove "Mity-Mite" upstream pressure regulator which was adjusted to maintain the reactor pressure at the desired level. This pressure reduction caused some cooling of the product stream. The water-cooler was adjusted to further reduce the temperature to below 300°F, as the pressure-regulator was rated at 350°F maximum. For mixtures rich in pentanes, the expansion across the regulator (essentially isenthalpic) resulted in a cooling of the product stream to well below ambient conditions (70-80°F). In some cases this resulted in a partial condensation of the hydrocarbons. A short heating coil attached to the sand-bath insulation was sufficient to bring the temperature back above 70°F and re-vaporize any condensate. Since all of the runs in this study were made at H_2/C_5 ratios above 0.7 moles of hydrogen per mole of pentane, no further condensation took place at room temperature. Thus, the entire product was taken off as a gas.

An ice-water bath was available for intentionally condensing some of the pentanes out of the gas stream in case the dew point of the reactor products happened to be above room temperature, but as was noted above, this was not used in this study of pentane hydroisomerization.

A continuous gas sampler (Figure 14, page 39) was used to obtain a representative sample during the "material balance" period. This was simply a 300 cc glass reservoir, initially filled with water.* A micro-metering valve was used to allow a continuous flow of gases into the reservoir, slowly displacing the water as the run progressed.

The flow of product gases (normally 4-5 SCFH) was measured by a wet-test meter, preceded by a water saturator.

G. Analytical Systems

Analyses of the product streams were carried out with a F&M Model 810R dual-column gas chromatograph. A 20-foot hexamethyl phosphoramide column, maintained at 25°C, was used for the separation of the hydrocarbon components. A 30/70 ratio of substrate/solids was used. A typical chart is shown in Appendix C, along with a detailed discussion of the calibration of the instrument, and a comparison with mass spectrometer analyses.

H. Safety Considerations

As the hydroisomerization reactions were carried out in the presence of hydrogen gas at elevated temperatures and pressures, the following special precautions were taken to insure safe operation of the entire system.

- The laboratory, about twenty feet square, was equipped with two fire extinguishers, an eye-wash fountain, and an emergency exit.

* MgSO_4 was added to reduce the H_2O vapor pressure.

- Gas cylinders were located outside of the building.
- Quick shut-off valves for the gas feed systems were located outside the hood, near the emergency exit.
- A fire blanket and another fire extinguisher were located in the hall immediately outside of the door.
- A 3000 cfm exhaust fan, built into the steel hood, was kept operating during all experimentation.
- Sliding safety-glass panels were used to close the hood* during runs.
- All electrical devices inside the hood were "explosion-proof," and met industrial Class I, Division 2 standards.
- Electrical circuit breakers for all power in the laboratory were located immediately outside of the door.

* Except for a 6" space at the floor to allow for an upward draft.

CHAPTER IV

STUDIES OF REACTOR FLOW PATTERNS

A. Introduction

The objective of this study was to characterize the flow patterns in the tubular reactors used in this research. A quantitative description of these flow characteristics was necessary before fundamental reaction rate constants could be calculated from the average conversion in the reactor effluent.

Tracer test methods were used to obtain these data. After an injection of a pulse of tracer at the reactor inlet, the concentration of tracer in the reactor effluent stream was monitored by a gas-ionization detector. Concentration vs. time curves obtained in this manner were used to estimate the amount of internal mixing (or "eddy diffusion") and to correlate this with the properties of the system.

These studies were carried out at the Esso Research Laboratories, shortly after the construction of the reactor systems.

B. Summary

Tracer tests, made with two types of packing, showed a very close approximation to plug flow. These data fitted an "eddy diffusion" model very well, showing Peclet numbers ranging from 40 to 273 under the conditions tested. The data also agree very well with a published correlation. Extrapolation of these data shows

that flow patterns closely approximating plug flow will result in actual operation of the units.

During these characterization studies, several additional results were obtained:

1. The recently published correlation of Bischoff⁽⁷⁾ was found to be reliable in predicting data in these small reactors.
2. A method of determining Peclet numbers from the geometry of tracer test curves was developed. While not a substitute for least squares curve fitting, it does allow more rapid estimation of Peclet numbers.
3. A quantitative chart for conveniently predicting conversions in non-ideal (diffusion model) reactors was drawn up. This is simply a plot of published equations, put in a more usable form.

C. Discussion

1. Experimental Procedure

As noted earlier, the reactor was constructed of 1/2" schedule 40 Inconel pipe, with an 8" packed space between micro-metallic frits. Two gas ionization detectors⁽⁴⁷⁾ were used, one at the reactor inlet and one at the outlet. Hydrogen was used as a carrier gas with argon as tracer.

2. Experimental Results

In general, the experimental data consisted of a strip recorder chart showing the tracer concentration at the inlet and outlet as a function of time, together with a record of the type of

packing used and the volumetric flow rate of the carrier gas.

Detailed data are presented in Table II (page 44). The following variables were derived from the tracer test curves:

p = the width of the input pulse (seconds)

at 1/2 its peak height

S = the width of the output pulse (seconds)

at 1/2 its peak height

U = the interval of time (seconds) between

the input peak and the output peak.

t_h = "nominal holding time"

= void volume/volumetric flow rate.

$S^* = S/t_h$

$U^* = U/t_h$

Peclet number (P) = a measure of the ratio of the directed motion of the bulk stream to the random motion in the mixing "eddies."

Re_p = particle Reynolds number.

d_p = particle diameter

L = length of catalyst bed

These variables were used in a preliminary analysis of the data. (Figure 15, page 45) shows the input and output traces for five selected runs.

TABLE II
TRACER TEST DATA

Run No.	Packing	Flow cm ³ /min	"U" sec	"S" sec	"p" sec	U/S	Peclet Number		Re _p	$\frac{L}{P_d}$
							Estimated*	Calculated**		
1	None	25	86	76	3.0	1.13	13.7	13.1		
2	"	25	84	78	3.0	1.08	12.2			
3	"	25	86	96	4.0	0.895	8.1			
4	"	25	97.7	68	4.0	1.43	23.0			
5	"	33	57	50	2.0	1.14	14.0			
6	Fine	35.6	52.9	27.4	0.4	1.93	40		0.0159	76.9
7	"	88.8	24.0	8.4	0.14	2.86	89		0.0397	34.6
8	"	88.8	22.5	8.6	0.12	2.62	75	62.5	0.0397	41.0
9	"	179	12.4	3.4	0.1	3.65	142		0.0800	21.6
10	"	179	12.5	3.3	0.03	3.78	152		0.0800	20.2
11	"	288	8.2	1.6	0.1	5.12	273		0.129	11.2
12	"	288	8.4	1.8	0.1	4.64	230		0.129	13.4
13	"	288	8.4	1.7	0.02	4.94	260	225	0.129	11.8
14	Coarse	303	4.64	1.4	0.2	3.3	119		1.97	1.33
15	"	303	4.00	1.3	0.2	3.07	102		1.97	1.55
16	"	385	3.62	1.0	0.16	3.62	141	128	2.51	1.12
17	"	96.8	15.0	6.6	0.7	2.28	56	40.6	0.63	2.83
18	"	96.0	15.0	6.4	0.7	2.35	60		0.625	2.74
19	Reactor Re-	129	0.76	0.76	0.74	1.0				
20	moved from	176	0.54	0.52	0.48	1.04				
21	System	469	0.16	0.18	0.14	0.89				

* Using Figure 18 (page 50).

** Using least squares fitting of analytical solution to output curve to actual experimental curve.

3. Preliminary Data Analysis

The tendency for the system to approach plug flow with increasing flow rate is shown in Figure 16 (page 47), where the "peak sharpness" (the ratio U/S) is plotted vs. flow rate of carrier gas. The fine packing (cracking catalyst with a 50% cut size of 0.053 mm) resulted in a better approach to plug flow than the coarse packing (crushed beads, screened between 14-35 mesh; 50% cut size of 0.79 mm), as would be expected. The empty reactor showed a very low "sharpness ratio." ($\frac{U}{S}$ = zero corresponds to perfect mixing.)

Figure 16 also shows a scale entitled: "Estimated Peclet Number." The Peclet number, which can be thought of as a ratio of "directed motion of the bulk stream" to "random motion in the diffusive eddies," is a dimensionless parameter used in describing the mixing behavior of a system. It appears in the partial differential equation describing the concentration of tracer in the reactor as a function of position and time⁽⁴⁵⁾.* The Peclet number corresponding to perfect mixing is zero, while that corresponding to plug flow is ∞ .

Since the geometrical properties of the output pulse are fixed by the Peclet number, these properties may be directly related to this mixing parameter. This is seen in Figure 17 (page 48) where several output concentration curves for the diffusion model

* In some analyses, a "dispersion group," $(\frac{D}{VL})$, is used as an index of the mixing intensity. The Peclet number is the reciprocal of the dispersion group.

are shown. These functional relationships, when written in terms of "normalized" variables (c/c_0 vs. t/t_h) are seen to depend only on the parameter P , the Peclet number. c is the measured concentration at the reactor outlet; c_0 is the initial concentration of tracer in the reactor (assumed to be evenly distributed throughout the vessel); t is the time after injection of the pulse; and t_h is the "nominal holding time" of the vessel. t_h is equal to the first moment of the experimental curve relating c to t .

The time required for the peak to emerge is seen to be a smooth function of the Peclet number. For a Peclet number of zero, the maximum value of c/c_0 occurs at $t^* = t/t_h = \text{zero}$. As the Peclet number approaches ∞ , the time (U^*) that the peak occurs approaches 1. Thus the "peak time" can be directly related to the Peclet number. It is not very useful in the case of high Peclet numbers, however, due to the asymptotic nature of the relationship. A more convenient geometrical variable to relate to the Peclet number is the ratio U^*/S^* , where $S^* = (S/t_h)$. This ratio varies from zero to infinity as the Peclet number varies from zero to infinity, because of the fact that S^* approaches zero at high Peclet numbers. This ratio has a further desirable property in that it can be measured directly from the original tracer curves, since

$$\frac{U^*}{S^*} = \frac{(U/t_h)}{(S/t_h)} = \frac{U}{S} \quad (1)$$

This relationship, shown in Figure 18 (page 50), is applicable to "axial diffusion" systems with inputs of negligible width.

Figure 18. Peclet Number vs. "Sharpness Ratio"

This curve will yield the Peclet number corresponding to the output curve from a diffusion-type system, without a time-consuming computer analysis. It will not replace such an analysis, however, in cases where a question exists as to whether a diffusion model is applicable to a given system. This simple approach was used in this study since a few limited computer runs had shown that a diffusion model fitted the data on these reactors reasonably well (see below).

4. Fitting of Peclet Numbers with Computer Program

The five runs shown in Figure 15 (page 45) were selected for a more elaborate data analysis. These runs (1, 8, 13, 16, and 17) were chosen to encompass a wide range of operating conditions. A high and a low gas flow rate was chosen for each packing (points falling nearest to the lines in Figure 16 (page 47)). Run 1 is a representative test on the empty reactor.

Figure 19 (page 52) shows the fitted (by least squares) "eddy diffusion" curves*, along with points taken from the actual output curves. The curve heights are normalized in that the total area under each curve is 1.0. The fraction of feed that remains in the system between t_1^* and t_2^* is simply the area below the curve between these two limits.

* These analyses were made on an IBM 7074 at Esso Research Laboratories in Baton Rouge, La., using computer programs developed by Dr. Paul McGinnis.

Figure 19. Normalized Output Curves
for Experimental Data

The diffusion model is seen to represent the data tolerably well, with the exception of Run 17 where more discrepancy is noted. The Peclet numbers corresponding to the fitted curves are slightly lower than the estimates made with Figure 18 due to the slight systematic departure from the model on the downward side of the curve (the experimental curves are slightly sharper than "fitted" curves).

5. Comparison with Published Correlation

The data in Table II (page 44) were expressed in dimensionless groups and compared with Bischoff's correlation⁽⁷⁾. This correlation, describing data taken in packed bed systems, is shown in Figure 20 (page 54). This figure relates a "mixing intensity" to the particle Reynolds number. This correlation represents the data well within the accuracy of the correlation. (In the published articles, the correlation line was dotted because of the scatter in the original data.) The points representing runs with the fine particles show that the correlation can be extended somewhat with a reasonable amount of confidence.

In calculating the dimensionless group $\epsilon L/Pd_p$ from the experimental data, a value of 0.615 was used for the void fraction of the coarse particles. This was estimated from the ratios of the actual average holding time (1st moment of experimental curve) to the "superficial holding time" (based on an empty reactor, with corrections for holdup time in the lines), using data for Run 21. A value of 0.8 was used for the fine particles.

Figure 20. Correlation of Dispersion Data

This was taken as an average of a value of 0.85 which was calculated as above from Run 8 data, and an experimental value of 0.75 (obtained by mixing 110 cc of dry particles with 142 cc water to yield 172 cc of mixture).

6. Extrapolation to Process Conditions

The correlation presented in Figure 18 (page 50) was used to estimate the Peclet numbers for typical process conditions to be used in this research project.

Use 15 cc catalyst, which corresponds to a bed height of 3.0 inches.

Catalyst - 15 cc, $\epsilon = 0.6$, $d_p = 0.63 \text{ mm} = 0.00207 \text{ ft.}$

Cross-Sectional Reactor Area - 0.00211 ft.^2

$L = 3.0 \text{ in.} = 0.25 \text{ ft.}$

Flow Rates - (8 v/v/hr, 4000 SCFB*)

$C_5 = 120 \text{ cc/hr} = 0.167 \text{ lb/hr} = 7.55 \cdot 10^{-4} \text{ barrels/hr}$

$H_2 = 3.02 \text{ SCFH} = \frac{0.016 \text{ lb/hr}}{0.183 \text{ lb/hr}}$
Total

$650^\circ\text{F} = 0.0147 \text{ centipoises} = 0.0356 \text{ lb/ft-hr}$

$$Re_p = \frac{0.00207(.183)}{.0356(.00211)} = 5.04$$

From Bischoff's correlation:

$$\frac{\epsilon L}{Pd_p} = 0.58$$

$$P = \frac{\epsilon L}{(.58)d_p} = \frac{0.60(.250)}{0.58(.00207)} = 125$$

* Standard cubic feet per barrel.

This reflects a close approximation to plug flow. In the past, a "rule of thumb" has been that Peclet numbers higher than 60 represent essentially plug flow systems.

In the operating range covered in this study, the Peclet number depended on the liquid feed rate and catalyst volume as is shown in Figure 21 (page 57).

7. Effect of Mixing Patterns on Conversion in Reactor

As is well known, a plug flow reactor will, in general, give a higher conversion in a given system than will a perfectly mixed reactor. As would be expected, reactors whose mixing patterns lie between these extremes will yield intermediate conversions.

For simple first order reactions, $A \rightleftharpoons B$, the average conversion at the outlet of a reactor can, in general, be calculated numerically by: (1) considering the feed stream to be composed of many small elements of feed, each with its own characteristic holding time, (2) calculating the conversion in each of these elements, and (3) combining the small elements to obtain the average conversion at the reactor outlet. If a mathematical description of the flow phenomena is available, an analytic solution is possible and can be obtained by applying methods of calculus in the above procedure. An alternate procedure is to include the reaction rate in a partial differential equation describing the performance of the reactor. This latter approach has been taken⁽⁴⁵⁾ to obtain the following equation for a reactor whose mixing pattern can be described by the diffusion model:

$$C^* = \frac{\text{Fraction of maximum possible conversion}}{4a} = \frac{P/2}{(1+a)^2 e^{aP/2} - (1-a)^2 e^{-aP/2}} \quad (2)$$

$$\text{where } a = \sqrt{1 + (4 k^*/P)}, \quad (3)$$

and $k^* = (\text{reaction rate constant})(\text{nominal holding time})$.

It is also of interest to note that this same relationship can be used with simple first order reversible reactions:

if the ordinate is taken as the fractional approach to equilibrium, and the abscissa, k^* , is taken as $(k + k')(\text{nominal holding time})$. This relationship is conveniently plotted in Figure 22 (page 59) where the fractional conversion is plotted as a function of k^* and P .

For these simple reactions, this figure can be conveniently used to determine the conversion if the reaction rate constant(s) and the Peclet number are known. Conversely, the sum, $(k + k')$, can be determined if the conversion and Peclet number are known.

As is seen in Figure 22, for operations at relatively large Peclet numbers (> 50), and at "moderate" conversions ($< 70\%$ of maximum), corrections to calculated rate constants for deviations from plug flow are negligible.

FIGURE 22. Conversion in Reactors with Longitudinal Dispersion

CHAPTER V

DISCUSSION OF EXPERIMENTAL DATA

This section will be devoted to a discussion of the methods used to obtain the original run data, and the reliability of the various sensing devices.

The following data were taken during the course of each run:

1. Reactor pressure.
2. Temperature of catalyst bed.
3. Feed rate of hydrogen gas.
 - (a) Time for $1/20 \text{ ft.}^3$ at wet test meter (pre-run calibration)
 - (b) Temperature of wet test meter
 - (c) Pressure of wet test meter
4. Time of material balance.
5. Volume of n-pentane fed during material balance period.
6. Total volume of product gases during material balance period.
7. Integrated areas of G.C. peaks corresponding to hydrocarbon components in product gases.

Each of these items will be discussed separately below.

A. Reactor Pressure

As is shown in Figure 11 (page 30), a pressure gauge was installed at the outlet of the catalyst bed. This was a Bourdon-type gauge, reading 0-500 psig. It was calibrated with a dead-weight tester, and found to be accurate to within 3 psi. Pressures used in the course of this research varied from 100 to 450 psig. The pressure was controlled manually by setting a Grove back-pressure regulator ("Mity-Mite"). This was adjusted to maintain the reactor pressure gauge to within 2 psi of its desired reading.

B. Catalyst Bed Temperature

The temperature of the catalyst bed was determined by side-entering thermocouples which protruded 1/4" into the catalyst bed. The temperature of the sand-bath was also monitored and was, in general, found to be one or two degrees higher than that of the catalyst bed.

A Leeds & Northrup temperature indicator was used to read the temperatures. This instrument, capable of reading up to twenty-four separate inputs, was calibrated with a potentiometer, and found to agree within one degree Fahrenheit.

Bed temperature was maintained constant ($\pm 2^{\circ}\text{F}$) by a Minneapolis-Honeywell temperature controller. This regulated the current to the second set of sand-bath heaters. The primary set, as noted in Chapter III, was manually adjusted to provide most of the heating, and was left on continuously.

C. Hydrogen Feed Rate

Prior to each run, after the reactor was loaded with catalyst, inserted in the sand-bath, and pressure tested, the hydrogen feed pressure (at rotameter) was set at 30-50 psi above the reactor pressure, and the control valve adjusted to yield the proper flow rate at the product gas wet test meter. This latter rate was determined by noting the time required for one revolution. The rotameter was used as an aid in determining the required valve setting, and as a visual indication as to whether the hydrogen rate was remaining constant during the course of a run.

The flow rate of hydrogen was kept constant by a differential-pressure regulator which tended to maintain a constant pressure drop across the control valve, regardless of any temporary downstream fluctuations. The excellent material balances ($100 \pm 2\%$) attest to the constancy of the hydrogen feed rate.

D. Time of Material Balance

Generally, material balance periods were one hour long, after snap samples had shown that the catalyst had "lined out" (see Figure 23, page 63). The actual timing was done by an electric interval timer which could be read to 1/100 minute.

E. n-Pentane Feed Rate

The liquid pentane was fed by means of a Ruska high pressure, low flow rate pump, capable of feeding between 2 and 240 cc/hr. In using this pump (see Figure 13, page 36), a feed rate was selected by manually changing the gear-drive system. Repeated runs at

Figure 23. "Line-Out" Periods for Typical Runs

"standard" run conditions showed an experimental error of only ± 0.2 cc/hr at a rate of 122.7 cc/hr. Prior to each run, the pump reservoir was cleared of entrapped air, and pressure-tested along with the rest of the system. The amount of n-pentane fed during a balance period was determined by a difference between two readings on the pump housing. These could be read to 0.01 cc.

F. Volume of Product Gases

All the runs reported in this study were made with sufficient hydrogen to assure that the product stream would be all gas-phase at ambient conditions. This entire product was passed through a water-saturator, and then through a 0.05 ft.³ wet test meter. The difference between the initial and final readings over the material balance period was corrected for temperature and water saturation, and was used as the total volume of reactor effluent.

G. Concentrations of Hydrocarbon Species in Product Gases

Generally, three or four snap samples of the product gas were taken during a material balance period. Each of these was injected separately into the gas chromatograph which, as noted earlier, produced a separate peak for each of the hydrocarbon components. The area under each peak, as determined by an internal ball-and-disc integrator, was proportional to the total amount of the corresponding component in the injected sample. The proportionality constants were determined experimentally for this system, and are discussed in Appendix C (page 217). Thus, the composition of the product stream, on a hydrogen-free basis, could be calculated. The actual composition

of the total product was calculated by adjusting the hydrocarbon compounds to force a carbon balance, and adjusting the hydrogen gas to force a hydrogen balance (some hydrogen was consumed in the saturation of cracked products). For a material balance, the total gram-moles of gas product as calculated above was compared to the total gram-moles of gas product as measured by the wet test meter. These balances normally ranged from 98 to 102%.

CHAPTER VI

MECHANISM STUDIES

A. Literature

As was discussed briefly earlier, experimental evidence on the isomerization of n-pentane is strongly in favor of a three-step mechanism involving two distinct species of active sites. The actual isomerization reaction is thought to occur as a normal olefin intermediate is isomerized to an isoolefin intermediate via a carbonium ion mechanism on an "acidic site." This type of site is normally included on the solid support, such as the surface (including internal pore surface) of silica-alumina catalysts. On the other hand, the sites on which the hydrogenation and dehydrogenation reactions take place are usually provided by the addition of a highly dispersed metallic component onto the solid catalyst particle.

Of the three postulated reactions, the relative independence of the overall reaction rate of the amount of dispersed metal^(56,76,77,95) indicated that neither the hydrogenation step nor the dehydrogenation step is rate-controlling. That the isomerization step is the slow step is also indicated by the data of Myers and Munns⁽⁵⁸⁾. This interpretation of the reaction mechanism has led to quite successful analyses of data obtained from noble-metal-supported solid catalyst. Although this three-step mechanism is currently believed to be the most correct, several other mechanisms have been postulated in efforts to explain data obtained in individual investigations.

Three alternate mechanisms, as summarized by Hutchins⁽³⁷⁾, include the following:

Dealkylation-Alkylation Mechanism, postulated by Parkas⁽²⁸⁾.

Free Radical Mechanism, postulated by Carter, et al.⁽¹⁴⁾.

Ester Formation with Catalyst, postulated by Ipatieff⁽³⁹⁾.

In the first two cases, subsequent data by other researchers have tended to refute the proposed mechanisms in favor of the three-step mechanism. The third mechanism postulates the existence of an intermediate complex composed of the acidic alumina hydrate and an adsorbed hydrocarbon molecule. This complex is presumably formed from the normal hydrocarbon. Upon dissociation of the complex, an isomeric hydrocarbon is given off. The original hydrocarbon was not specified, as it was postulated to be either pentane or pentene. If it were pentane, this would imply a single-site mechanism which would be contrary to more recent findings. On the other hand, if the original hydrocarbon were pentene, this mechanism would still be compatible with the three-step system described earlier, as this would simply offer a proposed mechanism for the "olefin-isomerization" step.

B. Analysis of Data from This Study

1. Introduction

As was noted in the literature review, the known "high activity" isomerization catalysts have serious drawbacks in that they are usually highly sensitive to impurities such as H_2O , H_2S and nitrogen compounds, and require corrosive, toxic process streams. In most cases, the aluminum halide catalysts require the

use of slurry processes. Thus, the advantages gained from low temperature operation are largely offset by processing difficulties. Solid "dual-function" catalysts, on the other hand, are relatively simple to handle, are easily regenerable, and show high selectivities. Their main drawback is the necessity of high temperature operation. This is detrimental both from an engineering consideration and also from an equilibrium standpoint.

The initial purpose of this research was to find a solid dual-function catalyst that would be active enough to allow operation at lower temperatures. The palladium-impregnated hydrogen mordenite system was the most active catalyst found at the time of this research project.

2. Baseline Runs with Linde MB-5390 Catalyst

Prior to the initiation of the exploratory runs, the most active commercial catalyst for the hydroisomerization of n-pentane was Linde's crystalline zeolite MB-5390⁽⁶⁵⁾. Several runs were made with this catalyst to provide a "baseline," or standard of comparison for future runs. The results of these runs are summarized below, where

W/W/Hr. = Pentane weight hourly space velocity, grams of
pentane fed per hour per gram of catalyst

i-C₅ = isopentane

p-C₅ = paraffinic C₅ (isopentane + n-pentane).

Run	<u>4</u>	<u>1A</u>	<u>2A</u>
Temperature, °F.	650	650	650
Pressure, psig	450	450	450
Feed Rate, W/W/Hr	9.49	4.91	9.82
H ₂ Rate, moles/mole	3.42	3.93	3.85
<u>Product Composition</u>			
% i-C ₅ in p-C ₅	50.2	58.3	45.7
Wt. % (C ₁ -C ₄)	0.4	0.7	0.3

As seen in the above table, at a pressure of 450 psig, it was necessary to operate at 650°F. to obtain a respectable conversion. A hydrogen rate of 3-4 moles/mole of pentane was used to prevent excessive coking of the catalyst. The results of these runs showed that the equipment was operating properly and that the techniques of catalyst activation were acceptable, for the data compared very favorable to previous data on the same system*.

3. Initial Simplified Model

In order to provide a more fundamental basis for comparing exploratory catalysts, a simplified model was used to provide a meaningful rate constant. The overall three-step reaction discussed earlier was assumed to consist of a single first order reversible reaction,

* Unpublished data from Esso Research Laboratories, Baton Rouge, La.

This is tantamount to assuming that the controlling step is the isomerization step in the three-step sequence. Due to uncertainties in the modes of action of the zeolite catalysts, particularly with regard to the intracrystalline diffusion, adsorption and reaction steps, the rate constant (k) in the following equation was assumed to be independent of the gas phase composition.

$$\text{Rate} = r = \frac{dN_i}{dW_c} = k \left[C_n - \frac{C_i}{K} \right] \quad (4)$$

where N_i = molar flow rate of isopentane
 W_c = mass of catalyst
 C_n = concentration of normal pentane, moles/unit volume
 C_i = concentration of isopentane, moles/unit volume
 K = thermodynamic equilibrium constant for n-pentane-iso-pentane system.
 r = gm moles i-pentane produced per unit time per unit mass of catalyst.

Let C_j = gm moles "j"/unit volume of gas

$$C_j = \frac{\text{Total moles}}{\text{unit volume of gas}} (\text{mole fraction of "j"}) = \frac{N_T}{V_T} y_j \quad (5)$$

where N_T = Total molar flow rate of gases
 V_T = Total volumetric flow rate of gases
 y_j = mole fraction of component "j"

Therefore,

$$\frac{dN_i}{dW_c} = k \left[\frac{N_T y_n}{V_T} - \frac{N_T y_i / K}{V_T} \right] = k \frac{N_T}{V_T} \left[y_n - y_i / K \right] \quad (6)$$

Also, since $N_i = N_T y_i$; (7)

$$dN_i = N_T dy_i \quad (8)$$

as N_T is constant for an isomerization reaction.

Substituting,

$$\frac{dy_i}{dW_c} = \frac{k}{V_T} \left[y_n - y_i/K \right] \quad (9)$$

Separating variables and integrating, with the restriction that the feed consists only of normal pentane and hydrogen (no isopentane),

$$\int_0^{y_i} \frac{dy_i}{[y_n - y_i/K]} = \frac{kW_c}{V_T} \quad (10)$$

Now, considering the hydrogen present,

$$V_T = \frac{F(1 + R_H)}{M \rho_G} \quad (11)$$

where F = mass flow rate of pentanes

M = molecular weight of pentanes

R_H = molar hydrogen/pentanes ratio

ρ_G = molar density of gas stream

Therefore,

$$\int_0^{y_i} \frac{dy_i}{(y_n - y_i/K)} = \frac{kW_c M \rho_G}{F(1 + R_H)} \quad (12)$$

At this point, it is convenient to change the concentration variables to a "hydrogen-free basis:"

$$y_i = \frac{Y_i}{(1 + R_H)} \quad (13)$$

Substituting into the left side of equation (12) yields simply

$$\int_0^{Y_i} \frac{dY_i}{(Y_n - Y_i/K)} = \frac{KW_c M \rho_G}{F(1 + R_H)} \quad (14)$$

$$\text{From } Y_n + Y_i = 1, \quad (15)$$

$$Y_n = 1 - Y_i, \quad (16)$$

$$\int_0^{Y_i} \frac{dY_i}{1 - Y_i \left[\frac{K+1}{K} \right]} = \frac{kW_c M \rho_G}{F(1 + R_H)} \quad (17)$$

Relating the thermodynamic equilibrium constant for the $n\text{-C}_5 \rightleftharpoons i\text{-C}_5$ reaction to the fugacities of the two components,

$$\begin{aligned} \frac{K}{K+1} &= \left[\frac{f_i}{f_i + f_n} \right]_{\text{eq.}} \\ &= \left[\frac{\nu_i^P y_i}{\nu_i^P y_i + \nu_n^P y_n} \right]_{\text{eq.}} = \left[\frac{\nu_i^Y y_i}{\nu_i^Y y_i + \nu_n^Y y_n} \right]_{\text{eq.}} \end{aligned} \quad (18)$$

Since the fugacity coefficients of isopentane and normal pentane are both close to unity, and are essentially equal at the conditions used in the study,

$$\frac{K}{K+1} = \left[\frac{Y_i}{Y_i + Y_n} \right]_{\text{eq.}} \quad (19)$$

Defining the above equilibrium mole fraction (hydrogen-free) of isopentane as Y_i^* , and substituting into equation (17) finally yields:

$$\int_0^{Y_i} \frac{(-dY_i)}{(Y_i^* - Y_i)} = - \frac{kW_c M \rho_G}{F(1 + R_H) Y_i^*} \quad (20)$$

Integrating,

$$L_n \left[1 - \frac{Y_i}{Y_i^*} \right] = - \frac{kW_c M \rho_G}{F(1 + R_H) Y_i^*} \quad (21)$$

Defining $\frac{F}{W_c} = W$ = mass flow rate, mass of pentane fed
per unit time per unit mass of catalyst, (22)

$$L_n \left[1 - \frac{Y_i}{Y_i^*} \right] = - \frac{kM \rho_G}{Y_i^* W (1 + R_H)}, \quad (23)$$

or

$$k = - \frac{W(1 + R_H) Y_i^*}{M \rho_G} L_n \left[1 - \frac{Y_i}{Y_i^*} \right] \quad (23A)$$

Upon rearrangement,

$$\frac{Y_i}{Y_i^*} = 1 - e^{-\frac{kM \rho_G}{Y_i^* W (1 + R_H)}} \quad (24)$$

The exponent can be related to the superficial holding time (t_H), since

$$\frac{M \rho_G}{W(1 + R_H)} = \frac{V \rho_B}{V_T} = \rho_B t_H; \quad (25)$$

where $\mathcal{V}$ = total volume of catalyst bed
 ρ_B = bulk density of catalyst
 V_T = volumetric flow rate of gases in reactor
 t_H = superficial holding time of gases in catalyst bed.

Thus,

$$\frac{Y_i}{Y_i^*} = 1 - e^{-(k \rho_B t_H / Y_i^*)} \quad (26)$$

which states that, at a given temperature, the fractional approach to equilibrium should be a function of only the superficial holding time of the reacting gases in the catalyst bed (assuming the bulk density remains constant).

Using this equation to define a "reaction rate constant," the activities of the various experimental catalysts could be compared. Subsequent testing of the most active catalyst would serve as a check on the applicability of this simple model.

4. Discovery of High Activity of Mordenite-Based Catalysts

When palladium-impregnated hydrogen mordenite was used at the conditions employed with the Linde MB-5390 catalyst, it was found to have such a high level of activity that up to 90% of the feed pentane was cracked to lighter products. These runs served only to indicate the exceptional activity of this catalyst, since the "side reactions" (cracking) precluded the calculation of any isomerization rate constants. The table below summarizes the results of these runs.

Run	<u>3A</u>	<u>3B</u>
Temperature, °F.	-----650-----	
Pressure, psig	-----450-----	
Feed Rate, W/W/Hr.	7.89	11.84
H ₂ Rate, moles/mole	3.23	2.15
<u>Product Composition</u>		
% i-C ₅ in p-C ₅	65.2	51.1
Wt. % (C ₁ -C ₄)	91.6	43.1

The fact that these product streams showed a high i-C₅/p-C₅ ratio did not necessarily imply that Pd on H-mordenite was an active isomerization catalyst. In order to test the isomerization activity of this catalyst without excessive cracking, runs 5 and 6 were made at 550°F., with other conditions the same as before. In these runs, the cracking was reduced to about 1%, while a high level of isomerization activity was shown.

Summarized data are shown below:

Run	<u>5</u>		<u>6</u>
Temperature, °F.	-----550-----		550
Pressure, psig	-----450-----		450
Feed Rate, W/W/Hr.	-----7.56		15.86
H ₂ Rate, moles/mole	3.45	0.71	0.69
<u>Product Composition</u>			
% i-C ₅ in p-C ₅	43.4	61.4	46.9
Wt. % (C ₁ -C ₄)	0.8	3.0	1.0
k, cm ³ /gm-sec	0.13	0.11	0.12

These results showed unquestionably that palladium on hydrogen mordenite was a much more active isomerization catalyst than was Linde's MB-5390. The data indicated that the former catalyst could match the latter's isomerizing capabilities, while more than 70°F. lower in temperature. As is normally found with solid catalysts, Pd on H-mordenite showed a high initial activity, then dropped rapidly to a "steady-state" level. Figure 24 (page 77) shows the calculated rate constants as a function of time for these two runs. Figure 25 (page 78) compares the rate constants, as calculated from the above runs, with earlier data obtained with the Linde catalyst.

As this discovery of the high isomerization capacity of the palladium-mordenite catalyst represented a significant breakthrough in the field of isomerization catalysis, a process variable study was initiated to further characterize this catalyst and to attempt to correlate the data with a meaningful mathematical model.

C. Mechanism Studies with Palladium on H-Mordenite

1. Effect of Mass Transfer on the Overall Isomerization Rate

The first phase of the mechanism studies in this research was concerned with an evaluation of the effects of mass transfer in the overall isomerization rate. This was accomplished by making a series of runs with widely different gas velocities. Other process conditions were kept relatively constant.

Figure 24. Line-Out Periods for Early Pd H-Mordenite Runs

Figure 25. Comparison of Linde MB-5390 Isomerizing Catalyst with Pd on H-Mordenite

This had the effect of significantly changing the rate of fluid-to-particle mass transfer, one of the series steps in the overall process. The tabulation below summarizes the results of this series of runs, in which gas velocities were varied over a four-fold range. As can be seen, the overall isomerization rates were relatively constant, as were the calculated rate constants. Had fluid-particle mass transfer been a limiting step in the process, the high-velocity run would have shown a significantly higher conversion than was observed at the conditions of lower gas velocity. These three runs show no such effects. Figure 26 (page 80) shows a plot of rate constants from runs made at 550°F and 450 psig, including the three runs mentioned above (open circles). This set of runs covered a four-fold range in gas velocities.

Run	<u>11</u>	<u>9</u>	<u>10</u>
Temperature, °F.	-----550-----		
Pressure, psig	-----450-----		
Feed Rate, W/W/Hr.	6.55	7.49	7.49
H ₂ Rate, moles/mole	3.45	3.45	3.56
Gas Velocity, cm/sec	0.49	0.99	2.02
<u>Product Composition</u>			
% i-C ₅ in p-C ₅	43.6	37.1	37.4
Wt. % (C ₁ -C ₄)	0.74	0.64	0.56
k, cm ³ /gms-sec	0.11	0.10	0.10

Thus, these runs and later runs at 550°F. and 450 psig were adequately correlated by the model discussed above. Had mass transfer been limiting, this simple model (which assumed no significant mass transfer resistance) would not have been adequate. The conversions would have been widely different in the three critical runs (9, 10, 11), and the calculated "rate constants" would not have been constant. Thus, these data were compatible with this simple model, and gave no reason to discard the hypothesis that mass transfer was not controlling.

2. Investigation of Diffusional Limitations

a. Properties of Mordenite Pore System

Since the introduction of crystalline zeolite catalysts, a new concept in solid catalysis has developed. As was noted earlier, the interstices within the crystal structures allow the reactant molecules to enter into a catalytic environment which is greatly

different from those normally encountered in conventional heterogeneous systems. For example, the internal "voids" in this intracrystalline realm bear little resemblance to the "pore volumes" of conventional solid catalysts.

The pores of more conventional catalyst particles are traditionally open, interconnected "channels" through which reactant molecules can pass relatively easily by simple diffusion without losing their "gas phase" characteristics. Two types of diffusion have been treated quite exhaustively in the literature⁽⁷²⁾. The first, "bulk diffusion," is normally characterized by extremely high (pore diameter/molecule diameter) ratios. In these systems, the pore diameters are much larger than the mean free path of the gas molecules, and the bulk reactant mixture behaves quite similar to an ordinary gas inside a tubular container. A second type of diffusion, important in catalytic systems, is called "Knudsen diffusion" which, while still characterized by relatively high (pore diameter/molecule diameter) ratios, occurs in systems wherein the pore diameter is much less than the mean free path of the molecules. Both of these diffusive mechanisms can be analyzed and described by an appropriate "diffusivity"⁽³⁴⁾. This coefficient is to be used in the diffusion equation

$$N_A = -D_e \frac{dC_A}{dx} \quad (27)$$

where N_A is the moles of A diffusing through unit area per unit time, D_e is the effective diffusion coefficient, and $\frac{dC_A}{dx}$ is the concentration gradient of component A.

For a binary gas mixture, with bulk diffusion prevailing, the diffusion coefficient can be estimated⁽⁶⁾ as a function of critical properties by

$$D_{AB} = a \left[\frac{T}{\sqrt{T_{CA}T_{CB}}} \right]^b \frac{(P_{CA}P_{CB})^{1/3}}{P_T} (T_{CA}T_{CB})^{5/12} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (28)$$

where D_{AB} is in cm^2/sec , P is in atmospheres, M is the molecular weight, and T is in $^\circ\text{K}$. T_{CA} is the critical temperature of A; P_{CA} is the critical pressure of A. Similarly for B. For non-polar gases, $a = 2.745 \times 10^{-4}$ and $b = 1.823$. Various modifications of the above relationships have been proposed for multicomponent systems⁽⁸⁶⁾.

In the case of Knudsen diffusion, where the major resistance to flow is provided by impacts with the pore walls rather than by collisions with other molecules, the diffusion coefficient⁽⁹⁰⁾ is

$$D_K = \frac{2r}{3} \sqrt{\frac{8RT}{\pi M}} \quad (29)$$

where r is the pore radius, R is the gas constant, T is temperature, $^\circ\text{K}$, and M is molecular weight.

The effects of system parameters on the diffusion coefficient for both types of diffusions are given below:

Variable	Diffusivity Proportional to	
	Knudsen	Bulk
Temperature	$T^{0.5}$	$T^{1.8}$
Pore Radius	r	Independent of r
Pressure	Independent of pressure	$1/P_T$

The above table graphically illustrates the striking manner in which the diffusion characteristics and the effects of system variables are modified by the geometry of the diffusion system.

When the geometrical restrictions imposed on the diffusing molecules inside the crystalline zeolite structures are examined, a third "diffusion regime" is found. In this regime, the "pore diameters" are not only less than the "mean free paths" of the reactant molecules, but are of the same order of magnitude as the molecular lengths. Diffusion in this regime, necessarily slower than in the two regimes discussed above, has not been characterized by general equations, and remains a virgin field for research.

In the case of mordenite, the "pores" are only $4-7\text{\AA}$ in diameter. When this crystal is used to isomerize n-pentane (over $6\text{\AA}$ long), a situation is encountered wherein the reactant molecules have to be oriented properly (parallel) in order for more than one to fit within the "pore" cross-section. A n-pentane molecule will even have trouble turning over inside the "pore." During the entire time inside the crystal, the pentane molecules are in such close proximity to the atoms forming the crystalline structure

("pore walls") that the pentane molecules are constantly influenced by electrostatic fields tending to strain, distort, and even break the carbon-carbon bonds. This, as noted earlier, results in a high level of reactivity and leads to a highly active catalyst species.

b. Application of Conventional Approach
to Heterogeneous Catalysis

Heterogeneous catalytic reactions have been, in many cases, quite satisfactorily analyzed by assuming that the individual steps can be described by their own rate equations, and that the rate of overall conversion process can be represented by a simultaneous solution of the individual equations⁽³⁵⁾. For example, the reactants must, via a "mass transfer process," travel from the gas phase to the surface of the catalyst particle. They must diffuse into the pores where they will be adsorbed onto "active sites," where the chemical reactions take place. The products, after desorbing from the active sites, must diffuse out through the pores to the surface, and then travel to the bulk stream flowing past the particle.

As an aid in discussing the intra-crystalline isomerization in mordenite, a brief discussion will be given of the relationships involved in "conventional" solid catalyzed reactions where diffusion and/or reaction rate controls.

For a simple $A \rightleftharpoons B$ reaction, with the bulk-stream concentrations such that C_A is higher than its equilibrium concentration, Figure 27 (page 85) qualitatively describes the concentration profile within a pore. The surface concentrations will be essentially

Figure 27. Concentration Profile Inside Catalyst Pore

those of the bulk stream, due to the relatively high rate of mass transfer across the "buffer layer." At steady state, the concentration gradients within the pores will be such that a net flow of A will be diffusing in, while a net flow of B will be diffusing out.

The rate of reaction (r) in any given differential area within the pore will be a function of the fluid concentrations of A and B in that vicinity⁽³⁵⁾. Where " k " is a reaction rate constant, C = concentration, and K is a thermodynamic equilibrium constant,

$$r = k \left[C_A - \frac{C_B}{K} \right] \quad (30)$$

Since the driving force $(C_A - \frac{C_B}{K})$ will decrease steadily within the pore, the rate of conversion of A will be greater near the surface than at any point within. For simple systems, the overall rate of reaction has been described mathematically⁽⁷⁸⁾, and conveniently presented by the use of an "effectiveness factor" which is simply the ratio of the overall rate of conversion within the pore to the hypothetical overall rate that would be obtained if all the fluid within the pores were at the same concentration as that of the surface (e.g., infinite diffusion coefficients).

For a uniform pore through a catalyst particle (as would, in principle, be expected in the mordenite crystal), the effectiveness factor, η , is calculated⁽⁷²⁾ to be

$$\eta = \frac{\tanh(\phi)}{\phi}, \quad (31)$$

$$\text{where } \phi = \frac{L}{2} \sqrt{\frac{(k + k')}{D_e}} \quad (31A)$$

L = pore length

k = first order reaction rate constant in forward direction

k' = first order reaction rate constant in reverse direction

D_e = effective diffusivity, assumed to be equal in both forward and reverse directions.

This function (η) approaches unity for small values of ϕ . In this case, the diffusivity term is large compared to $L^2(k+k')$, and the concentration gradients within the pore are almost nil. Thus, the entire surface area "sees" a fluid whose concentration is essentially that of the bulk stream. In this case, the reaction rate controls the overall rate, and the actual value of the diffusion coefficient need not be known quantitatively to calculate the overall reaction rate.

On the other hand, in cases in which ϕ is large (> 10), η approaches ϕ^{-1} . In this region, the diffusivity term is small compared to $L^2(k+k')$ and the concentration gradients at the pore entrance are very steep. At moderate distances in from the surface (less than halfway) the concentration profiles level out, approaching their equilibrium values⁽⁴⁵⁾. The remaining pore volume is ineffective for chemical reaction because of the absence of an appreciable driving force. Thus, at high values of ϕ , the diffusional

resistance significantly affects the overall conversion rate since it effectively limits the amount of product that can emerge from the pore.

However, in this case, even though diffusion is important, the overall rate of formation of the reaction product inside the pore is still a function of the surface reaction rate. A knowledge of the rate of the surface reaction is necessary to evaluate ϕ , from which the "effectiveness factor" is determined.

To summarize the above points:

- (1) At low value of ϕ , the surface reaction "controls;" $\eta \approx 1$ and is independent of ϕ . Diffusional resistance is negligible, and a knowledge of the actual diffusion coefficient is not necessary to determine the overall rate.
- (2) At high values of ϕ , although diffusional resistance is highly important, η is still a strong function of ϕ , so the surface reaction rate is still necessary to determine the overall rate. "Diffusion can never be said to control in the sense that it alone will determine the overall rate of reaction."⁽⁴⁵⁾

The above considerations are severely restricted (even for "isothermal" reactions in which no change in volume occurs) in that they assume that the reaction rate constant, k , in equation (30) is independent of the concentration of the fluid stream near the active sites. In general, for a simple $A \rightleftharpoons B$ reaction, assuming that only a single "site" is necessary for the isomeric conversion,⁽³⁵⁾

$$r = \frac{k_o(C_A - C_B/K)}{1 + K_A p_A + K_B p_B + \sum_j K_j p_j} \quad (32)$$

where p_i = partial pressure of component "i"
 K_i = adsorption equilibrium constant for component "i"
 A = reactant
 B = product
 j = one of other gas phase components, e.g., "inert"
 intermediates, "by-product," etc.
 k_o = hypothetical rate constant at zero pressure

Several relatively recent literature contributions have been made along these general lines with simplified models^(36,85,92), but very little work has been done on the more complex systems because of the mathematical complexity of the differential equations and because of the difficulty in obtaining sufficiently accurate data to adequately test these complex models.

As will be discussed later in more detail, a simplified model of this general type was adequate to correlate the isomerization data with a mordenite-based catalyst.

c. Effects of Intraparticle Diffusion

The original crystalline zeolite particles obtained from the Norton Company were from a single batch with a relatively narrow 1-5 micron particle size range. After being impregnated with palladium at Esso Research Laboratories, these minute particles were pilled and dried. Normally, the pilled particles were subsequently crushed to 20-40 mesh in order to assure proper flow patterns in the small reactors used in this study.

In order to determine whether there was any significant diffusional resistance in these crushed particles (average diameter about 0.6 mm.), runs were made with screened particles of three different ranges. These classified batches of catalyst covered a range from 0.1 to 1 mm. Runs 12-14 made up this series. Other than particle size, all other process variables were held essentially constant, with the exception of the liquid space velocity, which varied slightly because of the varying bulk densities of the different particle size samples (15 cc. charges were used in all cases).

The results of these runs are tabulated below:

Run	<u>13</u>	<u>12</u>	<u>9</u>	<u>14</u>
Temperature, °F.	-----550-----			
Pressure, psig	-----450-----			
H ₂ , moles/mole C ₅	-----3.4-----			
Gas Velocity, cm/sec	-----1.00-----			
Particle Size, mm.	.074-.149	.30-.42	.42-.84	.84-1.15
Feed Rate, W/Hr/W	10.85	7.27	7.49	6.87
<u>Product</u>				
% i-C ₅ in p-C ₅	29.4	43.7	37.1	42.9
k, cm ³ /gm-sec	0.11	0.12	0.10	0.11

Although there is some scatter in the calculated rate constants, there is definitely no trend toward a "more active" catalyst at smaller particle sizes (Figure 28, page 91). Since

the average particle diameters in this series covered a ten-fold range, it was concluded that there was no significant diffusional resistance in the crushed particles.

This leads to a very important point. Although the crushed particles showed no diffusional resistance, which indicates that in commercial applications the size of the piled particles will have little effect, this does not preclude the existence of diffusional limitations inside the crystalline lattices. This may be clarified when it is recalled that the basic crystalline particles in all cases were of the same order--1 to 5 microns.

As was noted earlier, the intra-crystalline structure contained "pores" of only 4-7Å diameter. These "micropores" can be compared to the void spaces between the 1-5 micron particles inside the packed macroparticle. These "macropore" diameters are of the order of magnitude of the microparticle diameters, 1-5 microns,

or 10,000-50,000Å. In the path of travel of the reactant molecules from the bulk gas stream to the active sites within the crystalline lattice, these two "pore systems" are in series. Of the two, intracrystalline pores obviously offer the controlling diffusional resistance. Thus, the conclusion concerning the absence of a significant diffusional resistance must be interpreted as referring to the "macropores" inside the crushed particle, and not to "micropores" inside the zeolite crystal structure. Another way of looking at the process is with reference to Figure 29 (page 93).

Regardless of the size of the macroscopic particles (0.1-1 mm), the component "microparticles" were always the same size (0.001 mm). The diffusional resistance inside the microparticles was orders of magnitude higher than the diffusional resistance inside the "pores" of the macroparticles. It was shown that there was essentially no mass transfer resistance between the bulk gas stream and the particle surfaces. Thus, the gas within the "macropores" always had the same composition as the bulk gas stream.

In the final analysis, as far as the reacting fluid was concerned, it "saw" the same size particles (1-5 microns) in each of the four runs listed above. The results of these runs show that there is no diffusional resistance due to the usage of different sized pills, but say nothing concerning the diffusional resistance inside the 4-7Å pores of the crystalline lattice. Based on geometric considerations alone, the diffusional resistance inside the mordenite lattice should be quite appreciable. However,

as was noted earlier, the assumptions underlying the Knudsen diffusion equations do not hold in this region. A considerable amount of uncertainty exists concerning the true nature of the intracrystalline mechanisms.

Thus, in the investigations reported in this dissertation, the reported "rate constants" will be descriptive of the overall reaction rate within the mordenite crystals, including the effect of these intracrystalline diffusional rates. The "effectiveness factors" for these microscopic pore diffusional processes are certainly much less than unity, but their exact determinations will have to await a more basic theoretical approach to "small-pore diffusion" and experimental data on zeolite crystals of varying particle sizes, when these become available.

3. Investigation of the Effects of Varying the Metal Content

In an effort to investigate the effects of varying palladium concentrations on the overall isomerization rate, a series of runs was made with varying concentrations of metals on the catalyst particles. Most of the runs in this series were made with palladium-impregnated catalysts. One was made with a platinum-impregnated catalyst and one was made with a sample of hydrogen mordenite with no impregnated metal. The results are tabulated below:

Run	<u>20</u>	<u>16</u>	<u>9</u>	<u>15</u>	<u>17</u>
Temperature, °F.	-----550-----				
Pressure, psig	-----450-----				
Impregnated Metal	None	Pd	Pd	Pd	Pt
Percent	0.0	0.2	0.5	1.0	0.5
Feed Rate, W/W/Hr.	9.73	7.95	7.50	7.66	7.84
H ₂ Rate, moles/mole	3.39	3.46	3.45	3.48	3.44
<u>Product Composition</u>					
% i-C ₅ in p-C ₅	40.2	39.4	37.1	40.1	39.2
Wt. % (C ₁ -C ₄)	2.4	1.0	0.75	1.0	0.74
k	0.14	0.12	0.10	0.12	0.11

These striking results show that the overall isomerization rate is independent of the concentration of the impregnated palladium, implying that the reactions on these sites (hydrogenation-dehydrogenation) are not rate-limiting. The overall rate was also unaffected by the substitution of platinum for palladium, again indicating that the reactions on the metal sites are not the controlling step in the process. These data are plotted in Figure 30.

An unexpected result of this series of runs is seen in the data from Run 20, in which no dispersed metal was impregnated into the mordenite crystal. The overall isomerization properties of this catalyst were as good as those of the metal-impregnated catalyst. This is a significant point.

Until the isomerizing properties of mordenite-based catalysts were discovered in the course of this research (and also independently by Shell Research), zeolite catalysts had to be impregnated with a hydrogenation component for the overall isomerization reaction to go to completion. In all the published cases, this hydrogenation component was a noble metal, usually platinum or palladium. This impregnated metal, as was discussed earlier, was necessary for the hydrogenation-dehydrogenation reactions in the stepwise isomerization, and also as a "coke inhibitor."

Although the hydroisomerization reactions of paraffinic hydrocarbons are remarkably "clean" reactions (very few side reactions), the isomerization sites tend to form polymeric material from the minute amounts of olefinic materials present, leading to carbonaceous, deactivating deposits on the catalyst surfaces. Also, as can be seen in the data from Run 20, the cracking rate was 2-3 times that observed in runs with palladium or platinum-containing catalysts. Thus, in addition to the above-mentioned effects, the impregnated metals tend to suppress cracking side reactions.

However, from the above data, it is evident that the absence of a noble metal inside the crystalline sieve did not affect the initial hydroisomerization rate. This can be due to any of several causes.

- (1) The mordenite crystalline structure may itself possess active sites capable of hydrogenation-dehydrogenation reactions. If this is true, this is a significant breakthrough in catalytic hydroisomerization.
- (2) From published data discussed earlier, the hydrogenation-dehydrogenation reactions are extremely rapid compared to the olefinic isomerization step (postulating the "three-step" mechanism discussed earlier). These reactions may be so rapid that the nickel in the reaction walls (the reactor was made of Inconel) was sufficient to supply the needed hydrogenation-dehydrogenation sites.

As the main purpose of this particular study was to investigate the properties of palladium-mordenite combinations, experimental runs with noble-metal-free mordenite were postponed for a later project. A contributing reason for this decision was the high probability of a greater coking rate (as evidenced by the higher cracking observed) which would lead to a shorter catalyst life under commercial process conditions. As was noted earlier, the equipment used for this study was not constructed for extended "catalyst life" runs, but was limited to relatively short (one day) experiments.

4. The Effects of Changing the Acidity Level of the Catalyst

The runs previously discussed showed that the dispersed-metal sites were not rate-controlling. As was discussed earlier, in addition to hydrogenation-dehydrogenation sites, a second type of site, generally called "acidic" has been found to be necessary for hydroisomerization reactions.

The positive sodium or calcium ions associated with the crystalline structure of zeolite catalysts are normally chemically exchanged by ammonium (NH_4^+) ions before the catalyst is used. A subsequent calcination drives off ammonia, leaving only protons to balance the charges in the crystal structure. These protons provide the required "acidic" sites.

Runs 7 and 8 were made with catalysts with lesser degrees of acidity than were used for the other runs in this research study. In these particular runs, magnesium mordenite and zinc mordenite were used. These catalysts were prepared at the Esso Research Laboratories by chemically exchanging the above positive ions for the ammonium ions. This resulted in zeolite crystals with much lower acidity levels. Summarized data from these runs are compared below with data from a hydrogen-mordenite run:

Run	9	7B	8B
Catalyst	0.5% Pd on H-mordenite	0.5% Pd on Mg-mordenite	0.5% Pd on Zn-mordenite
Temperature, °F.	-----550-----		
Pressure, psig	-----450-----		
Hydrogen, moles/mole	-----3.4-----		
Feed Rate, W/H/W	7.5	7.3	7.3
<u>Product Composition</u>			
% i-C ₅ in p-C ₅	37.1	13.6	10.9
Wt. % (C ₁ -C ₄)	0.6	0.4	0.2
k, cm ³ /gm-sec	0.10	0.028	0.022

These data show that the overall reaction rate is greatly influenced by the acidity of the catalyst, indicating that the reaction(s) taking place on these sites offer a controlling part of the overall resistance. If the current "three-step" mechanism is accepted, the conclusion must follow that the skeletal isomerization of the olefin intermediate on the acidic site is the rate-controlling step in the reaction sequence.

5. The Effect of Temperature on the Overall Isomerization Rate

One of the immediate advantages that was noted for mordenite-based catalysts was the fact that they could match the conversions on Linde's MB-5390 zeolite catalyst while at a much lower temperature. As was noted earlier, lower temperature operation is beneficial both from an equilibrium standpoint and also from an engineering materials standpoint. The evaluation of the temperature

effects, therefore, in addition to forming a necessary part of an adequate mechanism study, is of a great commercial importance.

Figure 31 (page 101) shows an Arrhenius plot of the rate constant (as calculated by equation 23A) for several zeolite catalysts used in this overall study. These runs were all made at 450 psig and 4000 SCFB hydrogen/barrel of feed (3.43 moles/mole).

The summarized data from the 1/2% Pd on H-mordenite runs are presented below:

Run	<u>18</u>	<u>25A</u>	<u>23D</u>	<u>9</u>	<u>19</u>	<u>25C</u>
Pressure, psig	-----450-----					
Hydrogen, moles/mole	3.43	3.42	3.39	3.45	3.51	3.40
Feed Rate, W/W/Hr.	4.08	3.97	8.11	7.49	16.5	15.9
Temperature, °F	500	500	525	550	600	600
<u>Product Composition</u>						
% i-C ₅ in p-C ₅	22.6	28.3	22.6	37.1	39.4	62.5
Wt. % (C ₁ -C ₄)	0.1	0.4	0.2	0.7	1.0	3.7
k, cm ³ /gm-sec	0.026	0.034	0.051	0.10	0.26	0.75

These data show quite a bit of scatter. Run 19 is considered somewhat suspect since a later run (25C) showed a considerably higher conversion. The repeated 600°F run gave a conversion that was very close to the corresponding equilibrium conversion. The rate constant calculated from this run is therefore subject to added uncertainty since it is highly dependent on the difference of these two numbers, which, being small, is very sensitive to analytical errors.

The overall conclusions from these data are relatively clear. The effect of temperature is roughly the same for all the zeolite catalysts used in this study. This effect (about "25°F. to double the rate" in this temperature range) corresponds to an "activation energy" of about 55,000 BTU/Lb mole. This is comparable to those reported by Hutchins⁽³⁷⁾ and by Lyster, et al.⁽⁴⁸⁾ from data taken with platinum-on-alumina catalysts.

The relatively large effect of temperature on the overall reaction rate cannot, in itself, be used to distinguish between reaction-rate-controlled systems and diffusion-controlled systems.* The following development shows that, even for a "diffusion-limited" process, the apparent "activation energy" is usually much higher than that expected from the temperature effect on the diffusion process alone.

With reference to the discussion of the "effectiveness factor" for a simple $A \rightleftharpoons B$ reaction (page 86), the ratio of the observed overall rate to the hypothetical rate (no diffusional resistance) approaches ϕ^{-1} when diffusion becomes limiting.

$$\eta = \frac{r}{r^*} = \phi^{-1} \quad (33)$$

From equation 31A,

$$\frac{r}{r^*} = \left[\frac{L}{2} \sqrt{\frac{k + k'}{D_e}} \right]^{-1} = \frac{2}{L} \sqrt{\frac{D_e}{k + k'}} \quad (34)$$

* The "activation energy" of the diffusion coefficient is of the order of 1,000-2,000 cal/gm-mole.

The hypothetical rate, written as a function of the surface concentrations, is

$$r^* = k \left[C_{AS} - \frac{C_{BS}}{K} \right] , \quad (35)$$

where C_{AS} = concentration of "A" at surface of particle.

C_{BS} = concentration of "B" at surface of particle.

Thus,

$$r = \frac{2k}{L} \sqrt{\frac{D_e}{k + k'}} \left[C_{AS} - \frac{C_{BS}}{K} \right] , \quad (36A)$$

or

$$r = \frac{2k}{L} \sqrt{\frac{D_e}{k(1 + \frac{1}{K})}} \left[C_{AS} - \frac{C_{BS}}{K} \right] \quad (36B)$$

$$= \frac{2}{L} \sqrt{\frac{kD_e}{(1 + \frac{1}{K})}} \left[C_{AS} - \frac{C_{BS}}{K} \right] . \quad (36C)$$

Expressing "k" and "D_e" in terms of their temperature dependence,

$$r = \frac{2}{L \sqrt{(1 + \frac{1}{K})}} \sqrt{k_o e^{-E_R/RT} D_o e^{-E_o/RT}} \left[C_{AS} - \frac{C_{BS}}{K} \right] , \quad (37)$$

or,

$$r = \left[\frac{2}{L} \sqrt{\frac{k_o D_o}{(1 + \frac{1}{K})}} e^{-\frac{1}{2} \left[\frac{E_R + E_o}{RT} \right]} \right] \left[C_{AS} - \frac{C_{BS}}{K} \right] . \quad (38)$$

The first group in brackets corresponds to the "observed rate constant," and will have an "activation energy" equivalent to the arithmetic mean of that of the actual reaction rate and that of

the diffusion constant (if the thermodynamic equilibrium constant, K , is very large and/or is relatively unaffected by temperature).

As will be shown in the following section, the "observed rate constant" is also, in general, a function of the partial pressures of the gas-phase components and their adsorption equilibrium constants. The "observed activation energy" will therefore also be affected by the temperature sensitivity of the adsorption constants.

Thus, the high observed value of the "activation energy" of the mordenite-based catalysts does not preclude the existence of diffusional limitations inside the catalyst pores.

6. The Effect of System Partial Pressures on the Overall Isomerization Rate

a. General Discussion

Thus far in this research program, a simplified model had been used, which assumed that the "reaction rate constant" (k) was a function of temperature only, and not of the partial pressures of the gas-phase components. If k were actually independent of the system partial pressures, the conversion of pure n -C₅ feed would be a function only of temperature and system "holding time," since for this model:

$$\frac{Y_1}{Y_1^*} = 1 - e^{- (k \rho_B t_H / Y_1^*)} \quad (39)$$

In general, however, the overall activity of a catalyst would be expected to decrease with increasing partial pressures⁽³⁵⁾,

due to a reduction in the number of available active sites. This reduction is a result of the increased number of adsorbed molecules which tend to "cover up" the active sites.

Assuming the applicability of Langmuir adsorption isotherms⁽³⁵⁾, for a simple first order, reversible system, this effect of partial pressures can be accounted for by writing the observed rate constant, k , as

$$k = k_o / (1 + K_i p_i + K_n p_n + K_H p_H) \text{ for a "single site" mechanism, and}$$

$$k = k_o / (1 + K_i p_i + K_n p_n + K_H p_H)^2 \text{ for a "dual site" mechanism;}$$

where

k_o = a constant, depending only on the type of catalyst and the temperature.

K_i, K_n, K_H = adsorption equilibrium constants for $i\text{-C}_5$, $n\text{-C}_5$, H_2 , respectively.

p_i, p_n, p_H = partial pressures of $i\text{-C}_5$, $n\text{-C}_5$, H_2 , respectively.

A "single-site" mechanism is descriptive of a reacting system wherein an adsorbed molecule can react while on a single "active site," regardless of the condition of nearby sites. A "dual-site" mechanism refers to a system wherein an adsorbed molecule can react only if it is on an active site that has a neighboring unoccupied site. The obvious reduction in the statistical chances for a reaction to occur leads to the larger denominator, which reduces the "effective reaction rate."

b. Effects of Hydrogen Partial Pressure and
Pentane Partial Pressure on Catalyst Activity

Since the data in this study were obtained with an integral reactor, partial pressures of the components were changing along the length of the catalyst bed during every run. However, the hydrogen partial pressure remained constant, and the sum of the isopentane and normal pentane partial pressures remained constant. Partial pressures of the intermediate and cracked products were so low as to be ignored in this analysis.

The general method of approach was to assume a single model and to test the data to determine whether it was compatible with the model. Nothing thus far had given reason to discard the hypothesis that the "rate constant" was not a function of system partial pressures. This assumption was not proven, for although the isopentane and normal pentane partial pressures were varying greatly, their sum ($p_i + p_n$) remained essentially constant. Thus, the general "corrected rate constant,"

$$k = k_o / (1 + K_i p_i + K_n p_n + K_H p_H)^n \quad (40)$$

would have been relatively constant, since K_i and K_n would be expected to be relatively close together.

Thus,

$$k_o / (1 + K_{C_5} (p_i + p_n) + K_H p_H)^n \quad (41)$$

would have been essentially constant.

Run 21 included a series of balances set up to test the model at different system partial pressures. In this series, p_{H_2} and p_{C_5} were varied without varying the superficial holding time. Had k been truly independent of system partial pressures, the conversion would have been the same in all four balances (equation 39).

These balances were made at 550°F with combinations of the following partial pressures: $p_{C_5} = 33.5$ and 67 psia, and $p_{H_2} = 200$ and 400 psia. Duplicate runs were made at each set of conditions.

The "holding time" was maintained constant by varying the conditions such that the ratio $p_{C_5}/(W/W/Hr)$ was constant. Summarized data are shown below:

Runs	<u>21A&E</u>	<u>21B&F</u>	<u>21C&G</u>	<u>21D&H</u>
Temperature, °F	-----550-----			
Total Pressure, psia	267	465	431	235
Feed Rate, W/Hr/W	7.66	7.66	3.83	3.83
Pentane Partial Pressure, psia	66	67	34	34
Hydrogen Partial Pressure, psia	201	398	397	201
H_2/C_5 , moles/mole	3.0	5.9	11.9	6.0
Superficial Holding Time, sec	4.9	5.0	5.0	5.0
<u>Product Composition</u>				
% i- C_5 in p- C_5	45.6	26.1	28.8	47.5
Wt. % (C_1-C_4)	1.2	0.4	0.4	1.3
k , $cm^3/gm\text{-}sec$	0.23	0.10	0.11	0.24

As can be seen in Figure 32 (page 109), an apparent effect of hydrogen partial pressure was noted, with no obvious effect of hydrocarbon partial pressure. However, due to the fact that $P_{C_5} + P_{H_2} = P_T$, and since these runs were made at relatively high H_2/C_5 ratios, the observed effect of P_{H_2} was confounded with an apparent effect of total pressure.

Runs 22A & B and 23B & D were made at 525°F, keeping total pressure and W/W/Hr constant, varying the H_2/C_5 ratio (from 0.75 to 3.4). The results of these runs showed the observed catalyst activity (k) to be essentially constant, even though the hydrogen partial pressure was almost doubled. This showed that the observed activity was not a simple function of hydrogen partial pressure, but still an apparent function of the total system pressure.

Run	<u>23B</u>	<u>22B</u>	<u>22A</u>	<u>23D</u>
Temperature, °F	-----525-----			
Total Pressure, psig	-----450-----			
Feed Rate, W/Hr./W	8.1	7.8	7.8	8.1
Pentane Partial Pressure, psia	265	237	127	106
Hydrogen Partial Pressure, psia	200	228	338	359
H_2/C_5 , moles/mole	0.75	0.96	2.7	3.4
<u>Product Composition</u>				
% i-C ₅ in p-C ₅	44.4	42.3	26.3	22.6
Wt. % (C ₁ -C ₄)	1.3	0.8	0.8	0.2
k, cm ³ /gm-sec	0.055	0.055	0.053	0.053

Earlier data (runs 5, 7, 8) in which the system pressure was maintained constant, showed corresponding increases in conversion when the hydrogen rate was reduced. As was the case in runs 22 and 23, the "k's" calculated under high and low hydrogen rates were relatively constant.

Data from runs 22 and 23 are shown in Figure 33 (page 111) along with data at lower pressures. These data, all at 525°F, can be correlated by the simple first-order reversible model presented earlier if the "catalyst activity" (indicated by "k") is assumed to be a function of total pressure.

c. Effect of Total Pressure on Conversion

As is evidenced by the data tabulated below and shown in Figure 34 (page 112), the effect of increased pressure is to decrease the conversion. These runs were made at 500°F, 4 W/Hr/W, 3.4 moles H₂/mole C₅.

<u>Run</u>	<u>Pressure</u>	<u>% i-C₅ in p-C₅</u>	<u>k</u>
24D	100	50.5	0.33
24C	150	42.5	0.17
25B	150	46.6	0.20
24B	250	34.8	0.079
24A	350	30.3	0.047
25A	450	28.3	0.034
18	450	22.6	0.026

These results and the results reported in the preceding section are compatible with the hydroisomerization results reported

by Ciapetta and Hunter⁽¹⁷⁾ from n-hexane runs with nickel-silica-alumina catalysts. At a constant pressure and superficial holding time, the ratio of hydrogen/hydrocarbon had no effect on the overall conversion of the n-hexane feed to isomers. On the other hand, runs in which holding time and hydrogen/hydrocarbon ratio were held constant showed a definite decrease in conversion with increasing total pressure.

Figure 35 (page 114) shows the observed rate constant as a function of temperature and total pressure. As noted above, the simplified model presented earlier has been found to adequately describe the data, with the simple modification of allowing the reaction rate constant to be a function of pressure as well as temperature. As can be seen, it increases with temperature and decreases with pressure.

Actually, this model predicts two effects of pressure on the reaction system, one tending to increase conversion and one tending to decrease conversion. In the simplified model,

$$\frac{y_i}{y_i^*} = 1 - e^{-k \rho_B t_H / y_i^*} = 1 - e^{-(k t_H) (\rho_B / y_i^*)}, \quad (42)$$

each factor in the product " $k t_H$ " is a function of pressure. The catalyst activity (k) decreases with pressure, while the holding time (t_H) increases with increasing pressure.

Figure 35. Effect of Temperature and Pressure on Rate Constant

7. Incorporation of Pressure Effects into Model

a. General Discussion

As was noted earlier, the observed "activity constant," k , was expected to be of the form

$$k = k_o / (1 + K_i p_i + K_n p_n + K_H p_H)^n \quad (43)$$

where $n = 1$ for "single site" mechanism

2 for "dual site" mechanism .

The data showing that k depends not on the individual partial pressures, but on the total pressure suggests that the adsorption constants K_i , K_n , and K_H are essentially equal, for if

$$K_i \approx K_n \approx K_H, \text{ and all are approximately equal to } K_o, \quad (44)$$

then

$$k = k_o / (1 + K_o [p_i + p_n + p_H])^n \quad (45)$$

or,

$$k = k_o / (1 + K_o p_T)^n, \quad (46)$$

showing a decrease in k with total pressure, but no explicit effects of individual partial pressures.

Although these constants would not be expected to be exactly equal, the data from this study are compatible with the foregoing assumption, and give no reason to disregard it for this particular mordenite-pentane-hydrogen system. Lyster, et al.⁽⁴⁸⁾ found that such "adsorption constants" for n-pentane, i-pentane and hydrogen on an alumina-based catalyst had the ratios 1.0:1.5:2.0, respectively. These ratios are far from the ratios that would be obtained from single-component adsorption measurements (K_H would be

expected to be different from K_1 or K_n by at least an order of magnitude). It has been noted, however⁽⁷⁴⁾ that the adsorption characteristics of solid catalysts, as exhibited in separate adsorption measurements, have no quantitative relationship to the "dynamic adsorption characteristics" shown in a reacting environment.

These "dynamic adsorption constants" should depend, to a large extent, on the particular type of catalyst being used, its method of preparation, its operating conditions (e.g., "fresh," "coked," "spent"), and the process conditions (temperature and concentrations of other components in the gas phase).

b. Single Site Mechanism

Figure 36 (page 117) is a plot which shows that the data are incompatible with a "single-site" model. This plot relates $\frac{1}{k}$ to P_T . This relationship should be linear (at a given temperature) with an intercept equal to $\frac{1}{k_o}$, since

$$\frac{1}{k} = \frac{1}{k_o} + \frac{K_o}{k_o} P_T. \quad (47)$$

These intercepts are negative, which would imply that k_o is negative, which is unrealistic.

c. Dual Site Mechanism

The assumption of a dual site mechanism is tested in Figure 37 (page 118) in which $\frac{1}{\sqrt{k}}$ is plotted vs P_T . This shows that the data are compatible with a dual site mechanism, assuming

Figure 36. Test of "Single-Site" Model

Figure 37. Test of "Dual-Site" Model

that the adsorption coefficients are equal, since

$$\frac{1}{\sqrt{k}} = \frac{1}{\sqrt{k_o}} + \frac{K_o}{\sqrt{k_o}} P_T \quad (48)$$

The slopes of the lines are $\frac{K_o}{\sqrt{k_o}}$. It is seen that this ratio (the slope) decreases with increasing temperature. The intercept appears to be a relatively weak function of temperature. Thus, the variation in the slope is mostly due to the effect of temperature on the adsorption equilibrium, and is in the expected direction; that is, less adsorption at higher temperatures.

The net effect of total pressure can be calculated from the mathematical model, since

$$k = k_o / (1 + K_i P_i + K_n P_n + K_H P_H)^2 = k_o / (1 + K_o P_T)^2, \quad (49)$$

Also,

$$t_H = \frac{\gamma}{v_T} = \frac{\gamma_M \rho_G}{F(1 + R_H)} = \frac{\gamma M P_T}{F(1 + R_H)RT} \equiv \beta P_T \quad (50)$$

Thus,

$$\frac{Y}{Y_i^*} = 1 - e^{-k_o \beta P_T / (1 + K_o P_T)^2} \quad (51)$$

This shows that the conversion approaches zero at low pressures and also at high pressures. As the pressure approaches zero, the holding time would, in effect, be so short that essentially no conversion would occur, even though the maximum number of active sites were available. At very high pressures, the fraction of available active sites would be so small that very little conversion would occur in spite of the longer holding times. A typical curve

calculated from this model is shown in Figure 38 (page 121). The optimum pressure can be calculated by differentiating equation (51) with respect to P_T , setting the derivative equal to zero, and solving for the critical value of P_T . This critical pressure is

$$P_{TC} = (1/K_O) \quad (52)$$

As is seen in the above figure, the data points from this study are all on the high pressure side of the maximum. This was done to avoid the coking problems that arise at low hydrogen partial pressures. At pressures below about 100 psig, coking reactions become appreciable, the catalyst tends to deactivate, and the simplified model does not apply.

This pressure effect can also be used to show that a "single-site" model does not fit the data. If a single-site model were to hold, the equation corresponding to (51) would be

$$\frac{Y}{Y_i^*} = 1 - e^{-k_O' \beta P_T / (1 + K_O' P_T)} \quad (53)$$

This function does not fall back to zero at high pressures, but increases from zero at low pressures and approaches the value $1 - e^{-k_O' \beta / K_O'}$ as the pressure is increased. Since the data obviously show a decreasing conversion at high pressures, the "single-site" model cannot be used to describe the system.

8. Discussion of Hydrogen Partial Pressure Effects Noted by Some Investigators

Data from several investigations of hydroisomerization reactions on other solid catalysts have shown separate, explicit effects of hydrogen partial pressure, in that conversion decreased

both at low hydrogen partial pressures and at high hydrogen partial pressures, with a maximum falling in the range of 200-400 psia. These findings are compatible with the general model that was used to fit the data from this study. The significant difference between the explicit effects of high hydrogen partial pressures in the above studies and the apparent absence of such explicit effects in this research lies in the relative magnitudes of the three "adsorption coefficients."

As an extreme example, assume that K_H was much larger than either K_I or K_n . Thus, the "rate constant," k , would approach

$$k = k_o / (1 + K_H p_H). \quad (54)$$

It is obvious that under these conditions, the reaction rate would decrease with increasing hydrogen partial pressures. The decrease at low hydrogen partial pressures could still be due to the increased coking rates.

A further extension of the general model can be made if the product $K_H p_H$ were much larger than unity. In this case, the reaction rate would vary inversely with the hydrogen partial pressure,

$$k = k_o / (K_H p_H) \quad (55)$$

The data of Sinfelt⁽⁷⁵⁾ were found to fit a similar model, as the rate of isomerization of n-pentane at low conversions were expressed as

$$r = k \left[\frac{p_n}{p_H} \right]^n. \quad (56)$$

Combining equations (4) and (55) results in

$$r = \frac{k_o}{K_H P_H} \left[C_n - \frac{C_i}{K} \right]. \quad (57)$$

Since Sinfelt's data were taken under conditions such that

$$\frac{C_i}{K} \ll C_n,$$

$$r = \frac{k_o}{K_H P_H} C_n = \frac{k_o}{K_H P_H} \frac{P_n}{RT} = \frac{k_o}{K_H RT} \left[\frac{P_n}{P_H} \right]^1, \quad (58)$$

or

$$r = k_T \left[\frac{P_n}{P_H} \right]^1, \quad (59)$$

which is a restricted form of the relationship described by Sinfelt.

9. Empirical Correlation of Data

Figure 39 (page 124) shows a correlation of the data, in which the conversion is plotted vs $\sqrt{P_T(W)(1 + R_H)}$. This plot shows a family of curves, one for each temperature. Such a relationship can be rationalized by the following reasoning:

Since

$$Y = Y_i^* \left(1 - e^{-k \rho_B t_H / Y_i^*} \right), \quad (60)$$

the conversion is a function of holding time (t_H), and temperature (as it affects k , Y_i^* , and to a lesser extent, t_H).

Figure 39. Empirical Correlation of Data

The relationship between k and P_T (Figure 37, page 118), at a given temperature, can be approximated by

$$\frac{1}{\sqrt{k}} = BP_T \quad (61)$$

or

$$k = \frac{1}{B^2} \left[\frac{1}{P_T^2} \right] \quad (62)$$

Also, from a continuity equation,

$$W_{C_5} = A\bar{V} \rho_{C_5}, \quad (63)$$

where W_{C_5} = mass flow rate of C_5 's
 A = cross-sectional area of reactor
 $\bar{V}$ = average velocity of C_5 's in reactor bed
 ρ_{C_5} = density of C_5 's in stream.

The holding time,

$$t_H = \frac{L}{\bar{V}} \quad (64)$$

where

L = length of catalyst bed.

$$\begin{aligned} t_H &= \frac{L}{\bar{V}} = \frac{LA \rho_{C_5}}{W_{C_5}} = \frac{\gamma \rho_{C_5}}{W_{C_5}} \\ &= \frac{\gamma \rho_{C_5}}{RT} \left[\frac{1}{W_{C_5}} \right] = \frac{\gamma}{RT} \left[\frac{\rho_{C_5}}{W_{C_5}} \right] \end{aligned} \quad (65)$$

where p_{C_5} = partial pressure of C_5 's

T = absolute temperature

R = gas constant

$\mathcal{V}$ = volume of catalyst bed.

Therefore,

$$\frac{k \rho_B^{t_H}}{Y_i^*} = \left(\frac{1}{B^2} \right) \left(\frac{1}{P_T^2} \right) \left(\frac{\rho_B}{Y_i^*} \right) \left(\frac{\mathcal{V}}{RT} \right) \left(\frac{p_{C_5}}{W_{C_5}} \right) \quad (66)$$

$$= \left(\frac{\rho_B}{B^2 Y_i^* RT} \right) \left(\frac{1}{P_T} \right) \left(\frac{p_{C_5}}{p_{C_5} + p_{H_2}} \right) \left(\frac{1}{W_{C_5}} \right) \quad (67)$$

or

$$\frac{k \rho_B^{t_H}}{Y_i^*} = \left(\frac{B}{B^2 Y_i^* RT} \right) \left(\frac{1}{P_T (1 + R_H) W_{C_5}} \right) \quad (68)$$

By definition,

$$W = \frac{W_{C_5}}{(\text{wt. catalyst})} = \frac{W_{C_5}}{\mathcal{V} \rho_B} \quad (69)$$

Therefore,

$$\frac{k \rho_B^{t_H}}{Y_i^*} = \left(\frac{1}{B^2 Y_i^* RT} \right) \left(\frac{1}{P_T (1 + R_H) (W)} \right) \quad (70)$$

Substituting in equation (5),

$$Y = Y_i^* \left[1 - e^{-\left[\frac{1}{B^2 Y_i^* RT} \frac{1}{P_T (1 + R_H) (W)} \right]} \right] \quad (71)$$

This says that the conversion (for a given temperature) should be a function of the group $[P_T(1 + H_2/C_5)(W)]$. This relationship is as shown in Figure 39 (page 124) where Y is plotted vs $\sqrt{P_T(1 + R_H)(W)}$. The correlation is very good, except for the 600°F data. This is

presumably due to two factors: (1) the scatter due to experimental factors is the greatest at this high temperature, (2) the assumption that $\frac{1}{\sqrt{k}} = BP_T$ is not too good at this high temperature.

10. Cracking Rates

In most of the runs, cracking (wt. % (C₁-C₄) in hydrocarbon products) was less than 1%, as is shown in Figure 40A (page 128). The high temperature runs (600°F), however, showed a higher level of cracking activity. These runs yielded relatively high conversion, which would be expected to result in higher cracking. The 450 psig data in Figure 40B (page 128) show that the 600°F runs may have the same cracking-conversion relationship as at lower temperatures; but additional data at high conversion and low temperatures will be required before definite conclusions can be made.

Figure 40C (page 128) shows the 550°F data at two pressure levels, 220-252 psig and 416-450 psig. All the variation in the cracking activity can be accounted for by the usual (C₁-C₄) vs conversion relationship, indicating that cracking is not significantly affected by pressure in this operating range.

Figure 40. Observed Cracking Rates

CHAPTER VII

ERROR ANALYSIS

A. Introduction

Mention has already been made of the reliabilities of the various instruments used in obtaining the basic data in this research. This section will be devoted to the development of a relationship between the random uncertainty in the basic data and the expected "scatter" in the final calculated quantities.

"Steady state" is usually defined for a chemical process as a condition characterized by the invariance (with respect to time) of macroscopic quantities at a given point. Examples of such quantities are temperature, flow rates, concentrations, etc. However, measurements of these quantities will vary, due to the uncontrollable random errors inherent in the measuring instruments. Thus, "m" repeated measurements, $X_1, X_2, X_3, \dots, X_m$, of a given quantity whose value is " μ ," will, as a rule, yield results which approximate μ , but which are not expected to be numerically equal to μ , due to experimental errors. The average of these measurements, $\bar{X} = \frac{\sum X_i}{m}$, is statistically a much better estimate of μ than any one of the original estimates.

B. Probability Distribution Functions

The concepts of probability and statistics can be used to describe such a "sampling process." The probability distribution function, " $P(X)$ " contains a complete description of the random nature of such a measurement. In general, $P(X)$ is a function of X somewhat similar to the example shown in Figure 41.

The properties of a probability distribution function are:

- (1) It is single-valued for all X .
- (2) It is always positive (or zero).
- (3) The area beneath the curve between any two given points is numerically equal to the probability that a given measurement will yield a value of X lying between the two points.

(4) The total area under the curve is unity (this follows directly from (3)).

(5) The "expected value" of the distribution is equal to the

first moment of the curve,
$$\int_{-\infty}^{\infty} X p(X) dX = \mu .$$

This "expected value" is identical to the actual value of the property being estimated (assuming no consistent bias errors in the measurement). Although the actual measurements will tend to cluster around μ , the possible results of measurement can vary over a wide range. For example, the probability of a measurement lying outside of B and C would be rather small.

This leads to the crux of the problem, for even at "steady state," repeated measurements of the various instruments will yield differing results--even though the actual quantity being measured is constant. Thus, it follows that any quantity (e.g., "Y") calculated from these measured "random" variables will itself be a random variable. Each different set of data will, in principle, yield a slightly different value of Y. As an example, even though the process is at steady state, and the catalyst is exhibiting a certain level of activity, our estimates of this activity will vary, since they are calculated from data which vary randomly with time.

Thus, the catalyst activity (Y), while not a basic measurement, will also be a "random" variable, and will have its own probability distribution function. The mean (first moment) of

this distribution, "y", will be the actual catalyst activity which would be calculated from the actual values of the basic measured quantities:

$$y = f(x_1, x_2, x_3 \dots x_n). \quad (72)$$

" x_i " is the actual value, of which " X_i " is an estimate. In our calculations, however, we are forced to estimate y from estimates of the x's:

$$Y = f(X_1, X_2, X_3 \dots X_n). \quad (73)$$

Y is then an estimate of y. As was the case with the X's, the average of several Y's will yield a better estimate of y than any of the single original estimates.

In principle, statistical theory can be used to calculate the probability distribution function of a calculated ("independent") variable if the probability distribution functions of the measured ("independent") variables and the functional relationship ("f") is known. For all but the simplest functions, however, the complexity of the mathematics normally precludes such an approach. An approximate approach is often used, since the probability distribution functions of the measured variables are seldom known with sufficient accuracy for a rigorous mathematical approach.

C. Mathematical Basis for Propagation of Errors Equation

If y, a dependent variable, can be related mathematically to a series of independent variables, $x_1, x_2, x_3 \dots x_n$, as

$$y = f(x_1, x_2, x_3, \dots x_n), \quad (74)$$

we can determine the sensitivity of y to changes to any single x_i by

calculating the partial derivative of y with respect to x_1 . We can also estimate the effect of changing several x 's by

$$\Delta y \approx \left[\frac{\partial y}{\partial x_1} \right] \Delta x_1 + \left[\frac{\partial y}{\partial x_2} \right] \Delta x_2 \dots = \sum_{i=1}^m \left[\frac{\partial y}{\partial x_i} \right] \Delta x_i. \quad (75)$$

This simple relationship is sometimes useful in estimating bias errors, or effects of known changes in the levels of the independent variables.

However, in the problem of immediate interest, we are concerned with random errors rather than definite changes. The probable errors in each independent variable are characterized by its probability distribution function. The mean of the distribution is the true value of the variable (no "bias" errors). A common measure of the "spread" of the distribution, or in other words, the "precision" of the data, is the standard deviation. In general, the "variance" (square of the standard deviation) is the second moment about the mean,

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \mu)^2 p(x) dx \quad (76)$$

For many common distributions, approximately 95% of the measurements will lie in the interval $x \pm 2\sigma$. For a "normal" distribution*, this percentage is 95.45.

$$* p(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2} \left[\frac{x-\mu}{\sigma} \right]^2}$$

Although σ_X is generally not known for any of the dependent variables, it can be estimated from repeated observations as

$$\sigma_X \approx s_X = \sqrt{\frac{\sum [X - \bar{X}]^2}{N - 1}}, \quad (77)$$

where N is the number of observations, and $\bar{X} = \frac{\sum X}{N}$.

As will be shown below, the standard deviation of a calculated variable can be estimated from (1) the standard deviations of the measured variables, and (2) the form of the mathematical relationship defining the dependent variable as a function of the independent variables.

If a set of process measurements were taken on a "steady state" chemical process, a value of Y could be calculated by equation (73). If this process were repeated a large number of times, N , the average of each X would approach its true value, x , and the average of Y would approach its true value, y . As $N \rightarrow \infty$, these averages would become equal to their respective true values. It can be shown statistically that the best estimate of any of these variables is the mean of the respective determinations. The actual relationship is:

$$y = f(x_1, x_2, \dots, x_m) \quad (78)$$

The relationship used in the calculation is:

$$Y = f(X_1, X_2, \dots, X_m) \quad (79)$$

The error in Y for a single calculation can be approximated by:

$$Y - y = \Delta y = \left(\frac{\partial y}{\partial x_1} \right) \Delta x_1 + \left(\frac{\partial y}{\partial x_2} \right) \Delta x_2 \dots + \left(\frac{\partial y}{\partial x_m} \right) \Delta x_m \quad (80)$$

where $\Delta x_i = X_i - x_i$.

If both sides of equation (80) are squared, a matrix of terms would be obtained on the right. Each term would be one of the possible combinations of the above terms taken two at a time. The terms would have the general form -

$$\left(\frac{\partial y}{\partial x_j} \right) \left(\frac{\partial y}{\partial x_k} \right) (\Delta x_j) (\Delta x_k) .$$

The diagonal elements would have the general form

$$\left(\frac{\partial y}{\partial x_i} \right)^2 (\Delta x_i)^2 .$$

Realizing that the $(\Delta x$'s) are random variables $(\Delta x = X - x)$, we could make a series of N runs, summing the $(\Delta y)^2$'s.

If both sides of the resulting summation were divided by $N-1$, the left side would become -

$$\frac{\sum_N (\Delta y)^2}{N-1}$$

while the right side would be a matrix similar to the previous one, except that the general terms would appear as:

$$\frac{\sum_N \left(\frac{\partial y}{\partial x_j} \right) \left(\frac{\partial y}{\partial x_k} \right) (\Delta x_j) (\Delta x_k)}{N-1}$$

For relatively small errors, the partial derivatives evaluated at the true value of the x 's can be taken as constants yielding m^2 terms of the following form:

$$\left(\frac{\partial y}{\partial x_j} \right) \left(\frac{\partial y}{\partial x_k} \right) \frac{\sum (\Delta x_j)(\Delta x_k)}{N-1}$$

The diagonal elements would appear as

$$\left(\frac{\partial y}{\partial x_i} \right)^2 \frac{\sum (\Delta x_i)^2}{N-1}$$

As N approaches infinity, the off-diagonal elements will approach zero (assuming the errors in the x 's are independent of each other), since both positive and negative Δx 's would be equally likely.

Also, by definition of σ^2 ,

$$\lim_{N \rightarrow \infty} \left[\frac{\sum (\Delta y)^2}{N-1} \right] = \sigma_Y^2 \quad (82)$$

and

$$\lim_{N \rightarrow \infty} \left[\frac{\sum (\Delta x_i)^2}{N-1} \right] = \sigma_{X_i}^2 \quad (83)$$

The resulting equation is therefore:

$$(3) \quad \sigma_Y^2 = \left(\frac{\partial y}{\partial x_1} \right)^2 \sigma_{X_1}^2 + \left(\frac{\partial y}{\partial x_2} \right)^2 \sigma_{X_2}^2 + \dots + \left(\frac{\partial y}{\partial x_m} \right)^2 \sigma_{X_m}^2 \quad (84)$$

or

$$\sigma_Y^2 = \sum_{i=1}^m \left(\frac{\partial y}{\partial x_i} \right)^2 \sigma_{X_i}^2 \quad (85)$$

The end result, equation (85), is a very useful relationship that has been used extensively, as will be discussed later. It is exact for linear functions, and may be taken as a good approximation for most non-linear functions when the standard deviations of the independent variables are less than 20% of their respective means.⁽²¹⁾ The equation relates the variance (σ^2) of Y to a series of terms, one for each independent variable. Each term in this summation is a direct measure of the amount of uncertainty in Y that is due to the probable errors in the observed value of the corresponding x.

The form of the terms is also interesting. Each term contains two factors, one a measure of the possible errors in measuring x, and the other a measure of the sensitivity of Y to errors in x. Thus, we can tell why a certain variable contributes significantly to the variance of Y; whether it is simply due to the errors as such, or whether it is due to the sensitivity of the mathematical relationships involved.

Although this does not directly yield an explicit function for the probability distribution of Y, it does relate the standard deviation of that distribution to the standard deviations of the distributions of the observed variables. The standard deviation can yield valuable information concerning the percentage of the time we would expect our errors to exceed a given level. This is, of course, a function of the specific probability distribution involved. In most cases, however, the errors in observed

variables are assumed to follow a "normal" distribution whose properties have been extensively tabulated. Thus, assuming the Δx 's are normally distributed, the σ_x 's can be estimated from repeated measurements on previous quality control samples, etc.

Assuming Y to have a distribution similar to the normal, we would expect about 95% of the calculated Y's to be in the range $y \pm 2 \sigma_y$. A more conservative estimate could be made using Tchebycheff's inequality which states that at least $1 - \frac{1}{h^2}$ fraction of a probability distribution will be within $\pm h \sigma$ from the mean, regardless of the distribution. This shows that at least 95% of the time we would measure a value Y inside the range $y + 4.5 \sigma_y$. As an approximation, we normally make estimates using tabulated properties of the normal distribution on the basis that a reasonable assumption as to the shape of the distribution of Y would lead to more accurate confidence statements than we would get by using an extreme limit such as Tchebycheff's inequality.

D. Analysis of Calculations for this Research

Typical experimental data used for the calculations in this research project are listed in Table III (page 139). The tabulated "two sigma limits" were estimated either from calibration data or from industrial experience with similar instruments.

A Fortran program was written to enable the propagation of error computations to be made on an IBM 7074 digital computer. This program determined the effects of errors in the process data on twenty-three calculated variables. The partial derivatives were

TABLE III
UNCERTAINTY IN TYPICAL DATA USED IN PROCESS CALCULATIONS

Observation	Value	Estimated "Two Sigma Limits"	
		Absolute	Percentage
1. C ₁ H ₄ G.C. Calibration Constant	3.765	0.0030	0.08
2. C ₂ H ₆ " " "	2.496	0.0070	0.28
3. C ₃ H ₈ " " "	2.006	0.0080	0.39
4. i-C ₄ H ₁₀ " " "	1.707	0.0044	0.26
5. n-C ₄ H ₁₀ " " "	1.685	0.0056	0.33
6. i-C ₅ H ₁₂ " " "	1.580	0.0200	1.26
7. n-C ₅ H ₁₂ " " "	1.495	0.0126	0.84
8. C ₆ " " "	1.352	0.0200	1.48
9. Density of n-C ₅ @ 75°F., 500 psig, gms./cc.	0.632	0.0060	0.95
10. Density of n-C ₅ @ 60°F., 1 atm., gms./cc.	0.631	0.0060	0.95
11. Catalyst Temperature, °F.	550.0	4.00	0.40(1)
12. Reactor Pressure, psig.	450.0	4.00	0.89
13. Feed Pump Difference, cc.	122.6	0.200	0.16
14. Wet Test Meter Calibration, min./(.05 ft. ³)	0.900	0.009	1.0
15. Wet Test Meter Temperature, °F.	80.00	2.00	0.37(1)
16. Wet Test Meter Difference, ft. ³	4.249	0.04	0.94
17. Time of Material Balance, min.	60.00	0.03	0.05
18. Volume of Catalyst, cc.	15.0	1.00	6.7
19. Weight of Catalyst, gms.	10.34	0.05	0.49
20. C ₁ C ₄ G.C. Area	0.00	0.05	--
21. C ₂ H ₆ " "	0.05	0.001	2.0
22. C ₃ H ₈ " "	0.34	0.0068	2.0
23. i-C ₄ H ₁₀ " "	0.30	0.0060	2.0
24. n-C ₄ H ₁₀ " "	0.55	0.011	2.0
25. i-C ₅ H ₁₂ " "	16.35	0.327	2.0
26. n-C ₅ H ₁₂ " "	22.00	0.440	2.0
27. C ₆ " "	0.00	0.050	--

(1) On absolute temperature basis.

calculated numerically by incrementing the various independent variables by one percent. The results of this analysis are tabulated in Table IV where the "expected two sigma" of each calculated variable is noted, along with the process observation(s) contributing the most to the indicated uncertainty. The actual computer printouts, reproduced in Table E-1 (page 239) give more details on the error analysis. For example, all the partial derivatives are printed out, as are the contributions (expressed in percent) of each observation to the variance of each calculated variable.

TABLE IV
SUMMARY OF RESULTS OF PROPAGATION OF ERROR ANALYSIS

Calculated Variable	Value	Estimated "Two Sigma Limits," %	Process Data Responsible for Most of Uncertainty
1. V/V/Hr.	8.19	6.75	Catalyst Volume
2. W/W/Hr.	7.49	1.18	Density of n-C ₅ Feed
3. H ₂ /C ₅ , mols./mol	3.45	1.59	Wet Test Meter Calibration
4. H ₂ /C ₅ , SCFB	4012	1.85	Wet Test Meter Calibration
5. Superficial Gas Velocity, cm./sec.	0.986	1.33	Reactor Pressure
6. Gms. H ₂ per 100 gms. n-C ₅ Fed	9.62	1.59	Wet Test Meter Calibration
7. " C ₁ H ₄ "	0.077	1.33	n-C ₅ G.C. Area ⁽¹⁾
8. " C ₂ H ₆ "	0.022	2.56	C ₂ H ₆ G.C. Area
9. " C ₃ H ₈ "	0.176	2.58	C ₃ H ₈ G.C. Area
10. " i-C ₄ H ₁₀ "	0.174	2.56	i-C ₄ H ₁₀ G.C. Area
11. " n-C ₄ H ₁₀ "	0.315	2.56	n-C ₄ H ₁₀ G.C. Area
12. " i-C ₅ H ₁₂ "	43.66	1.79	i-C ₅ H ₁₂ G.C. Area
13. " n-C ₅ H ₁₂ "	55.59	1.41	n-C ₅ H ₁₂ G.C. Area
14. " C ₆ "	0.0	0.03 ⁽²⁾	C ₆ G.C. Area
15. Conversion, %	44.41	1.76	n-C ₅ H ₁₂ G.C. Area
16. % i-C ₅ /p-C ₅	43.99	1.79	Both C ₅ G.C. Areas
17. Wt. % (C ₁ -C ₄)	0.76	1.87	n-C ₅ H ₁₂ G.C. Area
18. Selectivity %	98.31	0.09	C ₆ G.C. Area
19. Rate Constant, cm. ³ /gm.sec.	0.131	10.39	Catalyst Temperature
20. 1/√ Rate Constant	2.76	5.73	Catalyst Temperature
21. Holding Time, Seconds	7.77	6.80	Catalyst Volume
22. Void Fraction of Bed	0.577	4.85	Catalyst Volume
23. Material Balance	99.01	1.30	Wet Test Meter Difference

(1) Due to normalization and to empirical method of computation of CH₄.

(2) On absolute basis.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The hydrogen form of synthetic mordenite, with or without palladium impregnation, is an extremely active catalyst for the hydroisomerization of normal paraffins. For normal pentane, it is about eight times as active as Linde's MB-5390, the best commercially-available zeolite isomerization catalyst.
2. Data from this work indicate that, under typical industrial process conditions, reactions on the hydrogenation-dehydrogenation component (impregnated palladium or platinum) are not rate-limiting. The rate-controlling chemical step occurs on the active sites associated with the crystalline structure of the mordenite. According to the conventionally-accepted mechanisms, these acidic sites of the "dual-function" hydroisomerization catalysts are necessary to isomerize the olefinic hydrocarbon intermediates. Thus, these data are compatible with the assumption that isomerization is the rate-controlling step in the reaction sequence.

3. Under typical operating conditions, mass transfer from the fluid gas stream to the particle surface is not a rate-limiting step in the overall process.
4. Diffusion within the macroscopic pores of the filled particles used in this research is not rate-limiting. Diffusion inside the microscopic pores (4-7Å diameter) of the mordenite crystal structure was not systematically investigated. However, the data from this study are compatible with the assumption that this intra-crystal-line diffusion is a limiting factor, as would be expected from the fact that the diameters of the intra-crystalline pores and the lengths of the reactant molecules are essentially the same.
5. The experimental data on mordenite-based catalysts can be adequately correlated with simplified equations based on conventional approaches to heterogeneous catalysis. These correlations are compatible with a "dual-site" mechanism in which the dynamic adsorption constants for all three major components, n-pentane, isopentane, and hydrogen, are essentially equal. It is recognized that this method of correlation does not necessarily imply an exact knowledge of the mechanisms involved inside the mordenite crystalline structure, since the actual reactions take place in an entirely different environment from the type assumed in deriving conventional catalysis equations.

B. Recommendations

The basic data provided by this study have demonstrated the remarkable hydroisomerization activity of a small-pore crystalline zeolite whose "active sites" are inside of parallel intracrystalline pores, only 4-7 $\text{\AA}$ in diameter. This fact immediately suggests two extensions of this research.

The first is concerned with the highly interesting theoretical aspects of the intracrystalline reactions. This realm of diffusion-reaction mechanisms is unlike any other that has been systematically investigated at this time. The reactants must diffuse in and out of pores whose diameters are only 10-20% longer than the lengths of the reactant molecules. These "pores" are remarkably regular in their geometrical properties. A molecule within cannot be considered as being a "gas" molecule because of the severe restrictions placed on it by the pore walls. Even the Knudsen diffusion equations do not apply. The walls themselves are characterized by electrostatic fields that can affect the reactant molecules simultaneously from all sides. This environment obviously will present challenging and formidable problems for future research work.

The second recommendation concerns the shorter-range goals of capitalizing on the high activity of mordenite-based catalysts. As was noted earlier, this type of catalyst is considerably higher in activity than are conventional "large pore" solid catalysts--in spite of the necessarily severe diffusional limitations. Thus, there are some facets of the mordenite structure that correspond to "active

sites" whose catalytic activities are one or two orders of magnitude higher than those of conventional catalysts. Data from this research also suggest that, in addition to "acidic sites," mordenite also has active sites whose characteristics are similar to the "metallic sites" that are normally required for hydrogenation-dehydrogenation reactions. These interesting characteristics should be investigated, not only with regard to extending the isomerization studies to higher molecular-weight hydrocarbons, but also with regard to other chemical reactions.

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APPENDIX A
SUMMARIZED ISOMERIZATION DATA

TABLE A-1

SUMMARIZED ISOMERIZATION DATA

Catalyst	-----Pd on H-Mordenite-----										
	-----500-----						-----525-----				
Temperature, °F.											
Pressure, psia	115	165	165	265	365	465	465	265	365	465	465
Wt. % Metal on Catalyst	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed Rate, W/W/Hr.	4.04	4.04	3.96	4.04	4.04	3.96	4.07	8.11	8.11	8.11	7.84
H ₂ , mols/mol	3.36	3.36	3.42	3.36	3.36	3.42	3.43	3.05	1.22	0.753	0.962
H ₂ Partial Pressure, psia	88.6	127.1	127.6	204.2	281.4	359.8	360.2	199.6	200.7	200.0	228.5
C ₅ Partial Pressure, psia	26.4	37.9	37.4	60.8	83.6	105.2	104.8	65.4	164.3	265.0	237.5
Particle Size, mm (avg.)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Gas Velocity, cm/sec (superficial)	1.86	1.29	1.31	0.81	0.58	0.47	0.47	1.54	0.61	0.38	0.42
% i-C ₅ /p-C ₅	50.5	42.5	46.6	34.8	30.3	28.3	22.6	32.6	40.5	44.4	42.3
Wt. % C ₄ ⁻	0.8	0.6	0.6	0.3	0.3	0.4	0.1	0.6	1.2	1.3	0.8
Void Fraction	0.608	0.608	0.600	0.608	0.608	0.600	0.611	0.609	0.609	0.609	0.596
k, cc/gm-sec	0.33	0.17	0.20	0.079	0.047	0.034	0.026	0.14	0.74	0.055	0.055
1/√k	1.72	2.40	2.23	3.56	4.60	5.44	6.20	2.68	3.68	4.27	4.27
Run Number	24D	24C	25B	24B	24A	25A	18	23A	23C	23B	22B

TABLE A-1

SUMMARIZED ISOMERIZATION DATA

Catalyst	-----Pd on H-Mordenite-----										
Temperature, °F.	525	525	-----550-----								
Pressure, psia	465	465	235	235	267	267	431	431	465	465	465
Wt. % Metal on Catalyst	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.2	0.5	0.5
Feed Rate, W/W/Hr.	7.84	8.11	3.83	3.83	7.67	7.67	3.83	3.83	7.95	7.49	7.48
H ₂ , mols/mol	2.68	3.39	6.02	6.04	3.03	3.01	11.86	11.89	3.46	3.45	3.56
H ₂ Partial Pressure, psia	338.2	359.0	201.5	201.6	200.8	200.4	397.5	377.6	360.8	360.6	363.0
C ₅ Partial Pressure, psia	126.3	106.0	33.5	33.4	66.2	66.6	33.5	33.4	104.2	104.4	102.0
Particle Size, mm (avg.)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Gas Velocity, cm/sec (superficial)	0.80	0.95	1.54	1.54	1.56	1.55	1.54	1.54	0.99	0.99	2.02
% i-C ₅ /p-C ₅	26.4	22.6	45.8	49.0	46.8	44.4	28.2	29.4	39.4	37.1	37.3
Wt. % C ₄ ⁻	0.8	0.2	0.9	1.3	1.2	1.2	0.4	0.4	1.1	0.7	0.6
Void Fraction	0.596	0.509	0.587	0.587	0.587	0.587	0.587	0.587	0.601	0.577	0.577
k, cc/gm-sec	0.053	0.053	0.22	0.26	0.24	0.21	0.11	0.11	0.12	0.10	0.10
1/√k	4.35	4.35	2.13	1.97	2.05	2.17	3.00	3.00	2.88	3.17	3.12
Run Number	22A	23D	21D	21H	21A	21E	21C	21G	16	9	10

TABLE A-1

SUMMARIZED ISOMERIZATION DATA

Catalyst	-----Pd on H-Mordenite-----							
Temperature, °F.	-----550-----							
Pressure, psia	-----465-----							
Wt. % Metal on Catalyst	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.1
Feed Rate, W/W/Hr.	6.54	7.26	10.84	6.86	7.84	7.67	7.67	7.65
H ₂ , mols/mol	3.45	3.43	3.41	3.45	3.44	5.94	5.93	3.48
H ₂ Partial Pressure, psia	360.6	360.1	359.8	360.6	360.4	398.0	397.9	361.4
C ₅ Partial Pressure, psia	104.4	104.9	105.2	101.4	104.6	67.0	67.1	103.6
Particle Size, mm (avg.)	0.6	0.35	0.1	1.0	0.6	0.6	0.6	0.6
Gas Velocity, cm/sec (superficial)	0.49	0.98	1.00	0.99	0.99	1.54	1.54	0.99
% i-C ₅ /p-C ₅	43.7	43.5	29.4	42.5	39.2	26.8	24.6	40.3
Wt. % C ₄ ⁻	0.7	0.8	0.5	0.6	0.7	0.4	0.3	1.0
Void Fraction	0.540	0.564	0.589	0.538	0.596	0.587	0.587	0.586
k, cc/gm-sec	0.11	0.12	0.11	0.11	0.11	0.10	0.10	0.12
1/√k	3.00	2.90	3.00	3.00	3.00	3.12	3.12	2.90
Run Number	11	12	13	14	17	21B	21F	15

TABLE A-1

SUMMARIZED ISOMERIZATION DATA

Catalyst	-----Pd on H-Mordenite-----							
Temperature, °F.	550	550	550	600	600	600	600	600
Pressure, psia	465	465	465	165	265	265	365	465
Wt. % Metal on Catalyst	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed Rate, W/W/Hr.	7.56	7.56	15.86	16.17	16.17	15.87	16.17	16.53
H ₂ , mols/mol	3.45	0.714	0.687	3.39	3.39	3.40	3.39	3.51
H ₂ Partial Pressure, psia	360.8	195	190	127.4	204.6	204.7	282.0	362.0
C ₅ Partial Pressure, psia	104.2	270	275	37.6	60.4	60.3	83.0	103.0
Particle Size, mm (avg.)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Gas Velocity, cm/sec (superficial)	0.99	0.38	0.75	5.76	3.58	3.59	2.60	2.10
% i-C ₅ /p-C ₅	43.4	61.4	46.9	55.6	56.0	65.3	57.0	39.4
Wt. % C ₄ ⁻	0.8	3.0	1.0	5.3	3.3	4.5	3.0	1.0
Void Fraction	0.580	0.580	0.600	0.608	0.608	0.600	0.608	0.616
k, cc/gm-sec	0.13	0.11	0.12	1.39	0.89	1.36	0.67	0.26
1/√k	2.78	3.00	2.90	0.85	1.06	0.85	1.22	1.96
Run Number	5A	5B	6	24G	24F	25D	24E	19

TABLE A-1

SUMMARIZED ISOMERIZATION DATA

Catalyst	---Pd on H-Mordenite---			-----Linde MB-5390-----				
Temperature, °F.	600	650	650	650	650	650	650	650
Pressure, psia	-----465-----							
Wt. % Metal on Catalyst	0.5	0.5	0.5	--	--	--	--	--
Feed Rate, W/W/Hr.	15.87	7.89	11.84	4.91	4.91	9.82	9.82	9.49
H ₂ , mols/mol	3.40	3.23	2.16	3.93	0.778	3.86	0.783	3.42
H ₂ Partial Pressure, psia	359.3	355.0	318	370.8	203	369.4	205	360
C ₅ Partial Pressure, psia	105.7	110.0	147	94.2	262	95.6	260	105
Gas Velocity, cm/sec (superficial)	2.05	1.36	1.52	1.20	0.433	2.37	0.87	1.08
% i-C ₅ /p-C ₅	62.5	65.2	51.1	583	64.5	45.7	63.5	50.2
Wt. % C ₄	3.6	91.6	43.1	0.7	10.0	0.3	4.3	0.4
Void Fraction	0.600	0.610	0.610	0.644	0.644	0.644	0.644	0.666
k, cc/gm-sec	0.75	--	--	0.21	0.15	0.23	0.25	0.25
1/√k	1.16	--	--	2.15	2.60	2.09	2.02	2.02
Run Number	25C	3A	3B	1A	1B	2A	2B	4

APPENDIX B
DETAILED ISOMERIZATION DATA

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 1A

CATALYST	LINDE MB-5390
PARTICLE SIZE, MM.	0.42 - 0.84
TEMPERATURE, F	650.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	4.52
W/HR-W	4.91
HYDROGEN, MOLES/MOLE C5	3.936
SCFB	4579.
SUPERFICIAL	
HOLDING TIME, SEC.	11.54
GAS VELOCITY, CM/SEC.	1.202
VOID FRACTION	0.644
MINUTES ON FEED	80
PRODUCT	
GMS/100 GMS N-PENTANE	
HYDROGEN	10.98
METHANE	0.09
ETHANE	0.07
PROPANE	0.20
I-BUTANE	0.19
N-BUTANE	0.18
I-PENTANE	57.90
N-PENTANE	41.39
C6 PLUS	0.00
CONVERSION, %	58.61
IC5/PC5, %	58.31
WT % C4-	0.73
SELECTIVITY, %	98.78
RATE CONSTANT	
K, CC/GM-SEC	0.2154
$1/\sqrt{K}$	2.15
MATERIAL BALANCE, %	99.50

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 1B

CATALYST	LINDE MB-5390
PARTICLE SIZE, MM.	0.42 - 0.84
TEMPERATURE, °F	650.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	4.52
W/HR-W	4.91
HYDROGEN, MOLES/MOLE C5	0.778
SCFB	904.
SUPERFICIAL	
HOLDING TIME, SEC.	32.05
GAS VELOCITY, CM/SEC.	0.433
VOID FRACTION	0.644
MINUTES ON FEED	100
PRODUCT	
GMS/100 GMS N-PENTANE	
HYDROGEN	2.05
METHANE	0.32
ETHANE	0.21
PROPANE	1.82
I-BUTANE	6.14
N-BUTANE	1.57
I-PENTANE	57.06
N-PENTANE	31.38
C6 PLUS	1.62
CONVERSION, %	68.62
IC5/PC5, %	64.52
WT % C4-	10.04
SELECTIVITY, %	83.16
RATE CONSTANT	
K, CC/GM-SEC	0.1462
$1/\sqrt{K}$	2.62

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 2A

CATALYST	LINDE MB-5390
PARTICLE SIZE, MM.	0.42 - 0.84
TEMPERATURE, °F	650.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	9.04
W/HR-W	9.82
HYDROGEN, MOLES/MOLE C5	3.855
SCFB	4485.
SUPERFICIAL	
HOLDING TIME, SEC.	5.87
GAS VELOCITY, CM/SEC.	2.366
VOID FRACTION	0.644
MINUTES ON FEED	145
PRODUCT	
GMS/100 GMS N-PENTANE	
HYDROGEN	10.76
METHANE	0.05
ETHANE	0.03
PROPANE	0.11
I-BUTANE	0.03
N-BUTANE	0.06
I-PENTANE	45.57
N-PENTANE	54.16
C6 PLUS	0.00
CONVERSION, %	45.84
IC5/PC5, %	45.69
WT % C4-	0.28
SELECTIVITY, %	99.41
RATE CONSTANT	
K, CC/GM-SEC	0.2297
$1/\sqrt{K}$	2.09
MATERIAL BALANCE, %	99.88

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 28

CATALYST	LINDE MB-5390
PARTICLE SIZE, MM.	0.42 - 0.84
TEMPERATURE, °F	650.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	9.04
W/HR-W	9.82
HYDROGEN, MOLES/MOLE C5	0.783
SCFB	911.
SUPERFICIAL	
HOLDING TIME, SEC.	15.97
GAS VELOCITY, CM/SEC.	0.869
VOID FRACTION	0.644
MINUTES ON FEED	160
PRODUCT	
GMS/100 GMS N-PENTANE	
HYDROGEN	2.14
METHANE	0.21
ETHANE	0.08
PROPANE	0.72
I-BUTANE	2.58
N-BUTANE	0.75
I-PENTANE	58.96
N-PENTANE	33.86
C6 PLUS	2.88
CONVERSION, %	66.14
IC5/PC5, %	63.52
WT % C4-	4.34
SELECTIVITY, %	89.15
RATE CONSTANT	
K, CC/GM-SEC	0.2456
$1/\sqrt{K}$	2.02

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 3A

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 650.
 PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 7.95
 W/HR-W 7.89

HYDROGEN, MOLES/MOLE C5 3.233
 SCFB 3761.

SUPERFICIAL
 HOLDING TIME, SEC. 7.64
 GAS VELOCITY, CM/SEC. 1.362

VOID FRACTION 0.610

MINUTES ON FEED 15 50

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN 7.53 7.50

METHANE 0.32 0.32

ETHANE 7.99 7.71

PROPANE 50.50 53.56

I-BUTANE 15.94 14.48

N-BUTANE 17.06 16.94

I-PENTANE 5.64 5.47

N-PENTANE 3.06 2.92

C6 PLUS 0.99 0.12

CONVERSION, % 96.94 97.08

IC5/PC5, % 64.83 65.24

WT % C4- 90.46 91.62

SELECTIVITY, % 5.82 5.64

RATE CONSTANT

K, CC/GM-SEC 0.6082 0.7236

$1/\sqrt{K}$ 1.28 1.18

MATERIAL BALANCE, % 101.20

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 38

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 650.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 11.93
W/HR-W 11.84

HYDROGEN, MOLES/MOLE C5 2.156
SCFB 2507.

SUPERFICIAL
HOLDING TIME, SEC. 6.84
GAS VELOCITY, CM/SEC. 1.522

VOID FRACTION 0.610

MINUTES ON FEED 60 70

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 5.13 5.45

METHANE 0.49 0.47

ETHANE 3.28 1.87

PROPANE 28.69 16.57

I-BUTANE 17.21 14.62

N-BUTANE 12.07 9.78

I-PENTANE 20.21 26.60

N-PENTANE 16.42 25.42

C6 PLUS 2.52 5.23

CONVERSION, % 83.58 74.58

IC5/PC5, % 55.17 51.13

WT % C4- 61.20 43.07

SELECTIVITY, % 24.17 35.67

RATE CONSTANT

K, CC/GM-SEC 0.2780 0.2284

1/√K 1.90 2.09

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 4

CATALYST	LINDE MB-5390		
PARTICLE SIZE, MM.	0.42 - 0.84		
TEMPERATURE, °F	650.		
PRESSURE, PSIG	450.		
N-PENTANE, V/HR-V	8.19		
W/HR-W	9.49		
HYDROGEN, MOLES/MOLE C5	3.422		
SCFB	3981.		
SUPERFICIAL			
HOLDING TIME, SEC.	7.10		
GAS VELOCITY, CM/SEC.	1.077		
VOID FRACTION	0.666		
MINUTES ON FEED	10	30	105
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.55	9.55	9.55
METHANE	0.07	0.06	0.06
ETHANE	0.05	0.04	0.03
PROPANE	0.16	0.15	0.16
I-BUTANE	0.08	0.08	0.05
N-BUTANE	0.09	0.08	0.06
I-PENTANE	50.01	50.03	50.06
N-PENTANE	49.55	49.57	49.59
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	50.45	50.43	50.41
IC5/PC5, %	50.23	50.23	50.23
WT % C4-	0.45	0.40	0.36
SELECTIVITY, %	99.13	99.22	99.31
RATE CONSTANT			
K, CC/GM-SEC	0.2462	0.2462	0.2462
$1/\sqrt{K}$	2.02	2.02	2.02
MATERIAL BALANCE, %	98.68		

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 5A

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.56

HYDROGEN, MOLES/MOLE C5 3.451
SCFB 4015.

SUPERFICIAL
HOLDING TIME, SEC. 7.76
GAS VELOCITY, CM/SEC. 0.987

VOID FRACTION 0.580

MINUTES ON FEED 5 10 30 50

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.62 9.62 9.62 9.63

METHANE 0.10 0.11 0.09 0.08

ETHANE 0.16 0.14 0.13 0.10

PROPANE 0.21 0.25 0.21 0.17

I-BUTANE 0.13 0.20 0.16 0.14

N-BUTANE 0.43 0.49 0.37 0.25

I-PENTANE 51.24 48.99 45.80 43.08

N-PENTANE 47.75 49.85 53.27 56.19

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 52.25 50.15 46.73 43.81

IC5/PC5, % 51.76 49.56 46.23 43.39

WT % C4- 1.04 1.18 0.96 0.75

SELECTIVITY, % 98.06 97.69 98.00 98.33

RATE CONSTANT

K, CC/GM-SEC 0.1810 0.1653 0.1446 0.1292
1/√K 2.35 2.46 2.63 2.78

MATERIAL BALANCE, % 99.58

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 5B

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
 PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
 W/HR-W 7.56

HYDROGEN, MOLES/MOLE C5 0.714
 SCFB 830.

SUPERFICIAL
 HOLDING TIME, SEC. 20.15
 GAS VELOCITY, CM/SEC. 0.380

VOID FRACTION 0.580

MINUTES ON FEED 80 90 100

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN	1.96	1.96	1.95
METHANE	0.15	0.13	0.16
ETHANE	0.16	0.11	0.19
PROPANE	0.36	0.25	0.35
I-BUTANE	0.69	0.57	0.80
N-BUTANE	0.70	0.61	0.78
I-PENTANE	59.10	58.45	60.34
N-PENTANE	38.82	39.71	37.29
C6 PLUS	0.06	0.20	0.12

CONVERSION, %	61.18	60.29	62.71
IC5/PC5, %	60.36	59.54	61.80
WT % C4-	2.05	1.67	2.29
SELECTIVITY, %	96.61	96.94	96.22

RATE CONSTANT			
K, CC/GM-SEC	0.1048	0.1002	0.1142
$1/\sqrt{K}$	3.09	3.16	2.96

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 6

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	550.		
PRESSURE, PSIG	450.		
N-PENTANE, V/HR-V	16.41		
W/HR-W	15.86		
HYDROGEN, MOLES/MOLE C5	0.687		
SCFB	799.		
SUPERFICIAL HOLDING TIME, SEC.	10.22		
GAS VELOCITY, CM/SEC.	0.749		
VOID FRACTION	0.600		
MINUTES ON FEED	5	10	40
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	1.90	1.91	1.90
METHANE	0.10	0.09	0.09
ETHANE	0.08	0.06	0.06
PROPANE	0.16	0.11	0.14
I-BUTANE	0.36	0.31	0.32
N-BUTANE	0.29	0.29	0.40
I-PENTANE	50.93	48.49	46.37
N-PENTANE	47.89	50.01	52.49
C6 PLUS	0.22	0.67	0.15
CONVERSION, %	52.11	49.99	47.51
IC5/PC5, %	51.54	49.23	46.91
WT % C4-	0.98	0.85	1.02
SELECTIVITY, %	97.74	96.99	97.59
RATE CONSTANT			
K, CC/GM-SEC	0.1426	0.1297	0.1181
1/√K	2.65	2.78	2.91
MATERIAL BALANCE, %			95.11

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 7A

CATALYST 1/2% PALLADIUM ON MG-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 650.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.33

HYDROGEN, MOLES/MOLE C5 3.460
SCFB 4024.

SUPERFICIAL
HOLDING TIME, SEC. 7.04
GAS VELOCITY, CM/SEC. 1.086

VOID FRACTION 0.567

MINUTES ON FEED 5 10 30 40

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.51	9.52	9.48	9.49
METHANE	0.30	0.31	0.35	0.35
ETHANE	1.22	1.11	1.15	1.31
PROPANE	2.78	2.83	3.62	2.76
I-BUTANE	1.99	2.14	3.62	4.08
N-BUTANE	2.02	2.55	3.41	3.54
I-PENTANE	51.40	51.52	51.67	52.49
N-PENTANE	39.38	37.74	33.43	33.32
C6 PLUS	1.06	1.94	2.94	2.34
CONVERSION, %	60.62	62.26	66.57	66.68
IC5/PC5, %	56.62	57.72	60.72	61.17
WT % C4-	8.30	8.93	12.12	12.01
SELECTIVITY, %	84.79	82.76	77.62	78.72

RATE CONSTANT				
K, CC/GM-SEC	0.2631	0.2803	0.3439	0.3569
1/√K	1.95	1.89	1.71	1.67

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 7B

CATALYST 1/2% PALLADIUM ON MG-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
 PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
 W/HR-W 7.33

HYDROGEN, MOLES/MOLE C5 3.460
 SCFB 4024.

SUPERFICIAL
 HOLDING TIME, SEC. 7.74
 GAS VELOCITY, CM/SEC. 0.989

VOID FRACTION 0.567

MINUTES ON FEED 83

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN 9.66

METHANE 0.03

ETHANE 0.04

PROPANE 0.15

I-BUTANE 0.11

N-BUTANE 0.10

I-PENTANE 13.49

N-PENTANE 85.84

C6 PLUS 0.25

CONVERSION, % 14.16

IC5/PC5, % 13.58

WT % C4- 0.43

SELECTIVITY, % 95.25

RATE CONSTANT

K, CC/GM-SEC 0.0277

$1/\sqrt{K}$ 6.01

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 7C

CATALYST 1/2 %PALLADIUM ON MG-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
 PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
 W/HR-W 7.33

HYDROGEN, MOLES/MOLE C5 1.640
 SCFB 1907.

SUPERFICIAL
 HOLDING TIME, SEC. 13.08
 GAS VELOCITY, CM/SEC. 0.585

VOID FRACTION 0.567

MINUTES ON FEED 110

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN 4.57

METHANE 0.04

ETHANE 0.02

PROPANE 0.21

I-BUTANE 0.12

N-BUTANE 0.14

I-PENTANE 18.22

N-PENTANE 81.25

C6 PLUS 0.00

CONVERSION, % 18.75

IC5/PC5, % 18.31

WT % C4- 0.54

SELECTIVITY, % 97.17

RATE CONSTANT

K, CC/GM-SEC 0.0231

$1/\sqrt{K}$ 6.58

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 8A

CATALYST 1/2% PALLADIUM ON ZN-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 650.
 PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
 W/HR-W 7.34

HYDROGEN, MOLES/MOLE C5 3.406
 SCFB 3962.

SUPERFICIAL
 HOLDING TIME, SEC. 7.14
 GAS VELOCITY, CM/SEC. 1.073

VOID FRACTION 0.569

MINUTES ON FEED 5 10

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN	9.28	9.36
METHANE	0.35	0.32
ETHANE	3.66	1.45
PROPANE	2.17	2.34
I-BUTANE	1.09	2.12
N-BUTANE	1.40	2.61
I-PENTANE	57.98	57.19
N-PENTANE	32.37	32.44
C6 PLUS	1.21	1.68

CONVERSION, %	67.63	67.56
IC5/PC5, %	64.17	63.81
WT % C4-	8.65	8.83
SELECTIVITY, %	85.74	84.65

RATE CONSTANT		
K, CC/GM-SEC	0.5042	0.4739
1/√K	1.41	1.45

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 8B

CATALYST 1/2% PALLADIUM ON ZN-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
 PRESSURE, PSIG 450.
 N-PENTANE, V/HR-V 8.19
 W/HR-W 7.34
 HYDROGEN, MOLES/MOLE C5 3.406
 SCFB 3962.
 SUPERFICIAL
 HOLDING TIME, SEC. 7.84
 GAS VELOCITY, CM/SEC. 0.976
 VOID FRACTION 0.569

MINUTES ON FEED 102

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN 9.51
 METHANE 0.02
 ETHANE 0.03
 PROPANE 0.06
 I-BUTANE 0.03
 N-BUTANE 0.04
 I-PENTANE 10.89
 N-PENTANE 88.93
 C6 PLUS 0.00

CONVERSION, % 11.07
 IC5/PC5, % 10.91
 WT % C4- 0.18
 SELECTIVITY, % 98.39

RATE CONSTANT
 K, CC/GM-SEC 0.0215
 $1/\sqrt{K}$ 6.81

MATERIAL BALANCE, % 101.47

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 8C

CATALYST 1/2% PALLADIUM ON ZN-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	550.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	8.19
W/HR-W	7.34
HYDROGEN, MOLES/MOLE C5	1.226
SCFB	1426.
SUPERFICIAL	
HOLDING TIME, SEC.	15.52
GAS VELOCITY, CM/SEC.	0.493
VOID FRACTION	0.569

MINUTES ON FEED 120

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	3.41
METHANE	0.05
ETHANE	0.03
PROPANE	0.15
I-BUTANE	0.17
N-BUTANE	0.15
I-PENTANE	21.14
N-PENTANE	78.33
C6 PLUS	0.00

CONVERSION, %	21.67
IC5/PC5, %	21.25
WT % C4-	0.54
SELECTIVITY, %	97.55

RATE CONSTANT

K, CC/GM-SEC	0.0233
$1/\sqrt{K}$	6.55

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 9

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.50

HYDROGEN, MOLES/MOLE C5 3.450
SCFB 4012.

SUPERFICIAL
HOLDING TIME, SEC. 7.77
GAS VELOCITY, CM/SEC. 0.986

VOID FRACTION 0.577

MINUTES ON FEED 50 60 80 110

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.62 9.62 9.62 9.62

METHANE 0.09 0.08 0.07 0.07

ETHANE 0.07 0.02 0.04 0.06

PROPANE 0.15 0.18 0.11 0.11

I-BUTANE 0.15 0.17 0.18 0.15

N-BUTANE 0.34 0.32 0.36 0.25

I-PENTANE 49.86 43.66 41.79 36.89

N-PENTANE 49.36 55.59 57.46 62.48

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 50.64 44.41 42.54 37.52

IC5/PC5, % 50.25 43.99 42.11 37.13

WT % C4- 0.80 0.76 0.76 0.64

SELECTIVITY, % 98.46 98.31 98.25 98.32

RATE CONSTANT

K, CC/GM-SEC 0.1686 0.1312 0.1217 0.0997
 $1/\sqrt{K}$ 2.44 2.76 2.87 3.17

MATERIAL BALANCE, % 99.01

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 10

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	550.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	8.17
W/HR-W	7.49
HYDROGEN, MOLES/MOLE C5	3.556
SCFB	4136.
SUPERFICIAL	
HOLDING TIME, SEC.	7.60
GAS VELOCITY, CM/SEC.	2.015
VOID FRACTION	0.577
MINUTES ON FEED	120

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.92
METHANE	0.06
ETHANE	0.03
PROPANE	0.06
I-BUTANE	0.09
N-BUTANE	0.32
I-PENTANE	37.14
N-PENTANE	62.31
C6 PLUS	0.00
CONVERSION, %	37.69
IC5/PC5, %	37.35
WT % C4-	0.56
SELECTIVITY, %	98.54

RATE CONSTANT	
K, CC/GM-SEC	0.1029
1/√K	3.12

MATERIAL BALANCE, %	98.23
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 11

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 7.78
W/HR-W 6.55

HYDROGEN, MOLES/MOLE C5 3.448
SCFB 4010.

SUPERFICIAL
HOLDING TIME, SEC. 8.17
GAS VELOCITY, CM/SEC. 0.487

VOID FRACTION 0.540

MINUTES ON FEED	150	160	170	180
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.61	9.62	9.62	9.62
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METHANE	0.09	0.08	0.07	0.08
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ETHANE	0.11	0.08	0.06	0.08
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PROPANE	0.16	0.15	0.12	0.14
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I-BUTANE	0.17	0.17	0.12	0.11
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N-BUTANE	0.35	0.26	0.27	0.30
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I-PENTANE	44.61	41.64	42.88	44.04
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N-PENTANE	54.53	57.65	56.50	55.26
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C6 PLUS	0.00	0.00	0.00	0.00
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CONVERSION, %	45.47	42.35	43.50	44.74
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IC5/PC5, %	45.00	41.93	43.15	44.35
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WT % C4-	0.87	0.73	0.63	0.71
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SELECTIVITY, %	98.12	98.32	98.58	98.44
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RATE CONSTANT

K, CC/GM-SEC	0.1191	0.1056	0.1107	0.1161
1/√K	2.90	3.08	3.00	2.93

MATERIAL BALANCE, %				100.64
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 12

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.30-0.42

TEMPERATURE, °F	550.			
PRESSURE, PSIG	450.			
N-PENTANE, V/HR-V	8.18			
W/HR-W	7.27			
HYDROGEN, MOLES/MOLE C5	3.430			
SCFB	3989.			
SUPERFICIAL				
HOLDING TIME, SEC.	7.80			
GAS VELOCITY, CM/SEC.	0.981			
VOID FRACTION	0.564			
MINUTES ON FEED	110	120	140	160
PRODUCT				
GMS/100 GMS N-PENTANE				
HYDROGEN	9.57	9.56	9.57	9.57
METHANE	0.08	0.09	0.07	0.08
ETHANE	0.08	0.08	0.04	0.04
PROPANE	0.14	0.19	0.13	0.15
I-BUTANE	0.18	0.18	0.11	0.16
N-BUTANE	0.31	0.42	0.28	0.37
I-PENTANE	42.87	44.65	41.78	42.41
N-PENTANE	56.36	54.41	57.61	56.79
C6 PLUS	0.00	0.00	0.00	0.00
CONVERSION, %	43.64	45.59	42.39	43.21
IC5/PC5, %	43.20	45.07	42.03	42.75
WT % C4-	0.79	0.96	0.63	0.81
SELECTIVITY, %	98.23	97.94	98.55	98.17
RATE CONSTANT				
K, CC/GM-SEC	0.1227	0.1321	0.1171	0.1205
1/√K	2.85	2.75	2.92	2.88
MATERIAL BALANCE, %	98.90			

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 13

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.074-0.149

TEMPERATURE, °F 550.
PRESSURE, PSIG 440.

N-PENTANE, V/HR-V 11.51
W/HR-W 10.85

HYDROGEN, MOLES/MOLE C5 3.414
SCFB 3971.

SUPERFICIAL
HOLDING TIME, SEC. 5.45
GAS VELOCITY, CM/SEC. 1.000

VOID FRACTION 0.589

MINUTES ON FEED	90	100	110	120
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.52	9.53	9.53	9.53
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METHANE	0.06	0.06	0.05	0.05
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ETHANE	0.09	0.05	0.05	0.05
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PROPANE	0.15	0.11	0.10	0.11
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I-BUTANE	0.10	0.13	0.08	0.06
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N-BUTANE	0.19	0.30	0.19	0.18
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I-PENTANE	29.62	29.12	28.47	29.90
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N-PENTANE	69.81	70.25	71.07	69.66
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C6 PLUS	0.00	0.00	0.00	0.00
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CONVERSION, %	30.19	29.75	28.93	30.34
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IC5/PC5, %	29.79	29.30	28.60	30.03
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WT % C4-	0.59	0.65	0.47	0.45
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SELECTIVITY, %	98.10	97.87	98.42	98.54
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RATE CONSTANT

K, CC/GM-SEC	0.1070	0.1047	0.1013	0.1082
$1/\sqrt{K}$	3.06	3.09	3.14	3.04

MATERIAL BALANCE, %				100.42
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 14

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.84-1.15

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 6.87

HYDROGEN, MOLES/MOLE C5 3.452
SCFB 4016.

SUPERFICIAL
HOLDING TIME, SEC. 7.76
GAS VELOCITY, CM/SEC. 0.987

VOID FRACTION 0.538

MINUTES ON FEED 90 100 110 120

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.63 9.63 9.63 9.63

METHANE 0.08 0.07 0.06 0.08

ETHANE 0.09 0.06 0.05 0.05

PROPANE 0.19 0.10 0.06 0.15

I-BUTANE 0.15 0.12 0.13 0.18

N-BUTANE 0.30 0.25 0.19 0.33

I-PENTANE 42.84 42.39 42.08 41.62

N-PENTANE 56.36 57.02 57.44 57.61

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 43.64 42.98 42.56 42.39

IC5/PC5, % 43.19 42.64 42.28 41.95

WT % C4- 0.82 0.60 0.49 0.79

SELECTIVITY, % 98.16 98.63 98.87 98.18

RATE CONSTANT

K, CC/GM-SEC 0.1165 0.1140 0.1124 0.1109
 $1/\sqrt{K}$ 2.93 2.96 2.98 3.00

MATERIAL BALANCE, % 99.46

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 15

CATALYST 1.0% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.66

HYDROGEN, MOLES/MOLE C5 3.480
SCFB 4048.

SUPERFICIAL
HOLDING TIME, SEC. 7.71
GAS VELOCITY, CM/SEC. 0.993

VOID FRACTION 0.586

MINUTES ON FEED 120 130 140 150

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.70	9.70	9.70	9.71
METHANE	0.09	0.10	0.10	0.07
ETHANE	0.13	0.19	0.12	0.00
PROPANE	0.21	0.27	0.24	0.14
I-BUTANE	0.15	0.31	0.24	0.24
N-BUTANE	0.40	0.42	0.57	0.21
I-PENTANE	39.16	39.21	40.34	40.19
N-PENTANE	59.89	59.52	58.40	59.15
C6 PLUS	0.00	0.00	0.00	0.00
CONVERSION, %	40.11	40.48	41.60	40.85
IC5/PC5, %	39.53	39.71	40.85	40.46
WT % C4-	0.98	1.29	1.28	0.67
SELECTIVITY, %	97.62	96.88	96.99	98.39

RATE CONSTANT				
K, CC/GM-SEC	0.1130	0.1138	0.1191	0.1172
$1/\sqrt{K}$	2.97	2.96	2.90	2.92

MATERIAL BALANCE, % 101.36

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 16

CATALYST 0.2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.95

HYDROGEN, MOLES/MOLE C5 3.461
SCFB 4026.

SUPERFICIAL
HOLDING TIME, SEC. 7.74
GAS VELOCITY, CM/SEC. 0.989

VOID FRACTION 0.601

MINUTES ON FEED	140	150	160	170
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.65	9.65	9.65	9.65
METHANE	0.09	0.09	0.09	0.09
ETHANE	0.13	0.11	0.15	0.11
PROPANE	0.24	0.22	0.22	0.23
I-BUTANE	0.24	0.25	0.30	0.22
N-BUTANE	0.38	0.39	0.39	0.34
I-PENTANE	39.09	38.82	39.11	39.12
N-PENTANE	59.86	60.14	59.76	59.92
C6 PLUS	0.00	0.00	0.00	0.00

CONVERSION, %	40.14	39.86	40.24	40.08
IC5/PC5, %	39.50	39.23	39.55	39.50
WT % C4-	1.07	1.06	1.16	0.98
SELECTIVITY, %	97.38	97.40	97.19	97.60

RATE CONSTANT				
K, CC/GM-SEC	0.1168	0.1155	0.1170	0.1167
$1/\sqrt{K}$	2.93	2.94	2.92	2.93

MATERIAL BALANCE, %				101.07
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 17

CATALYST 1/2% PLATINUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.84

HYDROGEN, MOLES/MOLE C5 3.442
SCFB 4003.

SUPERFICIAL
HOLDING TIME, SEC. 7.77
GAS VELOCITY, CM/SEC. 0.985

VOID FRACTION 0.596

MINUTES ON FEED 140 150 160 170

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.60 9.60 9.60 9.60

METHANE 0.07 0.08 0.07 0.08

ETHANE 0.08 0.08 0.08 0.08

PROPANE 0.12 0.17 0.17 0.17

I-BUTANE 0.16 0.16 0.16 0.17

N-BUTANE 0.27 0.27 0.26 0.27

I-PENTANE 38.90 38.93 38.94 38.90

N-PENTANE 60.41 60.32 60.34 60.34

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 39.59 39.68 39.66 39.66

IC5/PC5, % 39.17 39.22 39.22 39.20

WT % C4- 0.71 0.76 0.74 0.77

SELECTIVITY, % 98.26 98.12 98.18 98.10

RATE CONSTANT

K, CC/GM-SEC 0.1131 0.1133 0.1134 0.1132

$1/\sqrt{K}$ 2.97 2.97 2.97 2.97

MATERIAL BALANCE, % 99.52

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 18

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 500.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 4.10
W/HR-W 4.08

HYDROGEN, MOLES/MOLE C5 3.432
SCFB 3992.

SUPERFICIAL
HOLDING TIME, SEC. 16.39
GAS VELOCITY, CM/SEC. 0.467

VOID FRACTION 0.611

MINUTES ON FEED 140 150 160 170

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.59 9.59 9.59 9.59

METHANE 0.02 0.02 0.02 0.02

ETHANE 0.01 0.01 0.01 0.02

PROPANE 0.02 0.03 0.01 0.02

I-BUTANE 0.02 0.03 0.02 0.03

N-BUTANE 0.02 0.03 0.02 0.03

I-PENTANE 21.96 22.03 23.26 23.11

N-PENTANE 77.95 77.85 76.65 76.77

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 22.05 22.15 23.35 23.23

IC5/PC5, % 21.98 22.06 23.28 23.13

WT % C4- 0.09 0.12 0.09 0.13

SELECTIVITY, % 99.60 99.47 99.65 99.47

RATE CONSTANT

K, CC/GM-SEC 0.0253 0.0255 0.0272 0.0270

$1/\sqrt{K}$ 6.28 6.27 6.06 6.09

MATERIAL BALANCE, % 99.67

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 19

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 600.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 16.39
W/HR-W 16.53

HYDROGEN, MOLES/MOLE C5 3.508
SCFB 4081.

SUPERFICIAL
HOLDING TIME, SEC. 3.65
GAS VELOCITY, CM/SEC. 2.098

VOID FRACTION 0.616

MINUTES ON FEED 80 90 110 120

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.78	9.78	9.78	9.78
METHANE	0.08	0.08	0.09	0.09
ETHANE	0.10	0.10	0.10	0.10
PROPANE	0.20	0.20	0.18	0.21
I-BUTANE	0.26	0.27	0.31	0.37
N-BUTANE	0.30	0.31	0.35	0.39
I-PENTANE	37.85	38.16	39.67	39.79
N-PENTANE	61.22	60.89	59.32	59.08
C6 PLUS	0.00	0.00	0.00	0.00

CONVERSION, %	38.78	39.11	40.68	40.92
IC5/PC5, %	38.20	38.52	40.08	40.25
WT % C4-	0.95	0.96	1.03	1.16
SELECTIVITY, %	97.60	97.58	97.51	97.23

RATE CONSTANT				
K, CC/GM-SEC	0.2477	0.2510	0.2674	0.2692
1/√K	2.01	2.00	1.93	1.93

MATERIAL BALANCE, % 98.02

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 20

CATALYST	H-MORDENITE			
PARTICLE SIZE, MM.	0.42 - 0.84			
TEMPERATURE, °F	550.			
PRESSURE, PSIG	450.			
N-PENTANE, V/HR-V	8.18			
W/HR-W	9.73			
HYDROGEN, MOLES/MOLE C5	3.391			
SCFB	3944.			
SUPERFICIAL				
HOLDING TIME, SEC.	7.88			
GAS VELOCITY, CM/SEC.	0.972			
VOID FRACTION	0.675			
MINUTES ON FEED	240	250	270	290
PRODUCT				
GMS/100 GMS N-PENTANE				
HYDROGEN	9.44	9.45	9.45	9.44
METHANE	0.14	0.12	0.13	0.13
ETHANE	0.06	0.07	0.08	0.06
PROPANE	0.51	0.32	0.37	0.34
I-BUTANE	1.52	1.17	1.29	1.37
N-BUTANE	0.53	0.40	0.46	0.46
I-PENTANE	39.06	37.33	39.54	39.80
N-PENTANE	57.68	60.20	56.53	56.98
C6 PLUS	0.54	0.43	1.63	0.89
CONVERSION, %	42.32	39.80	43.47	43.02
IC5/PC5, %	40.38	38.28	41.16	41.12
WT % C4-	2.76	2.07	2.33	2.36
SELECTIVITY, %	92.30	93.80	90.95	92.52
RATE CONSTANT				
K, CC/GM-SEC	0.1456	0.1339	0.1502	0.1500
1/√K	2.62	2.73	2.58	2.58
MATERIAL BALANCE, %	98.01			

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21A

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 252.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.68

HYDROGEN, MOLES/MOLE C5 3.030
SCFB 3524.

SUPERFICIAL
HOLDING TIME, SEC. 4.92
GAS VELOCITY, CM/SEC. 1.557

VOID FRACTION 0.587

MINUTES ON FEED	325	335	340	350
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	8.43	8.44	8.45	8.44
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METHANE	0.11	0.11	0.08	0.11
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ETHANE	0.23	0.23	0.12	0.15
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PROPANE	0.27	0.27	0.14	0.28
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I-BUTANE	0.31	0.30	0.15	0.35
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N-BUTANE	0.51	0.40	0.18	0.45
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I-PENTANE	45.91	45.73	46.04	47.51
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N-PENTANE	52.69	52.98	53.31	51.18
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C6 PLUS	0.00	0.00	0.00	0.00
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CONVERSION, %	47.31	47.02	46.69	48.82
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IC5/PC5, %	46.56	46.33	46.34	48.14
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WT % C4-	1.43	1.32	0.67	1.34
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SELECTIVITY, %	97.04	97.26	98.60	97.30
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RATE CONSTANT

K, CC/GM-SEC	0.2348	0.2325	0.2327	0.2501
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$1/\sqrt{K}$	2.06	2.07	2.07	2.00
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MATERIAL BALANCE, %				100.26
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21B1

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.68

HYDROGEN, MOLES/MOLE C5 5.941
SCFB 6910.

SUPERFICIAL
HOLDING TIME, SEC. 4.97
GAS VELOCITY, CM/SEC. 1.539

VOID FRACTION 0.587

MINUTES ON FEED 405 410 415 420

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 16.59 16.59 16.59 16.59

METHANE 0.04 0.05 0.05 0.06

ETHANE 0.06 0.05 0.07 0.09

PROPANE 0.10 0.09 0.07 0.09

I-BUTANE 0.08 0.08 0.07 0.12

N-BUTANE 0.07 0.10 0.18 0.24

I-PENTANE 27.62 30.80 28.32 28.73

N-PENTANE 72.03 68.86 71.25 70.69

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 27.97 31.14 28.75 29.31

IC5/PC5, % 27.72 30.90 28.44 28.90

WT % C4- 0.35 0.36 0.44 0.60

SELECTIVITY, % 98.77 98.88 98.49 98.01

RATE CONSTANT

K, CC/GM-SEC 0.1059 0.1225 0.1096 0.1119

$1/\sqrt{K}$ 3.07 2.86 3.02 2.99

MATERIAL BALANCE, % 100.03

TABLE 8-I
DETAILED ISOMERIZATION DATA

RUN 2182

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.68

HYDROGEN, MOLES/MOLE C5 5.941
SCFB 6910.

SUPERFICIAL
HOLDING TIME, SEC. 4.97
GAS VELOCITY, CM/SEC. 1.539

VOID FRACTION 0.587

MINUTES ON FEED	455	460	470	480
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	16.59	16.59	16.59	16.59
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METHANE	0.04	0.03	0.04	0.05
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ETHANE	0.07	0.03	0.06	0.12
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PROPANE	0.08	0.03	0.07	0.10
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I-BUTANE	0.10	0.06	0.06	0.06
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N-BUTANE	0.08	0.04	0.06	0.08
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I-PENTANE	23.87	25.05	24.41	24.60
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N-PENTANE	75.77	74.77	75.31	75.02
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C6 PLUS	0.00	0.00	0.00	0.00
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CONVERSION, %	24.23	25.23	24.69	24.98
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IC5/PC5, %	23.96	25.09	24.47	24.69
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WT % C4-	0.37	0.18	0.29	0.40
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SELECTIVITY, %	98.52	99.29	98.87	98.46
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RATE CONSTANT

K, CC/GM-SEC	0.0879	0.0932	0.0903	0.0913
1/√K	3.37	3.28	3.33	3.31

MATERIAL BALANCE, %				100.03
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21C

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 416.

N-PENTANE, V/HR-V 4.09
W/HR-W 3.84

HYDROGEN, MOLES/MOLE C5 11.857
SCFB 13792.

SUPERFICIAL
HOLDING TIME, SEC. 4.98
GAS VELOCITY, CM/SEC. 1.536

VOID FRACTION 0.587

MINUTES ON FEED	500	508	515	523
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	33.12	33.12	33.12	33.12
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METHANE	0.04	0.05	0.05	0.04
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ETHANE	0.05	0.11	0.11	0.05
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PROPANE	0.06	0.13	0.09	0.09
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I-BUTANE	0.07	0.11	0.11	0.07
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N-BUTANE	0.07	0.07	0.14	0.07
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I-PENTANE	28.07	28.43	27.73	28.63
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N-PENTANE	71.65	71.12	71.78	71.05
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C6 PLUS	0.00	0.00	0.00	0.00
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CONVERSION, %	28.35	28.88	28.22	28.95
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IC5/PC5, %	28.15	28.56	27.87	28.72
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WT % C4-	0.30	0.46	0.50	0.33
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SELECTIVITY, %	98.99	98.44	98.27	98.90
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RATE CONSTANT

K, CC/GM-SEC	0.1079	0.1100	0.1065	0.1109
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$1/\sqrt{K}$	3.04	3.01	3.06	3.00
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MATERIAL BALANCE, %				102.04
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TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 210

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	550.		
PRESSURE, PSIG	220.		
N-PENTANE, V/HR-V	4.09		
W/HR-W	3.84		
HYDROGEN, MOLES/MOLE C5	6.019		
SCFB	7001.		
SUPERFICIAL			
HOLDING TIME, SEC.	4.97		
GAS VELOCITY, CM/SEC.	1.539		
VOID FRACTION	0.587		
MINUTES ON FEED	540	546	555
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	16.80	16.78	16.79
METHANE	0.09	0.12	0.10
ETHANE	0.12	0.23	0.15
PROPANE	0.18	0.37	0.21
I-BUTANE	0.26	0.41	0.40
N-BUTANE	0.20	0.37	0.25
I-PENTANE	45.71	44.99	45.78
N-PENTANE	53.46	53.55	53.13
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	46.54	46.45	46.87
IC5/PC5, %	46.09	45.66	46.29
WT % C4-	0.85	1.50	1.11
SELECTIVITY, %	98.23	96.85	97.68
RATE CONSTANT			
K, CC/GM-SEC	0.2278	0.2239	0.2296
1/√K	2.10	2.11	2.09
MATERIAL BALANCE, %			100.49

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21E

CATALYST 1/2% PALLADIUM ON H-MORDENITE			
PARTICLE SIZE, MM. 0.42 - 0.84			
TEMPERATURE, °F	550.		
PRESSURE, PSIG	252.		
N-PENTANE, V/HR-V	8.19		
W/HR-W	7.68		
HYDROGEN, MOLES/MOLE C5	3.007		
SCFB	3498.		
SUPERFICIAL			
HOLDING TIME, SEC.	4.94		
GAS VELOCITY, CM/SEC.	1.548		
VOID FRACTION	0.587		
MINUTES ON FEED	605	610	- 615
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	8.38	8.38	8.38
METHANE	0.10	0.10	0.10
ETHANE	0.04	0.06	0.06
PROPANE	0.31	0.30	0.26
I-BUTANE	0.53	0.45	0.49
N-BUTANE	0.24	0.27	0.27
I-PENTANE	43.73	43.83	44.04
N-PENTANE	55.06	55.01	54.80
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	44.94	44.99	45.20
IC5/PC5, %	44.27	44.34	44.55
WT % C4-	1.23	1.18	1.18
SELECTIVITY, %	97.32	97.42	97.43
RATE CONSTANT			
K, CC/GM-SEC	0.2131	0.2138	0.2155
$1/\sqrt{K}$	2.17	2.16	2.15
MATERIAL BALANCE, %	100.55		

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21F

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.68

HYDROGEN, MOLES/MOLE C5 5.924
SCFB 6890.

SUPERFICIAL
HOLDING TIME, SEC. 4.99
GAS VELOCITY, CM/SEC. 1.535

VOID FRACTION 0.587

MINUTES ON FEED 650 665 670 680

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 16.55 16.54 16.54 16.54

METHANE 0.03 0.04 0.04 0.04

ETHANE 0.04 0.06 0.07 0.07

PROPANE 0.04 0.07 0.07 0.04

I-BUTANE 0.05 0.07 0.12 0.10

N-BUTANE 0.05 0.07 0.07 0.10

I-PENTANE 24.34 23.65 24.37 25.74

N-PENTANE 75.45 76.05 75.27 73.92

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 24.55 23.95 24.73 26.08

IC5/PC5, % 24.39 23.73 24.46 25.83

WT % C4- 0.21 0.31 0.38 0.36

SELECTIVITY, % 99.18 98.75 98.52 98.66

RATE CONSTANT

K, CC/GM-SEC 0.0897 0.0867 0.0900 0.0964

$1/\sqrt{K}$ 3.34 3.40 3.33 3.22

MATERIAL BALANCE, % 99.99

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21G

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 550.
PRESSURE, PSIG 416.

N-PENTANE, V/HR-V 4.09
W/HR-W 3.84

HYDROGEN, MOLES/MOLE C5 11.891
SCFB 13831.

SUPERFICIAL
HOLDING TIME, SEC. 4.97
GAS VELOCITY, CM/SEC. 1.540

VOID FRACTION 0.587

MINUTES ON FEED 735 745 750 755

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 33.21 33.21 33.21 33.21

METHANE 0.05 0.05 0.06 0.05

ETHANE 0.06 0.08 0.07 0.05

PROPANE 0.05 0.06 0.10 0.09

I-BUTANE 0.13 0.09 0.19 0.16

N-BUTANE 0.26 0.07 0.15 0.18

I-PENTANE 29.22 28.80 28.92 29.87

N-PENTANE 70.25 70.86 70.54 69.61

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 29.75 29.14 29.46 30.39

IC5/PC5, % 29.37 28.90 29.08 30.02

WT % C4- 0.55 0.35 0.56 0.53

SELECTIVITY, % 98.19 98.83 98.14 98.29

RATE CONSTANT

K, CC/GM-SEC 0.1145 0.1121 0.1130 0.1179

$1/\sqrt{K}$ 2.96 2.99 2.98 2.91

MATERIAL BALANCE, % 102.07

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 21H

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, F 550.
PRESSURE, PSIG 220.

N-PENTANE, V/HR-V 4.09
W/HR-W 3.84

HYDROGEN, MOLES/MOLE C5 6.036
SCFB 7021.

SUPERFICIAL
HOLDING TIME, SEC. 4.96
GAS VELOCITY, CM/SEC. 1.543

VOID FRACTION 0.587

MINUTES ON FEED 790 795 803 808

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 16.84 16.84 16.84 16.83

METHANE 0.11 0.11 0.11 0.12

ETHANE 0.17 0.16 0.11 0.16

PROPANE 0.32 0.32 0.29 0.45

I-BUTANE 0.44 0.53 0.54 0.54

N-BUTANE 0.22 0.25 0.25 0.36

I-PENTANE 48.39 48.00 48.15 48.78

N-PENTANE 50.38 50.66 50.58 49.61

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 49.62 49.34 49.42 50.39

IC5/PC5, % 48.99 48.65 48.77 49.58

WT % C4- 1.25 1.37 1.30 1.64

SELECTIVITY, % 97.53 97.28 97.42 96.82

RATE CONSTANT

K, CC/GM-SEC 0.2565 0.2530 0.2542 0.2627

$1/\sqrt{K}$ 1.97 1.99 1.98 1.95

MATERIAL BALANCE, % 100.54

TABLE B-1
DETAILED ISOMERIZATION DATA

RUN 22A1

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.84

HYDROGEN, MOLES/MOLE C5 2.676
SCFB 3112.

SUPERFICIAL
HOLDING TIME, SEC. 9.63
GAS VELOCITY, CM/SEC. 0.795

VOID FRACTION 0.596

MINUTES ON FEED 95 100 108 115

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 7.46 7.46 7.46 7.46

METHANE 0.06 0.06 0.06 0.06

ETHANE 0.11 0.10 0.11 0.11

PROPANE 0.13 0.12 0.13 0.13

I-BUTANE 0.17 0.14 0.22 0.21

N-BUTANE 0.28 0.25 0.29 0.28

I-PENTANE 27.14 26.74 26.01 25.53

N-PENTANE 72.14 72.60 73.19 73.70

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 27.86 27.40 26.81 26.30

IC5/PC5, % 27.33 26.92 26.22 25.73

WT % C4- 0.74 0.67 0.82 0.79

SELECTIVITY, % 97.40 97.60 97.02 97.05

RATE CONSTANT

K, CC/GM-SEC 0.0547 0.0536 0.0518 0.0506

$1/\sqrt{K}$ 4.28 4.32 4.39 4.45

MATERIAL BALANCE, % 100.31

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 22A2

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.84

HYDROGEN, MOLES/MOLE C5 2.676
SCFB 3112.

SUPERFICIAL
HOLDING TIME, SEC. 9.63
GAS VELOCITY, CM/SEC. 0.795

VOID FRACTION 0.596

MINUTES ON FEED 125 132 140 147

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	7.45	7.46	7.46	7.46
METHANE	0.08	0.07	0.07	0.06
ETHANE	0.15	0.14	0.14	0.11
PROPANE	0.21	0.19	0.18	0.13
I-BUTANE	0.28	0.25	0.25	0.17
N-BUTANE	0.39	0.35	0.34	0.28
I-PENTANE	26.03	25.36	26.54	26.02
N-PENTANE	72.88	73.66	72.50	73.24
C6 PLUS	0.00	0.00	0.00	0.00
CONVERSION, %	27.12	26.34	27.50	26.76
IC5/PC5, %	26.32	25.62	26.80	26.21
WT % C4-	1.11	1.00	0.98	0.75
SELECTIVITY, %	95.98	96.28	96.52	97.25

RATE CONSTANT				
K, CC/GM-SEC	0.0521	0.0503	0.0533	0.0518
$1/\sqrt{K}$	4.38	4.46	4.33	4.39

MATERIAL BALANCE, % 100.31

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 22B1

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.84

HYDROGEN, MOLES/MOLE C5 0.963
SCFB 1120.

SUPERFICIAL
HOLDING TIME, SEC. 18.04
GAS VELOCITY, CM/SEC. 0.424

VOID FRACTION 0.596

MINUTES ON FEED 180 210 215 225

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 2.67 2.68 2.67 2.67

METHANE 0.07 0.07 0.08 0.08

ETHANE 0.08 0.06 0.09 0.07

PROPANE 0.13 0.11 0.09 0.14

I-BUTANE 0.20 0.19 0.23 0.26

N-BUTANE 0.24 0.21 0.29 0.30

I-PENTANE 40.89 43.12 40.68 41.07

N-PENTANE 58.40 56.24 58.55 58.10

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 41.60 43.76 41.45 41.90

IC5/PC5, % 41.19 43.40 41.00 41.41

WT % C4- 0.72 0.65 0.78 0.84

SELECTIVITY, % 98.30 98.55 98.16 98.03

RATE CONSTANT

K, CC/GM-SEC 0.0524 0.0572 0.0520 0.0529

$1/\sqrt{K}$ 4.37 4.18 4.38 4.35

MATERIAL BALANCE, % 100.20

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 22B2

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 7.84

HYDROGEN, MOLES/MOLE C5 0.963
SCFB 1120.

SUPERFICIAL
HOLDING TIME, SEC. 18.04
GAS VELOCITY, CM/SEC. 0.424

VOID FRACTION 0.596

MINUTES ON FEED 230 240 250 260

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 2.67 2.67 2.67 2.68

METHANE 0.08 0.08 0.08 0.07

ETHANE 0.06 0.06 0.09 0.06

PROPANE 0.14 0.14 0.14 0.11

I-BUTANE 0.26 0.26 0.24 0.20

N-BUTANE 0.33 0.33 0.30 0.22

I-PENTANE 43.64 43.64 42.53 40.56

N-PENTANE 55.50 55.50 56.64 58.79

C6 PLUS 0.00 0.00 0.00 0.00

CONVERSION, % 44.50 44.50 43.36 41.21

IC5/PC5, % 44.02 44.02 42.88 40.83

WT % C4- 0.88 0.88 0.85 0.66

SELECTIVITY, % 98.06 98.06 98.08 98.44

RATE CONSTANT

K, CC/GM-SEC 0.0586 0.0586 0.0560 0.0517

$1/\sqrt{K}$ 4.13 4.13 4.23 4.40

MATERIAL BALANCE, % 100.20

TABLE B-1
DETAILED ISOMERIZATION DATA

RUN 23A

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 250.

N-PENTANE, V/HR-V 8.19
W/HR-W 8.11

HYDROGEN, MOLES/MOLE C5 3.054
SCFB 3552.

SUPERFICIAL
HOLDING TIME, SEC. 4.97
GAS VELOCITY, CM/SEC. 1.539

VOID FRACTION 0.609

MINUTES ON FEED 220 230 240

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 8.52 8.52 8.52

METHANE 0.06 0.06 0.06

ETHANE 0.08 0.08 0.10

PROPANE 0.12 0.14 0.15

I-BUTANE 0.16 0.19 0.13

N-BUTANE 0.16 0.18 0.13

I-PENTANE 31.82 33.10 32.21

N-PENTANE 67.62 66.26 67.24

C6 PLUS 0.00 0.00 0.00

CONVERSION, % 32.38 33.74 32.76

IC5/PC5, % 32.00 33.32 32.39

WT % C4- 0.58 0.66 0.56

SELECTIVITY, % 98.26 98.09 98.33

RATE CONSTANT

K, CC/GM-SEC 0.1352 0.1430 0.1375

$1/\sqrt{K}$ 2.72 2.64 2.70

MATERIAL BALANCE, % 102.43

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 238

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 525.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 8.19
W/HR-W 8.11

HYDROGEN, MOLES/MOLE C5 0.753
SCFB 876.

SUPERFICIAL
HOLDING TIME, SEC. 20.19
GAS VELOCITY, CM/SEC. 0.379

VOID FRACTION 0.609

MINUTES ON FEED	275	290	305	315
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PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	2.08	2.08	2.08	2.08
METHANE	0.09	0.10	0.09	0.11
ETHANE	0.09	0.09	0.06	0.07
PROPANE	0.17	0.25	0.22	0.29
I-BUTANE	0.44	0.57	0.53	0.66
N-BUTANE	0.29	0.33	0.27	0.33
I-PENTANE	44.71	44.31	40.46	45.73
N-PENTANE	54.22	54.36	58.38	52.84
C6 PLUS	0.00	0.00	0.00	0.00

CONVERSION, %	45.78	45.64	41.62	47.16
IC5/PC5, %	45.20	44.91	40.94	46.39
WT % C4-	1.09	1.35	1.17	1.46
SELECTIVITY, %	97.67	97.10	97.23	96.95

RATE CONSTANT				
K, CC/GM-SEC	0.0567	0.0560	0.0480	0.0594
$1/\sqrt{K}$	4.20	4.22	4.57	4.10

MATERIAL BALANCE, %				101.37
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TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 23C

CATALYST 1/2% PALLADIUM ON H-MORDENITE			
PARTICLE SIZE, MM. 0.42 - 0.84			
TEMPERATURE, °F	525.		
PRESSURE, PSIG	350.		
N-PENTANE, V/HR-V	8.19		
W/HR-W	8.11		
HYDROGEN, MOLES/MOLE C5	1.215		
SCFB	1414.		
SUPERFICIAL			
HOLDING TIME, SEC.	12.54		
GAS VELOCITY, CM/SEC.	0.610		
VOID FRACTION	0.609		
MINUTES ON FEED	350	365	380
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	3.37	3.37	3.37
METHANE	0.10	0.09	0.09
ETHANE	0.04	0.06	0.07
PROPANE	0.15	0.20	0.20
I-BUTANE	0.82	0.56	0.56
N-BUTANE	0.28	0.30	0.25
I-PENTANE	39.86	39.34	40.58
N-PENTANE	58.78	59.47	58.27
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	41.22	40.53	41.73
IC5/PC5, %	40.41	39.82	41.05
WT % C4-	1.39	1.21	1.17
SELECTIVITY, %	96.69	97.06	97.25
RATE CONSTANT			
K, CC/GM-SEC	0.0757	0.0739	0.0776
$1/\sqrt{K}$	3.64	3.68	3.59
MATERIAL BALANCE, %	101.48		

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 23D

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F		525.
PRESSURE, PSIG		450.
N-PENTANE, V/HR-V		8.19
W/HR-W		8.11
HYDROGEN, MOLES/MOLE C5		3.394
SCFB		3948.
SUPERFICIAL		
HOLDING TIME, SEC.		8.06
GAS VELOCITY, CM/SEC.		0.950
VOID FRACTION		0.609
MINUTES ON FEED	410	420
PRODUCT		
GMS/100 GMS N-PENTANE		
HYDROGEN	9.48	9.48
METHANE	0.03	0.00
ETHANE	0.02	0.00
PROPANE	0.03	0.00
I-BUTANE	0.10	0.00
N-BUTANE	0.07	0.00
I-PENTANE	23.53	21.64
N-PENTANE	76.23	78.36
C6 PLUS	0.00	0.00
CONVERSION, %	23.77	21.64
IC5/PC5, %	23.59	21.64
WT % C4-	0.25	0.00
SELECTIVITY, %	98.97	100.00
RATE CONSTANT		
K, CC/GM-SEC	0.0561	0.0505
$1/\sqrt{K}$	4.22	4.45
MATERIAL BALANCE, %		100.22

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 24A

CATALYST 1/2% PALLADIUM ON H-MORDENITE			
PARTICLE SIZE, MM. 0.42 - 0.84			
TEMPERATURE, °F		500.	
PRESSURE, PSIG		350.	
N-PENTANE, V/HR-V		4.09	
W/HR-W		4.04	
HYDROGEN, MOLES/MOLE C5		3.356	
SCFB		3904.	
SUPERFICIAL			
HOLDING TIME, SEC.		13.10	
GAS VELOCITY, CM/SEC.		0.584	
VOID FRACTION		0.608	
MINUTES ON FEED	135	145	150
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.37	9.37	9.37
METHANE	0.04	0.04	0.04
ETHANE	0.02	0.02	0.04
PROPANE	0.05	0.06	0.08
I-BUTANE	0.07	0.10	0.03
N-BUTANE	0.07	0.11	0.12
I-PENTANE	29.72	30.51	30.32
N-PENTANE	70.03	69.17	69.37
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	29.97	30.83	30.63
IC5/PC5, %	29.79	30.61	30.41
WT % C4-	0.26	0.33	0.32
SELECTIVITY, %	99.15	98.95	98.98
RATE CONSTANT			
K, CC/GM-SEC	0.0462	0.0479	0.0475
$1/\sqrt{K}$	4.65	4.57	4.59
MATERIAL BALANCE, %			99.70

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 248

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	500.		
PRESSURE, PSIG	250.		
N-PENTANE, V/HR-V	4.09		
W/HR-W	4.04		
HYDROGEN, MOLES/MOLE C5	3.356		
SCFB	3904.		
SUPERFICIAL			
HOLDING TIME, SEC.	9.51		
GAS VELOCITY, CM/SEC.	0.805		
VOID FRACTION	0.608		
MINUTES ON FEED	180	190	200
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.37	9.37	9.37
METHANE	0.04	0.04	0.04
ETHANE	0.03	0.02	0.05
PROPANE	0.05	0.06	0.05
I-BUTANE	0.06	0.07	0.06
N-BUTANE	0.11	0.10	0.09
I-PENTANE	34.83	34.67	34.40
N-PENTANE	64.88	65.05	65.31
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	35.12	34.95	34.69
IC5/PC5, %	34.93	34.77	34.50
WT % C4-	0.29	0.29	0.30
SELECTIVITY, %	99.19	99.20	99.16
RATE CONSTANT			
K, CC/GM-SEC	0.0794	0.0788	0.0780
$1/\sqrt{K}$	3.55	3.56	3.58
MATERIAL BALANCE, %	99.70		

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 24C

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	500.		
PRESSURE, PSIG	150.		
N-PENTANE, V/HR-V	4.09		
W/HR-W	4.04		
HYDROGEN, MOLES/MOLE C5	3.356		
SCFB	3904.		
SUPERFICIAL			
HOLDING TIME, SEC.	5.92		
GAS VELOCITY, CM/SEC.	1.294		
VOID FRACTION	0.608		
MINUTES ON FEED	220	227	240
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.36	9.36	9.36
METHANE	0.06	0.07	0.07
ETHANE	0.09	0.09	0.10
PROPANE	0.05	0.08	0.08
I-BUTANE	0.12	0.12	0.13
N-BUTANE	0.18	0.21	0.22
I-PENTANE	41.57	43.06	42.23
N-PENTANE	57.93	56.38	57.20
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	42.07	43.62	42.80
IC5/PC5, %	41.78	43.30	42.47
WT % C4-	0.51	0.58	0.59
SELECTIVITY, %	98.81	98.71	98.65
RATE CONSTANT			
K, CC/GM-SEC	0.1674	0.1776	0.1720
$1/\sqrt{K}$	2.44	2.37	2.41
MATERIAL BALANCE, %	99.70		

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 24D

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 500.
PRESSURE, PSIG 100.
N-PENTANE, V/HR-V 4.09
W/HR-W 4.04
HYDROGEN, MOLES/MOLE C5 3.356
SCFB 3904.
SUPERFICIAL
HOLDING TIME, SEC. 4.12
GAS VELOCITY, CM/SEC. 1.858

VOID FRACTION 0.608

MINUTES ON FEED 270 290 300

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN	9.36	9.36	9.36
METHANE	0.09	0.08	0.08
ETHANE	0.08	0.08	0.08
PROPANE	0.15	0.15	0.15
I-BUTANE	0.22	0.24	0.25
N-BUTANE	0.27	0.19	0.19
I-PENTANE	49.78	50.18	50.38
N-PENTANE	49.44	49.09	48.88
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	50.56	50.91	51.12
IC5/PC5, %	50.17	50.55	50.76
WT % C4-	0.81	0.74	0.76
SELECTIVITY, %	98.44	98.57	98.55

RATE CONSTANT			
K, CC/GM-SEC	0.3330	0.3380	0.3408
$1/\sqrt{K}$	1.73	1.72	1.71

MATERIAL BALANCE, % 99.70

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 24E

CATALYST 1/2% PALLADIUM ON H-MORDENITE			
PARTICLE SIZE, MM. 0.42 - 0.84			
TEMPERATURE, °F	600.		
PRESSURE, PSIG	350.		
N-PENTANE, V/HR-V	16.39		
W/HR-W	16.18		
HYDROGEN, MOLES/MOLE C5	3.387		
SCFB	3939.		
SUPERFICIAL			
HOLDING TIME, SEC.	2.94		
GAS VELOCITY, CM/SEC.	2.601		
VOID FRACTION	0.608		
MINUTES ON FEED	440	450	460
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.41	9.41	9.40
METHANE	0.18	0.18	0.19
ETHANE	0.45	0.36	0.55
PROPANE	0.65	0.54	0.67
I-BUTANE	0.86	0.89	0.85
N-BUTANE	0.87	0.91	0.88
I-PENTANE	55.39	54.92	54.66
N-PENTANE	41.03	41.56	41.85
C6 PLUS	0.63	0.70	0.40
CONVERSION, %	58.97	58.44	58.15
IC5/PC5, %	57.44	56.93	56.64
WT % C4-	3.00	2.87	3.14
SELECTIVITY, %	93.93	93.98	94.01
RATE CONSTANT			
K, CC/GM-SEC	0.6906	0.6721	0.6620
$1/\sqrt{K}$	1.20	1.22	1.23
MATERIAL BALANCE, %	100.04		

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 24F

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 600.
PRESSURE, PSIG 250.

N-PENTANE, V/HR-V 16.39
W/HR-W 16.18

HYDROGEN, MOLES/MOLE C5 3.387
SCFB 3939.

SUPERFICIAL
HOLDING TIME, SEC. 2.14
GAS VELOCITY, CM/SEC. 3.583

VOID FRACTION 0.608

MINUTES ON FEED 490 500 515

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.40 9.41 9.40

METHANE 0.20 0.17 0.19

ETHANE 0.51 0.38 0.51

PROPANE 0.75 0.58 0.67

I-BUTANE 1.33 0.87 1.29

N-BUTANE 0.84 0.79 0.76

I-PENTANE 53.71 54.10 53.75

N-PENTANE 41.98 42.21 42.42

C6 PLUS 0.75 0.94 0.47

CONVERSION, % 58.02 57.79 57.58

IC5/PC5, % 56.13 56.17 55.89

WT % C4- 3.63 2.80 3.42

SELECTIVITY, % 92.56 93.61 93.36

RATE CONSTANT

K, CC/GM-SEC 0.8889 0.8908 0.8785

$1/\sqrt{K}$ 1.06 1.06 1.07

MATERIAL BALANCE, % 100.04

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 24G

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	600.		
PRESSURE, PSIG	150.		
N-PENTANE, V/HR-V	16.39		
W/HR-W	16.18		
HYDROGEN, MOLES/MOLE C5	3.387		
SCFB	3939.		
SUPERFICIAL			
HOLDING TIME, SEC.	1.33		
GAS VELOCITY, CM/SEC.	5.759		
VOID FRACTION	0.608		
MINUTES ON FEED	530	545	560
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.38	9.39	9.38
METHANE	0.23	0.23	0.23
ETHANE	0.60	0.40	0.40
PROPANE	1.02	1.13	1.14
I-BUTANE	2.36	2.62	2.76
N-BUTANE	0.81	0.91	1.00
I-PENTANE	52.56	51.10	51.74
N-PENTANE	40.68	41.84	41.57
C6 PLUS	1.81	1.86	1.25
CONVERSION, %	59.32	58.16	58.43
IC5/PC5, %	56.37	54.98	55.45
WT % C4-	5.02	5.27	5.52
SELECTIVITY, %	88.61	87.86	88.54
RATE CONSTANT			
K, CC/GM-SEC	1.4465	1.3505	1.3815
$1/\sqrt{K}$	0.83	0.86	0.85
MATERIAL BALANCE, %	100.04		

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 25A

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 500.
PRESSURE, PSIG 450.

N-PENTANE, V/HR-V 4.09
W/HR-W 3.97

HYDROGEN, MOLES/MOLE C5 3.416
SCFB 3974.

SUPERFICIAL
HOLDING TIME, SEC. 16.46
GAS VELOCITY, CM/SEC. 0.465

VOID FRACTION 0.600

MINUTES ON FEED 85 95 105

PRODUCT
GMS/100 GMS N-PENTANE

HYDROGEN 9.54 9.54 9.54

METHANE 0.05 0.05 0.05

ETHANE 0.06 0.06 0.06

PROPANE 0.10 0.10 0.10

I-BUTANE 0.04 0.04 0.04

N-BUTANE 0.15 0.17 0.15

I-PENTANE 28.40 28.21 28.12

N-PENTANE 71.21 71.39 71.50

C6 PLUS 0.00 0.00 0.00

CONVERSION, % 28.79 28.61 28.50

IC5/PC5, % 28.51 28.32 28.23

WT % C4- 0.40 0.41 0.40

SELECTIVITY, % 98.65 98.61 98.65

RATE CONSTANT

K, CC/GM-SEC 0.0341 0.0338 0.0336

$1/\sqrt{K}$ 5.42 5.44 5.45

MATERIAL BALANCE, % 99.91

TABLE B-I
DETAILED ISOMERIZATION DATA

RUN 25B

CATALYST 1/2% PALLADIUM ON H-MORDENITE
PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	500.		
PRESSURE, PSIG	150.		
N-PENTANE, V/HR-V	4.09		
W/HR-W	3.97		
HYDROGEN, MOLES/MOLE C5	3.416		
SCFB	3974.		
SUPERFICIAL			
HOLDING TIME, SEC.	5.83		
GAS VELOCITY, CM/SEC.	1.312		
VOID FRACTION	0.600		
MINUTES ON FEED	200	210	220
PRODUCT			
GMS/100 GMS N-PENTANE			
HYDROGEN	9.53	9.53	9.53
METHANE	0.07	0.07	0.07
ETHANE	0.08	0.08	0.08
PROPANE	0.06	0.07	0.06
I-BUTANE	0.14	0.15	0.14
N-BUTANE	0.21	0.22	0.21
I-PENTANE	45.63	47.28	45.15
N-PENTANE	53.81	52.14	54.30
C6 PLUS	0.00	0.00	0.00
CONVERSION, %	46.19	47.86	45.70
IC5/PC5, %	45.89	47.56	45.40
WT % C4-	0.57	0.59	0.57
SELECTIVITY, %	98.79	98.80	98.79
RATE CONSTANT			
K, CC/GM-SEC	0.1952	0.2083	0.1916
1/√K	2.26	2.19	2.28
MATERIAL BALANCE, %	99.91		

TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 25C

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F	600.
PRESSURE, PSIG	450.
N-PENTANE, V/HR-V	16.39
W/HR-W	15.87
HYDROGEN, MOLES/MOLE C5	3.397
SCFB	3951.
SUPERFICIAL	
HOLDING TIME, SEC.	3.74
GAS VELOCITY, CM/SEC.	2.046
VOID FRACTION	0.600
MINUTES ON FEED	290 300

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN	9.43	9.42
METHANE	0.20	0.22
ETHANE	0.50	0.63
PROPANE	0.59	0.78
I-BUTANE	0.88	0.92
N-BUTANE	1.26	1.41
I-PENTANE	59.01	60.87
N-PENTANE	37.12	34.85
C6 PLUS	0.51	0.39
CONVERSION, %	62.88	65.15
IC5/PC5, %	61.39	63.59
WT % C4-	3.42	3.96
SELECTIVITY, %	93.85	93.42

RATE CONSTANT		
K, CC/GM-SEC	0.6769	0.8100
$1/\sqrt{K}$	1.22	1.11

MATERIAL BALANCE, %	99.99
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TABLE B-I

DETAILED ISOMERIZATION DATA

RUN 25D

CATALYST 1/2% PALLADIUM ON H-MORDENITE
 PARTICLE SIZE, MM. 0.42 - 0.84

TEMPERATURE, °F 600.
 PRESSURE, PSIG 250.

N-PENTANE, V/HR-V 16.39
 W/HR-W 15.87

HYDROGEN, MOLES/MOLE C5 3.397
 SCFB 3951.

SUPERFICIAL
 HOLDING TIME, SEC. 2.13
 GAS VELOCITY, CM/SEC. 3.592

VOID FRACTION 0.600

MINUTES ON FEED 325 335 350

PRODUCT
 GMS/100 GMS N-PENTANE

HYDROGEN 9.42 9.42 9.42

METHANE 0.23 0.23 0.23

ETHANE 0.54 0.53 0.52

PROPANE 0.89 0.87 0.86

I-BUTANE 1.43 1.39 1.38

N-BUTANE 1.48 1.44 1.43

I-PENTANE 59.49 59.55 59.81

N-PENTANE 34.67 34.76 34.61

C6 PLUS 1.34 1.31 1.22

CONVERSION, % 65.33 65.24 65.39

IC5/PC5, % 63.18 63.14 63.34

WT % C4- 4.57 4.45 4.43

SELECTIVITY, % 91.06 91.29 91.47

RATE CONSTANT

K, CC/GM-SEC 1.3689 1.3640 1.3887

$1/\sqrt{K}$ 0.85 0.86 0.85

MATERIAL BALANCE, % 99.99

APPENDIX C
CALIBRATION OF GAS CHROMATOGRAPH

APPENDIX C

CALIBRATION OF GAS CHROMATOGRAPH

A. Introduction

The product streams from the experimental runs in this research were, in general, composed of about 80 mole percent hydrogen and about 20 mole percent pentanes. In most cases, the amount of cracked product was relatively small (of the order of 1%). Only in a few instances were hydrocarbon components heavier than C₅ noted. The analysis of this type of gas stream was relatively simple, and was accomplished with a standard commercial gas chromatograph.

Figure C-1 (page 219) shows an output chromatogram obtained during calibration tests. These tests were carried out with research grade (99+ mole % purity) gas samples, obtained from the Matheson Company. No unsaturated hydrocarbons were used in the calibrations, since the reactor operating conditions assured an almost completely saturated hydrocarbon product. Cross-checks of actual product samples with a mass spectrometer verified this. As can be seen, an exceptionally clean separation was obtained, with the only exception being the small methane fraction that was not separated from the "fixed gases" peak (hydrogen and any air that may have been picked up during the sampling operation). The method that was used to estimate the amount of methane present in the products will be discussed later.

Figure C-1. Output Trace of Gas Chromatograph

B. Method of Calculation

The gas chromatograph consisted primarily of a thermal conductivity detector which was preceded by a packed column. The packing, due to varying adsorptivity constants, had a different "holdup-time" for each hydrocarbon component in the sample. Normally, a carrier gas (helium) was kept passing through the column, which had stabilized at the operating conditions. The gas sample was introduced as a "pulse" upstream of the column, and was swept through the packing by the carrier gas. Due to the clean separations that were effected, the gas stream passing through the detector at any given time normally consisted of a mixture of helium and a single hydrocarbon component.

The response of the thermal conductivity detector, a linear function of the instantaneous hydrocarbon concentration over wide ranges⁽⁵⁴⁾, was recorded as is shown in Figure C-1 (page 219). Thus, the instantaneous concentration of component "j" was simply

$$y_j = C'_j G_j \quad (C1)$$

where "y" = mole fraction, "G" = G.C. response, and C' is a calibration constant. The total amount of component "j" passing through the detection between times t_a and t_b was therefore

$$W_j = \int_{t_a}^{t_b} C'_j G_j dt = C'_j \int_{t_a}^{t_b} G_j dt \quad (C2)$$

A ball-and-disc integrator, built into the gas chromatograph system was used to perform this integration automatically as the analysis was being carried out. Thus, corresponding to each recorded "peak," a "peak area" was recorded, which was related to the hydrogen-free concentration of the corresponding component in the sample by the following equation:

$$Y_j = \frac{C_j Ar_j}{\sum_{k=1}^n C_k Ar_k} \quad (C3)$$

where C_j = an experimentally-determined calibration constant

Ar_j = "peak area" under peak "j"

$$= \int_{\text{peak "j"}} G_j dt$$

n = total number of components in hydrogen-free sample.

In order to extend the range of the gas chromatograph, an electronic "attenuator" was available to reduce the response of large peaks by selected factors. The final equation was therefore

$$Y_j = \frac{C_j Ar_j At_j}{\sum_{k=1}^n C_k Ar_k At_k} \quad (C4)$$

where At = "attenuation" used for the given peak.

C. Determination of Calibration Constants

During the calibration program, a 1 cc sample loop was used to inject precise volumes of each gas separately into the system. The corresponding peak area was noted for each gas. This integrated response (including the attenuation factor) was essentially a "calibration constant," as it represented the "area/cc of sample." The reciprocal of this number, a more convenient calibration constant, corresponded to the gram-moles of the given component per unit integrator reading. The calibration constants in Table C-1 (page 227) were determined as above, and are quantitatively:

$$C_j = \frac{1000}{(\text{integrator reading})_j (\text{attenuation})_j} \quad (C5)$$

The factor of 1000 was used simply for convenience. It did not affect the final results since, from equation (C4), it cancelled out in the calculation of the hydrogen-free concentrations.

Table C-1 (page 227) lists the mean calibration constants determined for each component, with the corresponding 95% confidence limits of each mean. Also listed in this table are calibration constants for the C₅ through C₇ liquids. These were determined with a liquid sampling valve which was used to inject precise volumes of pure liquids. The measured responses from these tests were put on the same molar basis as the above gases, and the resulting calibration constants were included in the table.

Figure C-2 (page 224) shows a graph of the calibration constants. This variation with molecular weight and composition (iso-paraffin vs. normal paraffins) is in agreement with results reported by Messner, et al. (54)

Since the actual response of the thermal conductivity detector was a function of the detector filament temperature, which was controlled by the rate of heat transfer from the heated filament, the "constants" were actually functions of all the system properties that could affect this heat transfer, in addition to the composition of the hydrocarbon-helium mixture. Thus, the absolute levels of the calibration constants depended also on the gas flow rate, detector temperature, and system pressure. However, for small deviations from "standard conditions," these corrections can be expressed as multiplicative factors, which cancel in the calculation of the gas composition. Thus the calibration constants in this table, although determined at a detector temperature of 100°C, a pressure of 50 psig, and a 100 cc/sec carrier gas flow, could be used in equation (C4) at other detector conditions as well as long as these conditions were kept constant for an entire sample mixture. Actually, all the analytical work was carrier out at or very near the conditions listed above.

D. Estimation of Methane Concentration

As was noted earlier, the methane peak was not separated from the hydrogen-air peak. The concentration of methane was therefore impossible to estimate from the gas chromatograph data, as it was normally less than 1/2% on a hydrogen-free basis. Since this

component was present in such a small concentration, and since small errors in its measurement would not affect the results of this study to any significant extent, an empirical correlation, developed from unpublished data from Esso Research Laboratories, was used. In this correlating method, the ratio of (methane)/(iso-pentane) was plotted vs. the ratio of (C_2 through C_4 paraffins)/(iso-pentane). These data, from the hydroisomerization runs with faujasite-based catalysts, showed that as the latter ratio increased, the ratio of $CH_4/(i-C_5)$ increased correspondingly. A line drawn through these data (Figure C-3, page 226) was used to estimate the relative hydrogen-free concentrations of methane in the product gases from this study.

E. Comparison with Mass Spectrometer Analysis

As a check on the analytical results obtained with this system, gas products from early runs were analyzed by a mass spectrograph at Esso Research Laboratories in Baton Rouge, La., as well as by the gas chromatographic system used for this research. The results of these analyses are shown in Table C-II (page 229). Comparisons are made both on a "total product" basis and also on a "fixed gas" (H_2 , CO , CO_2 , N_2) free basis. The former was the normal basis for a mass spectrometer analysis, while the latter was the normal basis for the "project analysis."

In both cases, it is seen that the results are quite close, in spite of the differences in the methods of analysis. In the M.S. analysis, the hydrocarbon components formed a small part of the

FIGURE C-3. Correlation of Methane Concentration

TABLE C-I

CALIBRATION CONSTANTS FOR PROJECT GAS CHROMATOGRAPH

Carbon Number	Normal Paraffins	Branched Paraffins	Olefins	Cyclics	C	
					Value	95% Conf. Limits
1	Methane				3.765	0.030
2	Ethane				2.496	0.019
			Ethylene		2.752	0.034
3	Propane				2.006	0.022
			Propylene		2.115	0.009
4	n-Butane				1.685	0.017
		Isobutane			1.707	0.013
			Butene-1			
			cis-Butene-2		1.789	0.003
			trans-Butene-2			
			Isobutylene			
			1,3-Butadiene		2.100	0.013
5	n-Pentane				1.495	0.035
		Isopentane			1.580	0.050
6	n-Hexane				1.278	0.04
		2,2-DMB			1.352	0.04
		2,3-DMB			1.352	0.04
		2-MP			1.308	0.04
		3-MP			1.318	0.04
				Methylcyclopentane	1.411	0.04
				Cyclohexane	1.471	0.04
				Benzene	1.582	0.04
7	n-Heptane				1.147	0.04

total sample, and therefore the relative accuracy of these components on a "hydrogen-free" basis were expected to be somewhat less than that expected of a normal M.S. analysis of a hydrogen-free sample ($2\sigma \approx 5\%$ of the quoted number). On the other hand, the G.C. samples were analyzed on a hydrogen-free basis.

The hydrogen concentration in the product gas stream was subsequently calculated from a material balance on the reactor system. As can be seen, the hydrogen concentrations are remarkably close, and the concentrations of the hydrocarbon components are essentially equal, within the limits of experimental error.

TABLE C-II

COMPARISON OF PROJECT ANALYSES WITH ERL-LA. ANALYSES

	"HIGH CRACKING" RUN				"LOW CRACKING" RUN			
	Total Output Stream		Mole %		Total Output Stream		Mole %	
	Mole %		(H ₂ , CO, CO ₂ , N ₂ -Free)		Mole %		(H ₂ , CO, CO ₂ , N ₂ -Free)	
	ERL M.S.	Project G.C.	ERL M.S.	Project G.D.	ERL M.S.	Project G.C.	ERL M.S.	Project G.C.
H ₂	70.15	70.06	--	--	80.49	79.84	--	==
CO, CO ₂ , N ₂	0.13	--	--	--	0.18	0.00	--	--
CH ₄	1.15	0.37	3.80	1.50	0.04	0.05	0.20	0.24
C ₂ H ₄	0.03	--	0.10	--	0.01	--	0.05	--
C ₂ H ₆	1.63	1.63	5.59	5.82	0.02	0.03	0.16	0.15
C ₃ H ₆	0.06	--	0.21	--	0.00	--	0.00	--
C ₃ H ₈	11.10	11.05	37.20	38.90	0.09	0.00	0.46	0.26
i-C ₄ H ₁₀	4.01	4.28	13.41	13.80	0.10	0.01	0.51	0.41
C ₅ H ₁₀	0.01	--	0.03	--	0.00	--	0.00	--
i-C ₅ H ₁₂	4.01	4.10	13.41	13.51	8.43	8.67	42.80	45.15
n-C ₅ H ₁₂	4.15	4.57	13.90	14.45	10.63	11.30	54.00	53.52
C ₆ H ₁₄	0.54	0.60	1.81	1.56	0.00	0.00	0.00	0.00

APPENDIX D
SAMPLE CALCULATIONS

APPENDIX D

SAMPLE CALCULATIONS

A. Typical Process Data

Temperature = 550°F

Pressure = 450 psig

Volume of n-Pentane fed = 122.6 cc

Calibration of hydrogen flow at wet test meter = 0.900 min/
(.050 ft³)

Wet test meter temperature = 80.0°F

Product gas volume at wet test meter = 4.249 ft³

Time of material balance = 60.0 minutes

Volume of catalyst = 15.0 cc

Weight of catalyst = 10.34 grams

Volume of gas sample = 250 cc = 0.00883 ft³

B. Analytical Data

<u>Component</u>	<u>G.C. Area</u>	<u>G.C. Attenuation</u>
CH ₄	--	1.0
C ₂ H ₆	0.05	1.0
C ₃ H ₈	0.34	1.0
i-C ₄ H ₁₀	0.30	1.0
n-C ₄ H ₁₀	0.55	1.0
i-C ₅ H ₁₂	16.35	4.0
n-C ₅ H ₁₂	22.00	4.0
C ₆ ⁺	0.00	1.0

C. Material Balance Calculations

Weight of n-pentane fed = 122.6 cc (0.631 gms/cc) = 77.48 gms.

Gm moles of n-pentane fed = 77.48/72.15 = 1.074 gm moles.

Barrels of n-pentane fed = 122.6 cc/(159,000 cc/barrel) =
0.772 10^3 barrels.

Gm atoms of carbon in n-pentane feed = 5.0 (1.074) = 5.37
gm atoms.

Gm atoms of hydrogen in n-pentane feed = 12.0 (1.074) = 12.89.

Liquid hourly space velocity:

$$(122.6 \text{ cc})(60 \text{ min/hr})/((60 \text{ min})(15 \text{ cc})) = 8.186 \text{ cc/hr cc.}$$

Weight hourly space velocity:

$$(77.48 \text{ gms})(60 \text{ min/hr})/((60 \text{ min})(10.34 \text{ gms})) = 7.494 \text{ gms/hr-gm.}$$

Total volume of gas product = 4.249 + 0.0088 = 4.2478 ft^3 .

Total volume of gas product at standard conditions:

$$4.2578 \frac{492}{460 + 80} \frac{29.92 - 1.03}{29.92} = 3.745 \text{ ft}^3$$

Total volume of feed hydrogen at standard conditions:

$$\frac{(60 \text{ min})(492)(29.92 - 1.03)}{(0.90 \text{ min}/.05 \text{ ft}^3)(460 + 80)} = 2.932 \text{ ft}^3$$

Gm moles of hydrogen gas fed:

$$\frac{(2.932 \text{ ft}^3)(453.6 \text{ gm moles/lb mole})}{(359 \text{ ft}^3/\text{lb mole})} = 3.705 \text{ gm moles}$$

Hydrogen/pentane molar ratio = (3.705)/(1.074) = 3.45 moles/mole.

Hydrogen/pentane ratio, (SCFB):

$$\frac{(2.932 \text{ ft}^3)(460 + 60)}{(.772 \times 10^{-3} \text{ barrels})(492)} = 4012 \text{ SCFB}$$

Gm atoms of carbon in product gases = 5.370 gm atoms.

Gm atoms of hydrogen in product gas = (12.89) + 2(3.705)
= 20.30 gm atoms.

Molar weighting factors for C_2^+ product components:

C_2H_6	:	(0.05)	(1.0)	(2.496)	=	0.1248
C_3H_8	:	(0.34)	(1.0)	(2.006)	=	0.6820
i- C_4H_{10}	:	(0.30)	(1.0)	(1.707)	=	0.5121
n- C_4H_{10}	:	(0.55)	(1.0)]	(1.685)	=	0.9268
i- C_5H_{12}	:	(16.35)	(4.0)	(1.580)	=	103.33
n- C_5H_{12}	:	(22.00)	(4.0)	(1.495)	=	131.56
C_6^+	:	(0.00)	(1.0)	(1.352)	=	0.00

Molar weighting factor for CH_4 , (empirical estimation):

0.493

$$CH_4 : 0.524 \frac{(.1248) + (.6820) + (.5121) + (.9268)}{(103.33)} \quad (103.33)$$

$$= 0.820$$

Sum of hydrocarbon weighting factors = 237.96

Hydrogen-free mole fractions of hydrocarbons:

CH_4	:	(0.820)/(237.96)	=	0.00344
C_2H_6	:	(0.1248)/(237.96)	=	0.000524
C_3H_8	:	(0.6820)/(237.96)	=	0.002866
i- C_4H_{10}	:	(0.5121)/(237.96)	=	0.002152
n- C_4H_{10}	:	(0.9268)/(237.96)	=	0.003895
i- C_5H_{10}	:	(103.33)/(237.96)	=	0.4342
n- C_5H_{10}	:	(131.56)/(237.96)	=	0.5529
C_6^+	:	(0.00)/(237.96)	=	0.00

Gm atoms of carbon per gm mole of hydrocarbon product:

CH_4	:	(1)	(0.00344)	=	0.00344
C_2H_6	:	(2)	(0.000524)	=	0.001048
C_3H_8	:	(3)	(0.002866)	=	0.008598
i- C_4H_{10}	:	(4)	(0.002152)	=	0.008608
n- C_4H_{10}	:	(4)	(0.003895)	=	0.01558
i- C_5H_{12}	:	(5)	(0.4342)	=	2.171
n- C_5H_{12}	:	(5)	(0.5529)	=	2.765
C_6^+	:	(6)	(0.00)	=	<u>0.00</u>
					4.9728 gm atoms

Gm moles of hydrocarbon components in gas stream:

CH_4	:	$(0.00344)(5.370)/(4.9728)$	=	0.00372
C_2H_6	:	$(0.000524)(5.370)/(4.9728)$	=	0.000566
C_3H_8	:	$(0.002866)(5.370)/(4.9728)$	=	0.003095
i- C_4H_{10}	:	$(0.002152)(5.370)/(4.9728)$	=	0.002324
n- C_4H_{10}	:	$(0.003895)(5.370)/(4.9728)$	=	0.004205
i- C_5H_{12}	:	$(0.4342)(5.370)/(4.9728)$	=	0.4689
n- C_5H_{12}	:	$(0.5529)(5.370)/(4.9728)$	=	0.5970
C_6	:	$(0.00)(5.370)/(4.9738)$	=	<u>0.00</u>
1.0798 gm moles				

Gm atoms of hydrogen in hydrocarbon products:

CH ₄	:	(4)	(0.00372)	=	0.01488
C ₂ H ₆	:	(6)	(0.00566)	=	0.03396
C ₃ H ₈	:	(8)	(0.003095)	=	0.02476
i-C ₄ H ₁₀	:	(10)	(0.004205)	=	0.02324
n-C ₄ H ₁₀	:	(10)	(0.004205)	=	0.04205
i-C ₅ H ₁₂	:	(12)	(0.4689)	=	5.627
n-C ₅ H ₁₂	:	(12)	(0.5970)	=	7.164
C ₆	:	(14)	(0.00)	=	<u>0.00</u>
					12.899

Gm moles of hydrogen gas in product stream:

$$1/2 \quad 20.30 - 12.899 = 3.6987 \text{ gm moles}$$

Total calculated gm moles in product gas:

$$(1.0798) + (3.6987) = 4.779 \text{ gm moles}$$

Total observed gm moles in product gas:

$$\begin{aligned} & (3.745 \text{ ft}^3)(28.316 \text{ liters/ft}^3)/(22.41 \text{ liters/ gm mole}) \\ & = 4.732 \text{ gm moles} \end{aligned}$$

Gas material balance:

$$100 (4.732)/(4.779) = 99.01\%$$

Gms of products per 100 gms of n-pentane fed:

H_2	:	(3.6987)	(2.016)	(100)/(77.48)	=	9.623
CH_4	:	(0.00372)	(16.04)	(100)/(77.48)	=	0.077
C_2H_6	:	(0.000566)	(30.07)	(100)/(77.48)	=	0.022
C_3H_8	:	(0.003095)	(44.09)	(100)/(77.48)	=	0.176
i- C_4H_{10}	:	(0.002324)	(58.12)	(100)/(77.48)	=	0.174
n- C_4H_{10}	:	(0.004205)	(58.12)	(100)/(77.48)	=	0.315
i- C_5H_{12}	:	(0.4689)	(72.15)	(100)/(77.48)	=	43.66
n- C_5H_{12}	:	(0.5970)	(72.15)	(100)/(77.48)	=	55.59
C_6	:	(0.00)	(86.17)	(100)/(77.48)	=	0.00

Wt. percent C_4 in hydrocarbon product:

$$100 (.077 + .022 + .176 + .174 + .315)/(100.01) = 0.764\%$$

$$\% \text{ i-}C_5 \text{ in p-}C_5 = 100(43.66)/(43.66 + 55.59) = 43.99\%$$

$$\text{Conversion} = 100 - 55.59 = 44.41\%$$

$$\text{Selectivity} = 100(43.66)/(100 - 55.59) = 98.31\%$$

$$\text{Catalyst solid density} = 1.63 \text{ gms/cc}$$

$$\text{Catalyst bulk density} = 10.34/15.0 = 0.6893 \text{ gms/cc}$$

$$\text{Void fraction in catalyst bed} = 1.0 - (0.6893)/1.63 = 0.577$$

Mole percent i-pentane (hydrogen-free) at equilibrium:

$$79.46 - 0.026428 (550) + 2125.1/(550) = 68.79\%$$

Density of reactor gases:

$$\frac{(450 + 14.7)(492)}{(14.7)(460 + 550)} \frac{1}{22,410} = 0.6871 \times 10^{-3} \text{ gm moles/cc}$$

Superficial holding time in reactor:

$$\frac{(77.48 \text{ gms pentane/hr})}{(72.15 \text{ gms/gm mole})(15 \text{ cc catalyst})} =$$

$$0.07159 \frac{\text{gm moles pentane}}{\text{hr cc}}$$

$$(0.07159)(1 + 3.45) = 0.3186 \frac{\text{gm moles gas}}{\text{hr cc}}$$

$$t_H = \left[\frac{(0.3186 \frac{\text{gm moles gas}}{\text{hr cc}})}{(.0006871 \frac{\text{gm moles gas}}{\text{cc}})} \right]^{-1} = 0.002157 \text{ hrs} = 7.77 \text{ sec}$$

Superficial gas velocity:

$$(15 \text{ cc}) / (1.96 \text{ cm}^2)(7.77 \text{ sec}) = 0.986 \text{ cm/sec}$$

Reaction rate constant:

$$\begin{aligned} k &= \frac{Y_1^*}{\rho_B t_H} \ln \left[1 - \frac{Y_1}{Y_1^*} \right] \\ &= \frac{(0.6879)}{(0.6893)(7.77)} \ln \left[1 - \frac{43.99}{68.79} \right] \\ &= 0.1311 \text{ cc/gm sec} \end{aligned}$$

APPENDIX E

RESULTS OF

PROPAGATION OF ERROR STUDY

TABLE E-I

TABLE OF PARTIAL DERIVATIVES

Independent Variable	Dependent Variables					
	1 8.185	2 7.392	3 3.449	4 4012.	5 0.9855	6 9.623
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	-0.0
3	0.0	0.0	0.0	0.0	0.0	-0.002
4	0.0	0.0	0.0	0.0	0.0	-0.001
5	0.0	0.0	0.0	0.0	0.0	-0.002
6	0.0	0.0	0.0	0.0	0.0	0.001
7	0.0	0.0	0.0	0.0	0.0	0.005
8	0.0	0.0	0.0	0.0	0.0	0.0
9	12.953	11.856	-5.404	-6286.028	0.350	-15.100
10	-12.845	0.0	0.0	6358.969	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	-0.002	0.0
13	0.066	0.061	-0.027	-32.404	0.0	-0.077
14	0.0	0.0	-3.794	-4414.166	-0.840	-10.603
15	0.0	0.0	-0.010	-12.281	-0.002	-0.029
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-0.135	-0.123	0.057	66.874	-0.003	0.160
18	-0.540	0.0	0.0	0.0	0.0	0.0
19	0.0	-0.717	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0	0.0	-0.021
22	0.0	0.0	0.0	0.0	0.0	-0.012
23	0.0	0.0	0.0	0.0	0.0	0.006
24	0.0	0.0	0.0	0.0	0.0	-0.006
25	0.0	0.0	0.0	0.0	0.0	0.0
26	0.0	0.0	0.0	0.0	0.0	0.0
27	0.0	0.0	0.0	0.0	0.0	0.003

TABLE E-I

TABLE OF PARTIAL DERIVATIVES

Independent Variable	Dependent Variables					
	7	8	9	10	11	12
	0.07701	0.02197	0.1761	0.1743	0.3154	43.66
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.008	0.0	0.0	0.0	0.0
3	0.005	-0.0	0.087	-0.0	-0.0	-0.039
4	0.004	-0.0	-0.0	0.101	-0.0	-0.046
5	-0.0	-0.0	-0.0	0.0	0.186	-0.084
6	0.003	-0.006	-0.048	-0.047	-0.086	15.491
7	-0.028	0.008	-0.065	-0.064	-0.116	-16.145
8	0.0	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	0.041	0.439	0.0	0.0	0.0	0.0
22	0.033	-0.0	0.417	-0.0	-0.001	-0.235
23	0.028	-0.0	-0.001	0.579	-0.001	-0.263
24	0.028	-0.0	-0.001	-0.001	0.571	-0.259
25	0.0	-0.0	-0.004	-0.004	-0.008	1.496
26	-0.001	-0.0	-0.004	-0.004	-0.007	-1.097
27	-0.0	-0.0	-0.001	-0.001	-0.002	-0.299

TABLE E-I

TABLE OF PARTIAL DERIVATIVES

Independent Variable	Dependent Variables					
	13	14	15	16	17	18
	55.58	0.000	44.41	43.99	0.7647	98.31
1	0.0	0.0	0.0	0.0	0.0	0.0
2	-0.005	0.0	0.005	0.0	0.009	-0.020
3	-0.050	0.0	0.050	0.0	0.092	-0.202
4	-0.058	0.0	0.058	0.0	0.106	-0.234
5	-0.107	0.0	0.107	0.0	0.194	-0.429
6	-15.306	0.0	15.205	15.525	-0.186	0.991
7	16.422	0.0	-16.422	-16.389	-0.282	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	-0.256	0.0	0.256	0.0	0.477	-1.012
22	-0.299	0.0	0.299	0.0	0.547	-1.193
23	-0.335	0.0	0.335	0.0	0.605	-1.333
24	-0.330	0.0	0.330	0.0	0.597	-1.317
25	-1.479	0.0	1.479	1.500	-0.017	0.095
26	1.115	0.0	-1.115	-1.113	-0.019	0.0
27	-0.380	0.681	0.380	0.0	-0.005	-1.515

TABLE E-I

TABLE OF PARTIAL DERIVATIVES

Independent Variable	Dependent Variables				
	19 <u>0.1311</u>	20 <u>2.761</u>	21 <u>7.765</u>	22 <u>0.5770</u>	23 <u>99.01</u>
1	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0
4	0.0	0.00	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0	0.0
6	0.080	-0.845	0.0	0.0	0.0
7	-0.084	0.896	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0
9	0.046	-0.490	-2.755	0.0	-35.130
10	0.0	0.0	0.0	0.0	0.0
11	-0.003	0.037	-0.007	0.0	0.0
12	-0.0	0.002	0.016	0.0	0.0
13	0.0	-0.002	-0.014	0.0	-0.181
14	-0.111	1.184	6.674	0.0	85.098
15	-0.0	0.003	0.018	0.0	-0.068
16	0.0	0.0	0.0	0.0	23.254
17	-0.0	0.005	0.028	0.0	-1.269
18	0.0	0.0	0.517	0.027	0.0
19	-0.012	0.133	0.0	-0.040	0.0
20	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0
23	0.0	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	0.0	0.0
25	0.007	-0.081	0.0	0.0	0.0
26	-0.005	0.060	0.0	0.0	0.0
270.0	0.0	0.0	0.0	0.0	0.0

TABLE E-II

TABLE OF CONTRIBUTIONS TO VARIANCE OF DEPENDENT VARIABLES

Independent Variable	Dependent Variable					
	1	2	3	4	5	6
	8.186	7.493	3.449	4012.	0.9855	9.623
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0	0.0	0.0
7	0.0	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0
9	1.975	64.277	35.135	25.843	2.590	35.135
10	1.953	0.0	0.0	26.446	0.0	0.0
11	0.0	0.0	0.0	0.0	8.925	0.0
12	0.0	0.0	0.0	0.0	41.358	0.0
13	0.058	1.897	1.037	0.763	0.076	1.037
14	0.0	0.0	38.983	28.673	33.528	38.983
15	0.0	0.0	14.901	10.960	12.816	14.901
16	0.0	0.0	0.0	0.0	0.0	0.0
17	0.537	17.477	9.941	7.312	0.704	9.941
18	95.486	0.0	0.0	0.0	0.0	0.0
19	0.0	16.347	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0	0.0
23	0.0	0.0	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	0.0	0.0	0.0
25	0.0	0.0	0.0	0.0	0.0	0.0
26	0.0	0.0	0.0	0.0	0.0	0.0
27	0.0	0.0	0.0	0.00	0.0	0.0
σ^2	0.0764	0.00196	0.000748	1376.	0.0000426	0.00584
2σ , Abs.	0.552	0.0887	0.0547	74.19	0.0130	0.152
2σ , %	6.75	1.18	1.58	1.84	1.32	1.58

TABLE E-II

TABLE OF CONTRIBUTIONS TO VARIANCE OF DEPENDENT VARIABLES

Independent Variable	Dependent Variable				
	7 0.02197	8 0.1761	9 0.1743	10 0.3154	11 43.66
1	0.0	0.0	0.0	0.0	0.0
2	0.003	1.195	0.0	0.0	0.0
3	0.195	0.0	2.385	0.0	0.0
4	0.045	0.0	0.0	1.010	0.0
5	0.248	0.0	0.0	0.0	1.666
6	0.423	4.610	4.564	4.628	4.606
7	12.230	3.300	3.266	3.312	3.296
8	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0
21	0.166	60.781	0.0	0.0	0.0
22	4.921	0.0	59.975	0.0	0.0
23	2.754	0.0	0.0	60.820	0.0
24	9.010	0.0	0.0	0.0	60.348
25	1.057	11.509	11.393	11.554	11.498
26	68.875	18.583	8.396	18.655	18.565
27	0.066	0.017	0.017	0.017	0.017
σ^2	0.00000026	0.00000008	0.00000515	0.00000498	0.00001638
2σ , Abs.	0.001026	0.000563	0.00453	0.00446	0.00809
2σ , %	1.33	2.56	2.57	2.55	2.56

TABLE E-II

TABLE OF CONTRIBUTIONS TO VARIANCE OF DEPENDENT VARIABLES

Independent Variable	Dependent Variable					
	12 43.66	13 55.58	14 0.0	15 44.41	16 43.99	17 0.7649
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0.002
3	0.0	0.0	0.0	0.0	0.0	0.268
4	0.0	0.0	0.0	0.0	0.0	0.106
5	0.0	0.0	0.0	0.0	0.0	0.581
6	15.728	15.314	0.0	15.314	15.554	6.750
7	6.781	6.996	0.0	6.996	6.878	6.190
8	0.0	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0	0.0	0.111
22	0.0	0.0	0.0	0.0	0.0	6.761
23	0.0	0.0	0.0	0.0	0.0	6.428
24	0.001	0.002	0.0	0.002	0.0	21.053
25	39.265	28.229	0.0	28.229	28.829	16.852
26	38.185	39.397	0.0	39.397	38.737	34.858
27	0.036	0.059	100.000	0.059	0.0	0.033
σ^2	0.1525	0.152	0.000290	0.152	0.154	0.0000512
2σ , Abs.	0.781	0.782	0.0340	0.782	0.787	0.0143
2σ , %	1.78	1.40		1.76	1.78	1.87

TABLE E-II

TABLE OF CONTRIBUTIONS TO VARIANCE OF DEPENDENT VARIABLES

Independent Variable	Dependent Variable					
	18 98.31	19 0.1311	20 2.761	21 7.765	22 0.5770	23 99.01
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0.0
3	0.035	0.0	0.0	0.0	0.0	0.0
4	0.014	0.0	0.0	0.0	0.0	0.0
5	0.077	0.0	0.0	0.0	0.0	0.0
6	5.267	1.408	1.142	0.0	0.0	0.0
7	0.0	0.610	0.509	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0
9	0.0	0.042	0.034	0.098	0.0	2.674
10	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	89.329	91.216	0.335	0.0	0.0
12	0.0	0.673	0.561	1.602	0.0	0.0
13	0.0	0.001	0.001	0.002	0.0	0.078
14	0.0	0.545	0.453	1.294	0.0	35.310
15	0.0	0.208	0.172	0.489	0.0	1.121
16	0.0	0.0	0.0	0.0	0.0	52.082
17	0.0	0.011	0.009	0.026	0.0	8.731
18	0.0	0.0	0.0	96.150	99.466	0.0
19	0.0	0.212	0.127	0.0	0.533	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
21	0.013	0.0	0.0	0.0	0.0	0.0
22	0.882	0.0	0.0	0.0	0.0	0.0
23	0.857	0.0	0.0	0.0	0.0	0.0
24	2.812	0.0	0.0	0.0	0.0	0.0
25	13.148	3.516	2.850	0.0	0.0	0.0
26	0.0	3.439	2.870	0.0	0.0	0.0
27	76.890	0.0	0.0	0.0	0.0	0.0
σ^2	0.00186	0.0000353	0.00625	0.0595	0.000194	0.415
2σ , Abs.	0.0863	0.0136	0.158	0.527	0.0279	1.28
2σ , %	0.0878	10.3	5.72	6.79	4.85	1.30

APPENDIX F

NOMENCLATURE

APPENDIX F

NOMENCLATURE

- a - Dimensionless variable, $\sqrt{1 + 4k^*/P}$
- A - Subscript denoting "reactant"
- A - Cross-sectional area of empty reactor
- B - Subscript denoting "product"
- B - Subscript denoting "bulk" (when used as ρ_B)
- C - Concentration of tracer, measured at reactor outlet
- C_A - Concentration of reactant (or "component A")
- C_{AS} - Concentration of component "A" at surface of catalyst particle
- C_B - Concentration of product (or "component B")
- C_{BS} - Concentration of component "B" at surface of catalyst particle
- C_H - Concentration of hydrogen
- C_I - Concentration of isopentane
- C_n - Concentration of normal pentane
- C_o - Initial concentration of tracer (assuming instantaneous mixing throughout reactor)
- C^* - Fraction of maximum possible concentration
- d_p - Diameter of particle
- D - Longitudinal dispersion coefficient
- D_{AB} - Diffusion coefficient of "A" in "B"
- D_e - Effective diffusion coefficient
- D_o - Factor (non-temperature-dependent) in effective diffusion coefficient

- D_K - Knudsen diffusion coefficient
- f - Fugacity
- F - Feed rate of n-pentane
- G - Subscript denoting "gas"
- h - Subscript denoting "actual" (when used as t_h)
- H - Subscript denoting "superficial" (when used as t_H)
- i - General index variable
- j - General index variable
- k - First order forward reaction rate constant (equation 23A), including any effects of system partial pressures
- k_0 - Hypothetical first order forward reaction rate constant at zero pressure
- k' - First order reverse reaction rate constant, including any effects of system partial pressures
- k^* - Dimensionless variable, defined as $(k + k')t_n$
- K - Thermodynamic equilibrium constant
- K_{CS} - Dynamic adsorption coefficient for C_5 hydrocarbons
- K_H - Dynamic adsorption coefficient for hydrogen
- K_I - Dynamic adsorption coefficient for isopentane
- K_n - Dynamic adsorption coefficient for n-pentane
- L - Pore length (in equations 31A-38)
- L - Length of catalyst bed
- $\ln$ - Natural logarithm
- M - Molecular weight of n-pentane
- M_A - Molecular weight of component "A"
- M_B - Molecular weight of component "B"
- N - Number of independent sets of measurements

- N_i - Flow rate of isopentane
- N_n - Flow rate of n-pentane
- N_T - Total molar flow rate of gases
- p - Width of input pulse at 1/2 its maximum height in tracer test experiment
- P_H - Partial pressure of hydrogen
- P_i - Partial pressure of isopentane
- P_n - Partial pressure of n-pentane
- ρ - Probability distribution function
- P - Peclet number
- P - General pressure term in equation 28
- P_{CA} - Critical pressure of component "A"
- P_{CB} - Critical pressure of component "B"
- P_T - Total pressure
- r - Reaction rate (averaged over all active sites in particle)
- r^* - Reaction rate at surface of particle
- R - Gas constant
- Re_p - Particle Reynolds number
- R_H - Molar ratio of hydrogen/pentanes
- s_X - Standard deviation of measured variable
- s_Y - Standard deviation of calculated variable
- S - Width of output pulse at 1/2 its maximum height in a tracer test
- S^* - S/t_h
- t - Time
- t_h - "Actual holding time" (void volume)/(volumetric flow rate)

- t_H - "Superficial holding time"
- t^* - t/t_H
- T - Temperature, degrees Rankine, unless otherwise specified
- T_{CA} - Critical temperature of component "A"
- T_{CB} - Critical temperature of component "B"
- u - Fluid viscosity
- U - Emergence time of output peak, measured from input peak
- U^* - U/t_H
- V_T - Total volumetric flow rate of gases at reactor conditions
- $\bar{V}$ - Average velocity, L/t_H
- $\mathcal{V}$ - Catalyst volume
- w - Total weight rate of flow through reaction system
- W - Pentane feed rate, gms/hr/gm catalyst--"W/Hr/W."
- W_c - Weight of catalyst in reactor
- x - Axial distance along catalyst bed
- x - Actual value of measured quantity (Chapter VII)
- X - Measured value of random variable
- $\bar{X}$ - Arithmetic mean of several measurements
- y - Actual value of calculated quantity (Chapter VII)
- y - Mole fraction
- y_H - Mole fraction of hydrogen
- y_i - Mole fraction of isopentane
- y_n - Mole fraction of n-pentane
- y_i^* - Mole fraction of isopentane at equilibrium
- Y - Value of calculated dependent variable, as calculated from actual measurements of independent variables (Chapter VII).

Y - Hydrogen-free mole fraction
 Y_i - Hydrogen-free mole fraction of isopentane
 Y_n - Hydrogen-free mole fraction of n-pentane
 Y_i^* - Hydrogen-free mole fraction of isopentane at equilibrium

β - A group of terms, not dependent upon pressure, in equations 50-53
 ϵ - Void fraction
 η - Effectiveness factor
 μ - Viscosity
 μ - Expected value of probability distribution function
 ν - Fugacity coefficient
 ρ_g - Molar density of gas stream
 ρ_b - Bulk density of catalyst bed
 σ - Standard deviation
 ϕ - Thiele modulus

AUTOBIOGRAPHY

Philip Auburn Bryant was born on October 23, 1935, in Baton Rouge, Louisiana. In 1953, he was graduated from Catholic High School in Baton Rouge. After serving in the United States Marine Corps, he returned to Baton Rouge and in 1959 received a Bachelor of Science Degree in chemical engineering from Louisiana State University. In 1961, he received a Master of Science Degree from the same university.

After his sophomore year at Louisiana State University, he was employed for the summer by the Solvay Process Division of Allied Chemical and Dye Works at Baton Rouge, Louisiana. This was followed by successive periods of summer employment at Ethyl Corporation in Baton Rouge, Louisiana; Humble Oil and Refining Company in Baytown, Texas; and Dupont in Wilmington, Delaware. Upon completion of his M.S. work, he was employed by Esso Research Laboratories in Baton Rouge, Louisiana.

After four years at Esso Research Laboratories, he returned to Louisiana State University to complete his work toward a PhD degree in chemical engineering, after which he returned to Esso Research Laboratories in Baton Rouge.

In 1957, he married the former Fay Ensminger, and is now the father of two children.

EXAMINATION AND THESIS REPORT

Candidate: Philip Auburn Bryant

Major Field: Chemical Engineering

Title of Thesis: Hydroisomerization of Normal Pentane Over a Zeolite Catalyst

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 14, 1966