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James Jerome Spivey
Louisiana State University and Agricultural & Mechanical College

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Hydroisomerization of Pentane and Hexane Mixtures on Zeolite Catalysts

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

The Department of Chemical Engineering

by

James Jerome Spivey

B.S., Chem. Eng., N.C. State University, 1972
M.S., Chem. Eng., N.C. State University, 1974

August, 1980
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Abstract

Pure component and mixtures of pentane and hexane were hydroisomerized on Pd-H-mordenite and Pd-H-faujasite at 465°F, 100 to 300 psig, 6.2 to 6.6 w/hr/w, and 10/1 to 18/1 H₂/hydrocarbon mole ratio. The activity of both these catalysts was comparable to other developmental catalysts reported in the literature. Results showed that on the mordenite catalyst, the first order rate constant for n-C₅ decreased on dilution with n-C₆ while the n-C₆ rate constant increased on dilution with n-C₅. On the faujasite catalyst, the rate constant for both n-C₅ and n-C₆ decreased from the pure component values on dilution.

Models were proposed for the rate constants as functions of adsorption parameters and the partial pressures of the reactants and of hydrogen. These models were based on a Langmuir-Hinshelwood adsorption function. Statistical analysis of the various models indicated that on Pd-H-mordenite, n-C₆ is preferentially adsorbed. On Pd-H-faujasite, the analysis showed that neither n-C₅ nor n-C₆ predominates in adsorption and that the adsorption parameters for both reactants must be included in the model. The hydrogen adsorption parameter was negligible compared to both the pentane and hexane adsorption parameters on both catalysts.
Introduction

Hydroisomerization of low molecular weight paraffins has become an increasingly important conversion process in recent years. This is due to the phase-down of antiknock concentrations in motor gasoline and the resulting need for higher octane, i.e., more branched hydrocarbon constituents. The research octane number (RON) of streams containing C₅ and C₆ mostly straight chain hydrocarbons can be boosted from about 70 to over 80 with the extent of improvement depending on the isomerization temperature and C₅/C₆ ratio (1).

Zeolite catalysts have been employed almost exclusively in new efforts in this area. Paraffin isomerization requires a stable catalyst with high activity to take advantage of the higher equilibrium conversions to branched products at lower temperatures (2). Zeolites have been shown to be highly active for this type of reaction and have additional advantages such as relative insensitivity to moisture, sulfur, nitrogen (3).

The earliest investigations into zeolite catalyst activity were acid-base type reactions such as cracking, isomerization, alkylation, and dehydration of alcohols. These reactions were also known to be catalyzed by amorphous aluminosilicates. Zeolites, being crystalline aluminosilicate compounds, were found to have special properties compared to amorphous catalysts. It was found that noble-metal free zeolites catalyze n-C₆ isomerization while the amorphous aluminosilicates do not (4). This is attributed to the unique adsorptive and acidic surface properties of zeolites. Modified zeolites have appeared in which ion exchange and deposition of a hydrogenating noble metal such as Pd are used to enhance specific reactions. Hydroisomerization of alkanes on
such catalysts is generally considered to proceed through a mechanism in which dehydrogenation of the alkane at a metallic site is followed by skeletal rearrangement at an acidic zeolite site via a carbonium ion intermediate. The resulting isomer is hydrogenated at a metallic site to complete the reaction.

Problems currently being investigated in this field include the structure of the active centers (both metal and acid sites), intradiffusional inhibition due to intramolecular channels, and the nature of catalyst deactivation (3). Little has been reported in the literature on systematic studies of mixed n-C₅ and n-C₆ feeds although it is this type of feed that is typical of hydroisomerization feed stocks for octane enhancement. In fact, C₅ and C₆ hydrocarbons comprise 15-20% of the total motor gas pool (5). Any anomalies observed in hydroisomerization of such mixed feeds are important in the design of commercial systems and in the investigation of the mechanism and dynamics on a molecular level.

This study was designed to examine the kinetics of n-C₅/n-C₆ hydroisomerization of both mordenite and faujasite catalysts. The objectives were:

1. Using a simplified kinetic model, describe the effects of temperature and reactant partial pressures on the rate constant for both a mordenite and faujasite catalyst typical of developmental catalysts.

2. Explain any anomalies in terms of fundamental kinetic quantities such as adsorption parameters.

3. Compare the performance of the mordenite and faujasite catalysts in terms of the kinetic models developed.
Literature Review

Zeolites are a special class of crystalline aluminosilicate compounds which have specific pore dimensions and pore structure. Their value in heterogeneous catalysis lies in the ability to tailor the pores to exclude certain reactants and thus obtain high selectivity; and in the special acidic and adsorptive properties of the zeolite surface which promote specific conversion reactions such as hydroisomerization.

In this section, the available literature on faujasite and mordenite zeolites will be examined as follows. First, the structure and physical properties for each catalyst will be described. Second, studies carried out involving specific reactions on these catalysts will be reviewed especially as they relate to the particular types of catalysts used in this study. Finally, studies which have compared the activities of mordenite and faujasite catalyst, particularly as differences in performance may be related to physical and chemical characteristics, will be reviewed.

Structure

There are more than 30 different crystalline zeolites occurring in nature. Over 100 additional zeolites have been manufactured synthetically in order to obtain enhanced chemical or sorptive properties. Whether synthetic or natural, all zeolites may be represented by the empirical formula (6):

\[ M_{x/n} 0 \left[ \left( Al \ 0_2 \right)_x \left( Si \ 0_2 \right)_y \right] \cdot w H_20 \]

In this formula, M is the cation of valence n, w is the number of water molecules, and y/x has values of 1-5 depending on the structure.
This structure consists of an infinitely extending three dimensional network of $\text{AlO}_4$ and $\text{SiO}_4$ tetrahedra linked to each other by sharing all of the oxygens.

In spite of the many varieties of natural and synthetic zeolites available, only few have practical importance at the present. Many zeolites, after dehydration, have very small channels which do not penetrate the particle and which are serious mass transfer blocks. In other cases, dehydration irreversibly disrupts the structure and the positions of the metal cations, causing the framework to collapse. To be of use, the structure must remain intact after dehydration. Breck (6) has summarized and classified the important synthetic and natural zeolite properties.

**Faujasite**

Faujasite is both a naturally occurring and synthesized zeolite. Type X and Y have been used to designate two synthetic faujasites which have received special attention. The empirical formulas for a typical oxide are given by Breck (6),

\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5 \text{SiO}_2 \cdot 6 \text{H}_2\text{O} \quad \text{Type X.}
\]

\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.8 \text{SiO}_2 \cdot 8.9 \text{H}_2\text{O} \quad \text{Type Y.}
\]

The basic structure of the faujasite, both X and Y, is that of a truncated tetrahedron as shown in Figure 1. Each vertex in the Figure represents a silicon or aluminum atom and each line represents a linking oxygen atom. Access to the inner pores is by way of four 12-sided windows with a diameter of \(\sim 9\)Å. The inner cavity has a diameter of \(\sim 11\)Å. The metal cation, such as $\text{Na}^+$, is located within the cavities as shown in Figure 2. By decationization or ion exchange, it can be seen that the
Figure 1. Structure of Type X or Type Y Zeolite.
Figure 2. Three-Dimensional Structure of Sodalite Unit.

The truncated octahedron and three of the four hexagonal prisms are shown together with the cation sites along one of the four tetrahedral axes. The cation sites are: I at the center of a hexagonal prism, I' displaced from a shared hexagonal face into the sodalite cage, II' displaced from an unshared hexagonal face into the sodalite cage, III slightly displaced into the supercage, and II displaced considerably into the supercage. From Smith (7).
catalytic properties of a given structural X or Y faujasite can be altered. In addition, when it is recognized that the structural framework of the faujasite may be changed by such methods as steam leaching \((8/\)) , it becomes apparent that a great deal of latitude exists in which to tailor the faujasite structure for a given reaction.

It has been found that the introduction of Group VIII transition metals into polyvalent or decationized faujasite yields catalysts very active for isomerization. It has been found that Pd-faujasite enables a 50-100°C lower temperature to be used when compared to conventional bifunctional catalysts \((3/\)) . These metals provide a hydrogenation and a dehydrogenation function described earlier. A catalyst such as palladium-type Y-H-faujasite \((\text{Pd-H-Y})\) is called bifunctional, as it contains both metallic and acidic sites.

The method of preparation of such catalysts as Pd-Na-Y and the effect of catalyst pretreatment prior to use in reactions has been investigated extensively. This is due to the large effect that differences in preparation can have on structure and consequently on activity. For example, Minachev, et al., found that the method of introduction of the metal can greatly effect activity. He found that Pt-Na-Y prepared by ion exchange has a greater activity than the same catalyst prepared by impregnation with chloroplatinic acid \((3/\)) .

After ion exchange, the catalyst is typically activated under air or \(\text{N}_2\) followed by reduction in \(\text{H}_2\) to further enhance its activity, specifically the nature of the surface and the metallic sites. It is found that activity in \(\text{n-C}_5\) isomerization falls off rapidly for catalysts reduced at \(>380^\circ\text{C}\) \((3/\)) . Another study investigated the effect of pretreatment of Pd-Ca-Y in air, \(\text{N}_2\), and \(\text{H}_2\) \((9/\)) . Below \(250^\circ\text{C}\) the Pd was found
not to be sufficiently reduced by H₂ and its dehydrogenation activity was low. However, when this catalyst was subsequently used in an isomerization reaction, the conversion increased during the course of the 1 hour run from 8 to 20%. This indicates that the metal was activated during the run.

This same study investigated the effect of HCl treatment on the catalyst. The catalyst acidity increased with increasing HCl treatment, mainly as a result of increase in the medium to strong acidic sites.

**Mordenite**

Mordenite is unique among zeolites in that the structure consists of parallel elliptical channels which do not intersect. These channels have major and minor diameters of 6.95 and 5.81 Å respectively, as shown in Figure 3. Of primary interest is the fact that the effective pore dimensions of mordenite can be adjusted by ion exchange with a cation of suitable radius (10, 11, 12). Voorhies, et. al., found that acid leaching of mordenite produces an Al-deficient structure with decreased diffusional resistance (36). This procedure raises the SiO₂/Al₂O₃ ratio in mordenite by extracting aluminum atoms. It appears that the silica tetrahedra do not replace the alumina tetrahedra on extraction. As the aluminum is removed, the acidity decreases. However, since decreased diffusional resistance results, there exists an optimum SiO₂/Al₂O₃ ratio for a given reaction.

The preparation of H-mordenite has been studied by several investigators in order to find optimum activation conditions. Maile and Weisz found that treatment with O₂ or H₂ at 1000°F enhances the activity (13). Gray and Cobb found that maximum activity was produced by calcination at 510°C (14). These authors also studied the effect of the degree of ion exchange of Group VIII metals. They found that activity...
Figure 3
CROSS-SECTIONAL VIEW OF MORDENITE

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increases rapidly above 80% exchange.

The nature of the metallic component of Pd-H-Mordenite was examined by Chick, et al. (2). They found that small metal crystallites uniformly distributed are best. In H-mordenite, .5 wt% Pd gives about one Pd atom per 180 Å of pore length. This level appeared to be optimum. Braun, et al., sintered a Pt-H-M catalyst which simultaneously increased the mean particle size of the metal and decreased the specific metal surface area (15). They found that the activity per unit surface area passed through a maximum at about 100 Å metal particle size. This supports the idea of a "structure sensitive" reaction being dependent on metal particle size.

**Isomerization Reactions**

Although the exact nature of the zeolite surface and the effects of crystallographic and physicochemical variables on reaction kinetics are somewhat unresolved, several aspects have been studied. It has been shown that both Lewis and Bronsted acid sites must be present and that optimum activity results when there are an equal number of these sites (16). Lewis acid sites are electron pair acceptors associated with the Al atoms of the faujasite. Bronsted acid sites are proton donors such as H atoms which are incorporated into the catalyst by ion exchange described in the next section. In addition, it has been found that increasing reduction temperature of decationized zeolite causes the Bronsted sites to go through a maximum while the Lewis sites begin to increase about 500°C (9). These independent results could explain why the activity of faujasite goes through a maximum with respect to reduction temperature. In addition, there is such a large degree of cooperation between the acidic and metallic sites that the activity
reaches a point of diminishing returns after a certain metal concentration is reached (16). The performance of the catalyst is highly dependent on the ratio of acidic to metallic sites and on the efficiency of each (17). The metallic sites, by their hydrogenation function, serve to keep the acidic sites free of coke precursors (16).

Specific studies on catalysts similar to those used in this study will be reviewed next.

**Faujasite**

Faujasite catalysts in the monovalent cationic form have no activity in carbonium ion reactions (3). It is necessary to modify the faujasite by ion exchange with NH$_4^+$ or Ca$^{+2}$, for example. If NH$_4$ is used and the NH$_3$ is driven off by heating, the "hydrogen", H$^-$, or decationized faujasite is left. This form is active for isomerization reactions.

For isomerization, the incorporation of 0.5–2.0 wt% Group VIII metals in the monovalent form of faujasite results in a catalyst active for hydrogenation but not for isomerization (3).

It is apparent then that a dual function faujasite catalyst, one with both metallic and acidic sites, would be active for isomerization in addition to having the stability offered by the metallic sites. The metallic sites not only aid in isomerization but are thought to hydrogenate coke precursors keeping the surface active longer.

Minachev has studied the contributions of the metallic and acidic sites on Pt-Ca-X and Pt-Ca-Y at 280 - 350°C, 30 atm (3). He examined the effect of Pt concentration while maintaining a constant acidic function. The isomerization rate of cyclohexane increased with Pt concentration.
until above .5 wt% Pt, the rate did not change with metal content. This implies that at above .5 wt%, this particular reaction is limited by rearrangement occurring on the acidic sites. Further evidence was obtained as follows. By isomorphic replacement of Al by Si atoms in .5 wt% Pd-X, i.e. changing Pd-X toward Pd-Y by increasing the SiO2/Al2O3 ratio from 2.5 to 4.8, it was observed that the activity for n-C6 isomerization increased substantially. Increasing SiO2/Al2O3 ratio corresponded to increasing acidity. This result thus indicated that the acidic site isomerization of the intermediate olefin is rate limiting at these conditions. Comparing X and Y forms, it was found that if the two have the same crystal lattice and metal content, the hydrogenating activity was the same, as judged by the hydrogenation of C2H5. However, the hydrogenation activity was highly dependent on the metal chosen. Pt was more active than Pd. Both Pt and Pd were more active than Ni.

Topchieva, et al., have investigated the isomerization of n-C6 on Ca-H-Y at 250-350°C, 30 kg/cm², and H2/n-C6 molar ratio of 3.5 (18). They found that the maximum yield of hexane isomers occurred at 330-340°C, corresponding to 93% of equilibrium. At higher temperatures, cracking became significant while at lower temperatures the yield was lower due to slower reaction rate. As the yield increased, the monomethyl isomer concentration, 2- and 3- methyl pentane (2MP, 3MP), decreased while the dimethyl isomers, 2, 2 and 2, 3 dimethylbutane (2,2 DMB, 2,3 DMB) increased. This indicates that secondary isomerization from mono to dimethyl products on the acidic sites increases with conversion. Further increases in reaction temperature beyond 330-340°C caused the intermediates to crack, and then hydrogenate, rather than hydrogenate as C6 isomers. The authors noted that as the total pressure was decreased at a fixed
H₂/n-C₆ ratio, the cracking rate increased. This may be due to decreasing hydrogen partial pressure and hence surface hydrogen concentration which favored the further reaction (cracking) of the olefin intermediate. The authors also found that at 30 kg/cm², 220°C, and 1 hr⁻¹ space velocity, no decrease in activity was found for a period of 2500 hr.

Yegiazarov, et al., looked at Pd-H-Y at 310°-390°C, 30 atm, and H₂/n-C₅ of 3/1 (19). Their catalyst had 18-20 wt% binders used as mechanical support for the catalyst. They found that HCl leaching of the catalyst increased n-C₅ isomerization activity up to 4.8 hours treatment time. They postulated that further leaching hindered the yield by retarding desorption of the olefin intermediate from strong acid sites that were created. This retarded desorption apparently led to increased cracking rates which the authors observed at severe leaching conditions. This paralleled the results of Topchieva discussed earlier (18). Yegiazarov also found that increasing the space velocity increased the product selectivity (isomerized versus cracked products) but reduced overall yield.

Garanin, et al., have studied n-C₅ isomerization on .5 wt% Pd-Ca-Y at 300°-360°C, 1 to 50 atm, 1 hr⁻¹, and 3.2/1 H₂/n-C₅ (20). They found a maximum i-C₅ yield at 360°C and 10-20 atm, corresponding to 90% of equilibrium yield or 57 mole % i-C₅. Above 360°C, hydrocracking began, although hydrocracked products were less than 2 mole %. At each reaction temperature the i-C₅ yield passed through a maximum at 5-15 atm total pressure and then decreased slowly. The author states that as the total pressure is changed, Pₙ-C₅, Pₖ₂, and the contact time all change. Additional experiments to determine the effect of these three factors separately showed that the isomerization rate, g-mole /g catalyst/hr, passed through a sharp maximum with respect to Pₖ₂ at ~ 3 atm at constant
while the rate asymptotically approached a limiting value with respect to $P_{C5}$ at $\sim 8$ atm at constant $P_{H2}$. Up to 6 atm, the rate was linear with $P_{C5}$, indicating first order kinetics, with zero order kinetics above 6 atm. The authors stated that the initial low rate at low $P_{H2}$ is due to coke deposition on the catalyst surface. Above 3 atm, the hydrogen diluted the $n$-$C5$ feed lowering its concentration and thus the overall rate. These results are consistent with the generally accepted mechanism of isomerization on a dual functional catalyst. This mechanism involves rapid dehydrogenation of the paraffin on the metallic site, rate-limiting isomerization on the acidic site followed by hydrogenation of the iso-olefin. Thus, the equilibrium olefin concentration and hence the overall rate depends on the initial partial pressures of the hydrogen and hydrocarbon. The authors show that their reaction rate is linear with $P_{C5}/P_{H2}$ over the range .1 $-$ .3, in agreement with the assumed mechanism and the rate law $r = k \frac{P_{C5}}{P_{C6}}$. It is also important to note that the authors found no variation in rate with catalyst particle size in the range of 1 $-$ 4 mm which implies that gas to particle mass transfer is not rate-affecting.

An interesting study by Bolton and Lanewala questions the traditional concept of the olefin intermediate in hydrocarbon isomerization (4). Noting the close similarity in the initial products in the isomerization of $n$-$C6$ and the hydrogenolysis of methylcyclopentane (MCP), they propose a cyclic intermediate in the isomerization reaction. Using a .5 wt\% Pd-Y catalyst at 285$^\circ$C, 500 psig, $H2$/hydrocarbon ratio of 5-20/1, and 2-90 hr$^{-1}$, they found that cracking always accompanied isomerization of $n$-$C6$, with typical cracked product concentration of .04 - 2.0%. By using each of the 5 hexane isomers as initial feed materials and carrying out
the reactions at differential conversion levels, the authors studied the reaction paths of each intermediate in the conversion of n-C\textsubscript{6}. They postulate the following reaction scheme based on their results:

![Reaction Scheme Diagram]

This scheme differs from the generally accepted bifunctional mechanism due to the direct formation of 2, 3 DMB from n-C\textsubscript{6}, the formation of 2 MP from 2, 2 DMB and the absence of n-C\textsubscript{6} from the primary products of 2 MP. A simple molecular rearrangement of a carbonium ion intermediate does not explain these results. A cyclic reaction mechanism proposed by Barron, et al.,\cite{Barron21} involving an MCP intermediate is unsatisfactory since it does not allow for the direct formation of 2, 3 DMB from n-C\textsubscript{6}. Since cracking accompanied each reaction, the mechanism must account for cracking as well as isomerization. Based on their results, the authors propose that isomerization and cracking proceed through a common surface transition state involving adjacently adsorbed hexane molecules. The thermodynamically favored six member ring is formed involving two hexane molecules. From this configuration, it is shown that the all experimental results can be accounted for, including cracking and isomerization reaction products. This is consistent with the results of Anderson \cite{Anderson22} who found that hydrocracking and isomerization occurring on Pt and Pd films have the same activation energy. Bolton and Lanewala conclude by
stating that further analysis of the hydrocracked products is needed to verify their proposal.

Weeks, et al., in studying the labeled n-C₅(3-C¹³) reactions on .42 wt% Pd-H-Y at 325°C concluded that hydroisomerization occurs as a single reaction sequence rather than from repeated contact with the surface. In the absence of H₂, it has been shown that isomerization proceeds both through intra and intermolecular rearrangement (24). However, hydroisomerization was found to be entirely intramolecular. In studies carried out to determine the effect of H₂ on the mechanism, it was found that hydroisomerization products differed substantially from simple isomerized products. The authors conclude that a random distribution of product resulting from isomerization may be explained by a cyclopentyl intermediate while one additional pathway occurs in hydroisomerization, resulting in a more ordered product distribution.

Saito and Iwasaki studied n-C₅ hydroisomerization at 270-330°C, 1 to 50 atm on .05 - 1.0 wt% Pt-H-Y (8). They examined the effect of Pt content and reaction conditions. They found that below .3 wt% Pt, the rate was limited by dehydrogenation of n-C₅ or hydrogenation of iso-C₅ whereas above .3 wt%, rearrangement on the acidic site was limiting. They postulate that this rearrangement occurs on active Pt sites which are kinetically influenced by adjacent protonic acid sites. Further, they feel that hydrocracking, which accompanies the isomerization reaction, takes place on different active sites. They thus conclude that due to molecular influence, there is a varying degree of cooperation between the metallic and acidic components resulting in different types of active sites some of which seem to preferentially promote isomerization or cracking. Based on their results, they propose the following scheme for hydroisomeri-
Mordenite

Mordenite has the highest SiO$_2$/Al$_2$O$_3$ ratio of any zeolite, 10/1, and it may be expected that a higher acid catalytic activity would result. Experiments have shown that mordenite is the most active catalyst discovered so far for isomerization of saturated hydrocarbons (3). In addition, mordenite will hydrogenate benzene at 250°C and 30 atm completely even without Group VIII metals (3). It will not dehydrogenate cyclohexane (25).

The former study also showed that as the Na$^+$ ion concentration was decreased on decationization, the hydrogenation activity decreased, implying that the Na$^+$ may have some hydrogenation activity in mordenite(3). Group VIII metals are not necessary for paraffin isomerization on H-mordenite (H-M) and their presence has been reported to have no effect (3) or to only increase activity slightly (2).

Minachev, et al., have studied isomerization and hydrogenation activity of H-mordenite. They state that since the first step in isomerization on both bifunctional and metal zeolite catalysts is dehydrogenation as reported by others (26, 27), and since isomerization on H-M does not require a metal, another type of mechanism is indicated. They postulate that isomerization occurs without a dehydrogenation step.
Specifically, for $n$-$C_5$ isomerization

$$n-C_5H_{12} + H-M \xrightleftharpoons{k_1} n-C_5 H_{11}-M + H_2 \quad (1)$$

$$n-C_5 H_{11}-M \xrightleftharpoons{k_2} i-C_5 H_{11}-M \quad (2)$$

$$i-C_5 H_{11}-M + H_2 \xrightleftharpoons{k_3} i-C_5 H_{12} + H-M. \quad (3)$$

If (2) is rate determining, the authors show that the rate is represented by

$$R = \frac{g\text{-mole}}{g\text{-cat-hr}} = \frac{k_2 K_1}{1 + K_1} \frac{P_{n-C_5}}{P_{H_2}^0} - \frac{k_2}{K_3} \frac{P_{i-C_5}}{P_{H_2}^0}$$

where $K_i$ is the equilibrium constant for reaction $i$. This rate expression implies that the dependence of the rate on $P_{H_2}^0/P_{n-C_5}$ takes the form of a Langmuir isotherm. Experimental results agreed with this model.

They also studied the activity of other cationic forms of mordenite, namely Li, Na, Mg, Ca, Cd, and Al. They found that H-M had much higher activity, as measured by cyclohexane isomerization, than any other form. This may have been due to reduction of the effective pore diameter due to the size of the cations with respect to the H form.
Chick, et al., investigated deactivation of 12.5/1 SiO₂/Al₂O₃ H-M during n-C₆ isomerization at 250°C, and P_H₂ of 1 atm (2), varying amounts of Pd from .106 - 1.47 wt%. Earlier qualitative results had shown that metal free H-M deactivates rapidly whereas high P_H₂ or the addition of a noble metal stabilizes the catalyst (28-33). Noble metal addition was also known to decrease cracking activity (32,34,35). The author's experimental results showed that on metal free H-M, the rate of cracking was initially high but decreased rapidly. Increasing the Pd content in stages to .7 wt% caused the cracking rate to decrease and the isomerization rate to increase. It was noted that above .1 wt% Pd, no olefins were formed although significant C₃ was present below .1 wt%. This reflects the hydrogenation activity of the Pd. The authors found that the deactivation behavior for both cracking and isomerization could be represented by

\[
R = R₀ \exp (-A_j t)
\]

where
\[
R = \text{reaction rate (for cracking, } j=c; \text{ for isomerization, } j=i) \\
R₀ = \text{initial reaction rate} \\
t = \text{time on stream} \\
A_j = \text{deactivation time constant}
\]

Thus, deactivation during both reactions could be compared using A_j.

A_c and A_i both decreased rapidly up to .5 - .6 wt% Pd and changed little thereafter with Pd content. The overall deactivation rate increased rapidly with cracking rate and the associated deposition of coke on the catalyst. The addition of Pd resulted in a sharp decrease in cracking rate and thus deactivation. Thus, cracking rate was directly related to deactivation rate. The authors stated that this was
due to polymerization of olefinic products resulting in coke. This coke blocked the pores of the catalyst and inhibited activity. By contrast, the relatively slower deactivation observed in isomerization was attributed to slow poisoning of the active sites. The authors propose that since the isomerization rate increases with Pd content and the cracking rate decreases, isomerization proceeds independently but parallel to cracking. Cracking normally produces a small quantity of coke or coke precursors which are not hydrogenated at the Pd sites. By acting to reduce the cracking rate, the Pd sites thus stabilize the catalyst. The stability given by Pd is thus the result of a reduction of cracking rate rather than direct hydrogenation of coke or coke precursors or the establishment of more favorable olefin-paraffin carbonium ion ratios. Paraffin reaction is thought to begin with hydride abstraction at a Lewis acid site or protonation at strong acid sites, perhaps adjacent to Lewis acid sites. The authors postulate that suppression of cracking and deactivation by the addition of Pd may result from a reduction in the number or strength of these sites. Suppression of cracking may also result from a reduction in carbonium ion lifetime associated with a greater reactivity of hydrogen in the presence of Pd. This is not simply an occupation of the acidic sites by Pd since increased $\text{H}_2/n-\text{C}_5$ ratios led to reduced cracking rates and increased isomerization rates. While the authors do not rule out the generally accepted bifunctional mechanism, they suggest that deactivation is a direct result of cracking, i.e., the addition of Pd reduces the deactivation rate by reducing cracking rate rather than by hydrogenation of coke or coke precursors. Thus, Pd greatly influences the surface acid properties and may be used to alter the catalyst selectivity.
The effect of surface acidity as influenced by SiO$_2$/Al$_2$O$_3$ ratio has been investigated. It has been shown by Beecher and Voorhies that acid extracted H-M with a SiO$_2$/Al$_2$O$_3$ of 64/1 has increased activity for cracking of cumene and hydrocracking of n-C$_{10}$ and decalin (36). Weller and Bauer showed that n-C$_6$ cracking activity increased with SiO$_2$/Al$_2$O$_3$ up to 17.5/1 (66). However, Kranich has reported that at high ratios, the removal of aluminum resulted in a loss of cumene cracking activity (37). Voorhies, et al., investigated the effect of SiO$_2$/Al$_2$O$_3$ ratio on the properties of mordenite by studying the hydroisomerization of n-C$_5$ as well as physical and adsorption characteristics of the modified catalysts (38). They found that the unit cell of a 66/1 H-M was smaller than for a 12/1 catalyst. This may be expected due to the shorter Si-O bond length. Their results show that acidity is the dominant factor in determining n-C$_5$ hydroisomerization activity. The authors were able to correlate acidity, as measured by NH$_3$ adsorption, with isomerization activity. While the changes in pore structure associated with increased acidity had no effect on n-C$_5$ isomerization, it was proposed that the smaller pores may inhibit the reaction of a larger molecule. Related work by Voorhies and Beecher (36) on cyclohexane and n-C$_5$ hydroisomerization showed that the isomerization activity initially increased and then decreased with SiO$_2$/Al$_2$O$_3$ ratio. This maximum of activity may be related to a reduction in acid sites with a reduction in alumina content for acid extracted mordenites. Though no intraparticle diffusion limitations were noted on the standard 10.8/1 mordenite, the activation energy for cyclohexane decreased with increasing SiO$_2$/Al$_2$O$_3$ ratio. This may have been due to possible intrapore structural or chemical changes, noted earlier (37) on a similar catalyst, which caused mass transfer resistance. It has been noted that the
interaction of surface acidity and pore accessibility may account for conflicting reports on the effect of alumina deficiency on catalytic activity (37). The authors were able to represent their rate constant with a Langmuir-Hinshelwood dual site adsorption model.

Lopez, et al., studied cracking and isomerization of n-C6 on H-M and .6 wt% Pt-H-M at 250 and 400°C (39). At 400°C on H-M, no isomerization was observed and the selectivity was that which was predicted from the classical dual function theory with adsorption-desorption as the rate determining step. At 250°C on H-M, isomerization and cracking rates were approximately equal. No olefins were observed at 250°C while substantial olefins were present at 400°C. On Pt-H-M, isomerization and cracking occurred at both temperatures indicating that the rate controlling step was isomerization and β-scission of the intermediate carbonium ion. They propose the following reaction scheme for n-C6 cracking and isomerization of n-C6:

\[
\begin{align*}
n\text{-C}_6 & \rightarrow \text{i-C}_6 \quad \text{n-C}_6 \\
n\text{-C}_6 & \rightarrow \text{i-C}_6 \\
n\text{-C}_6 & \rightarrow \text{i-C}_6 \\
\text{n-C}_6 & \rightarrow \text{i-C}_6
\end{align*}
\]

where \(1 \leq x \leq 4\).

The authors conclude that the classical carbonium ion mechanism is consistent with results on both catalysts. At 400°C, the formation and desorption of carbonium ions is rate determining. Isomerization does not
occur since it is slow relative to scission. Decreasing the temperature or adding Pt improves the adsorption and desorption rate of the intermediate and favors isomerization over cracking.

Comparison of Mordenite and Faujasite

Several studies comparing the activity and properties of mordenite and faujasite catalysts have been carried out. Gray and Cobb state that the active sites of mordenite are similar to their faujasite counterparts (40). Despite similarities, each has its own peculiarities. For example, steric effects are more pronounced on mordenite since it has a smaller pore size than type Y (25,41,42,43). Addition of a noble metal does not increase n-C5 isomerization activity on H-M as it does on H-Y (25,33,35,43-45). Fetting and Schoeneberger examined the influence of structural parameters of H-M and Ca-Y on the activity and selectivity in n-C5 and n-C6 hydroisomerization (15). The H-M was found to have 7-8 Å primary and 10,000 Å secondary pore diameters while Ca-Y had 9 Å and 4000 Å diameters respectively. These properties were found to be unaltered after metal loading. The authors defined activity as the temperature dependence of the conversion and selectivity as the fraction of isomers of the total conversion. Various cations; Re, Ni, Ru, Rh, Pd, Pt, were selected to determine the effect of the metal type on activity and selectivity. Pd and Pt had the highest isomerization selectivity while Re had the highest activity. Ru, Rh, and Ni had high initial hydrogenating activity but also had high deactivation rates. Pt-H-M had a higher n-C6 isomerization activity than Pd-H-M while this order of metal influence was reversed on Ca-Y. Ni-H-M was found to be active for cracking as was Ni-Ca-Y. However, on Ni-Ca-Y, the major product was CH4 while on
Ni-H-M, C₃ and C₄ isomers were the main products. This agrees with the results of Boudart (46), and may reflect the higher acidity of H-M associated with its higher SiO₂/Al₂O₃ ratio. In examining the effect of catalyst type at the same metal loading, Fetting and Schoeneberger found that Pt-H-M had an activity and selectivity at 523-583°K that Pt-Ca-Y did not exhibit until 613-693°K. This was true for both n-C₅ and n-C₆ isomerization.

The authors suggested that this was due to a secondary pore resistance i.e., that associated with the spaces between zeolite crystals, on Pt-Ca-Y. The effectiveness factor was found to decrease with catalyst particle size resulting in a decrease in apparent activation energy from 97 to 67 kJ/g-mole. The authors found that Pt-H-M had a higher activity at low temperatures than did Pt-Ca-Y.
Experimental Procedure

The equipment described is located in the Petroleum Processing Laboratory of the Chemical Engineering Department of Louisiana State University in Baton Rouge. The equipment was obtained primarily through donation of apparatus or funds by Exxon Research and Development Labs in Baton Rouge. The .5% Pd-H-M catalyst used in this study, batch LJJ-289, as well as the .5% Pd-H-Y, a physical mixture of two identically prepared batches HJE-243 and HJE-244, were provided by Exxon Labs.

A schematic flow diagram of the equipment is shown in Figure 4. With the exception of the hydrocarbon feed pumps, gas cylinders, and control panel board, the equipment was located in a walk-in hood with a 3000 CFM exhaust fan and sliding safety glass window. The gas cylinders, containing high purity electrolytic hydrogen, were located remotely from the laboratory.

The hydrogen was fed through a Pd-Al2O3 catalyst bed maintained at 350°F by thermostatic control to convert any O2 in the stream to H2O. The water was subsequently removed in beds containing 3A molecular sieves and indicating Drierite desiccant.

Hydrogen flow was regulated by a Foxboro flow control valve coupled with an indicating flow controller located on the panel. A Foxboro DP cell equipped with a .006-in. integral orifice was used to measure the H2 flow and provide an input signal to the flow controller. A Matheson pressure regulator assured a relatively constant hydrogen supply pressure immediately upstream of the control valve. A Mity-Mite back pressure regulator provided a constant pressure downstream of the orifice.
Figure 4. Simplified Flow Plan.
Three hydrocarbon feed pumps were used to feed n-C5, n-C6, and mixtures to the reactor. The n-C5 and n-C6 were Phillips reagent grade (99+ mole % minimum) materials. Gas chromatographic analysis confirmed their purity. The feed pumps were positive displacement Ruska pumps, each having a 250 cc capacity. The feed rate could be varied from 2 to 240 cc/hr by changing gears in the drive system. The motors for these pumps were explosion proof.

The reactor was a fixed bed tublar type. Figure 5 shows a detailed cross section of the reactor with catalyst in place. The reactor is made of ½-in. sch 80 Inconel pipe with a 40 cc capacity. The catalyst was physically mixed with inert mullite to avoid hot spots in the catalyst bed by enhancing heat transfer. The volume of the catalyst plus mullite charges was 10 cc. This charge was located between glass wool plugs which filled the remaining reactor volume. A single iron constantan thermocouple located in the middle of the catalyst charge was used to monitor the reaction temperature. The reactor was sealed using a replaceable steel O-ring held in place by a temperature compensating coupling.

An air-fluidized sand bath, heated by six 500 watt strip heaters surrounding the submerged reactor was used to control the reaction temperature. The air fluidizing rate was controlled by a rotameter. Three of the strip heaters were controlled manually by a Variac rheostat while the remaining three were controlled automatically by a Eurotherm temperature controller. Both the Variac and Eurotherm controls were located on the panel. The sandbath temperature was monitored by an iron-constantan thermocouple, which provided input to the Eurotherm controller,
Figure 5. Reactor System in the Sand Bath Vessel.
located in a top-entering thermowell. The reactor, sandbath, and other routinely monitored temperatures were displayed on a Doric digital temperature indicator located on the panel. A West Guardsman temperature safety device located on the panel shut off hydrogen and hydrocarbon flows and sandbath heat in the event of an unsafe reactor temperature.

The hydrocarbon liquid feed was mixed with the hydrogen, fully vaporized, and brought to the reactor temperature by passing through a coiled length of tubing submersed in the sandbath. The reactor pressure was set and controlled by a Mity-Mite back pressure regulator downstream of the reactor. Pressure gauges 0-1000 psig, were located at the reactor inlet and exit to monitor reactor pressure. Mercoid pressure switches for shutting off hydrogen and hydrocarbon feeds as well as sandbath heat in the event of excessively low/high air supply pressure or low/high reactor pressure were located in the hood. The reactor was also protected by a 1000 psig pressure relief valve.

Since the dew point of the reactor effluent gas was well below ambient temperature, the product gas was measured and sampled as follows. The effluent was passed through a counterflow fixed bed Rashig ring water saturator and then through a .05 ft/rev. wet test meter. The gas was then vented through the exhaust fan to the atmosphere. The gas was sampled for GC analysis through a septum located between the reactor outlet and the water saturator. Glass syringes used to extract samples were Teflon sealed and gas tight. The reactor effluent gas was analyzed on a dual column Perkin-Elmer model 990 gas chromatograph equipped with hot wire detectors. The column was 10 foot by 1/4-inch aluminum tubing packed with 20% Ucon HB-280X on 60/80 Chromasorb W.
of the peaks was carried out on a Varian CDS III integrator and recorded on a Varian 9176 recorder. Proportionality constants relating peak areas to mole fractions were obtained from a previous study (33) and confirmed in this study. These factors are shown in Appendix 1.

Catalyst Preparation

The catalyst used in this study was prepared for use in the isomerization studies as follows:

1. About 100 cc of the catalyst was placed in a quartz glass open container which was then placed in a 2-inch O.D. glass tube. This glass tube lay inside a horizontal electric oven with both ends extending past the ends of the furnace.

2. An iron-constantan thermocouple was inserted through one end of the glass tube and rested in the catalyst charge to measure its temperature.

3. Air flow over the catalyst was begun as soon as heating started. The air served to remove moisture from the calcining catalyst. The air was treated to remove any traces of hydrocarbons by passing it through a copper oxide catalyst bed at 1000°F. The air was then dried by passing through 13 X molecular sieves and indicating Drierite before entering the oven. The air flow rate was controlled by a rotameter.

4. The temperature of the oven was programmed as follows:
   a. Increase from ambient to 350°F at a maximum rate of 100°F/hr.
b. Maintain at 350°F for 16 hours.
c. Increase from 350°F to 1000°F at a maximum rate of 125°F/hr.
d. Maintain at 1000°F for 3 hours.
e. Cool to 350°F as rapidly as practical.

5. The temperature was monitored by a Doric digital temperature indicator. The hot calcined catalyst was placed in a desiccator to cool to ambient temperature. The catalyst was stored in the desiccator until needed.

6. Inert mullite used to dilute the catalyst charges was calcined in an open ceramic dish in a muffle furnace at 1000°F for 24 hours. The calcined mullite was cooled to 350°F at ambient conditions and stored in a desiccator for later use.

Catalyst Loading

The catalyst was weighed with a Mettler analytical balance and mixed with sufficient mullite to make 10 cc volume. The reactor was charged with a section of glass wool and then the catalyst mixture was placed in the reactor. A second section of glass wool was inserted behind the catalyst charge. The reactor was sealed using a temperature compensating coupling and a steel O-ring coated with copper based anti-seize compound. The reactor was pressure tested with hydrogen at a pressure at least 50% higher than the run pressure. It was then depressurized, placed in the sandbath, and connected to the feed and product lines. The reactor was then checked at the run pressure for any leaks in the connecting lines. The sandbath was then heated rapidly to 465°F.
with hydrogen flowing through the reactor. This activation of the catalyst was carried out for 1/2 hour to reduce the noble metal imregnated in the catalyst.

**Run Procedure**

The runs were carried out as follows:

1. The hydrogen flow rate was set on the automatic flow controller.

2. After about 15 minutes for equilibration, the flow rate was measured on the wet test meter and recorded.

3. Pure pentane was fed to the reactor using a positive displacement pump. Mixtures of pentane and hexane were fed from a second pump. These mixtures were prepared using volumetric flasks and pipettes. Pure hexane was fed from a third pump.

4. The runs were made in the following order; pure pentane, mixtures, pure hexane, then a repeat pure pentane run to determine if there had been any catalyst deactivation. None was found in any run on either catalyst.

5. For each run, a material balance was made after 3/4 to 1 hour on feed. This was done by noting the hydrocarbon feed rate, reactor effluent flow rate, and reactor effluent composition. The material balance procedure is outlined in Appendix 1.

6. Gas samples were taken after the 3/4 to 1 hour equilibration period and analyzed on the gas chromatograph.

7. After obtaining the material balance and samples, the hydrocarbon feed was stopped. The hydrogen flow rate was
allowed to return to the set conditions and re-checked.

Run Data

Data necessary for the material balance and rate constant calculation is shown below:

1. Barometric pressure was measured using a mercury barometer. The room temperature was measured using a thermometer.

2. Elapsed time for a .05 ft³ revolution of the wet test meter along with the wet test meter water temperature were measured at the beginning, during, and end of each run.

3. For the material balance, the wet test meter reading and temperature and the displaced volume of the Ruska positive displacement pumps were taken both at the beginning and end of each run.

4. For each reactor effluent sample, the reactor, sandbath, and wet test meter temperatures along with the reactor pressure and time for a .05 ft³ revolution were taken. The corresponding time on feed was also noted.

5. For each gas sample, the concentrations were calculated automatically and recorded.
Kinetic Model

It is of primary interest in this study to develop a kinetic model for both catalysts. Such models can be used not only to compare the two catalysts but to predict performance as a function of feed concentrations and reaction conditions.

There are basically two types of kinetic models. A theoretical model may be derived directly from a postulated mechanism. By assuming certain steps to be rate controlling, various forms of the rate expression may be obtained and checked experimentally. In order to formulate a theoretical model, a complete reaction mechanism must be postulated. Once verified, a theoretical model may be used to extrapolate to conditions beyond experimental data. In addition, valuable insight into a given reaction can often lead to more general applications of the findings in related reaction studies. However, there are limits to the use of theoretical models. Complete mechanisms are known with certainty for few reactions. Also, there are often so many parameters to be found that they cannot be determined with acceptable accuracy. Empirical models are those which use experimental data together with simplified forms of the theoretical model to extract a rate expression. Such models are valuable in that they are soundly based on experimental data. However, extrapolation beyond the range of the data is generally not valid.

In this study, theoretical models will be developed to determine the form of the rate expression. Certain groups of parameters will be lumped and simplifying assumptions made in order to make statistical analysis of the data tractable and
determination of the lumped parameters valid.

In this section, the theoretical basis of the kinetic model for the hydroisomerization of n-C₅ and n-C₆ will be developed. Simplifying assumptions will be made to arrive at a final model. Methods of statistical analysis of the data will be discussed.

Heterogeneous reactions have been described by Langmuir-Hinshelwood equations and are presented by Hougen and Watson (47). The phenomena of solid-gas reactions may be described by the following steps:

1. Mass transfer of reactants from the bulk gas phase to the exterior surface of the catalyst bed.
2. Diffusion of the reactants from the catalyst surface through the pores.
3. Adsorption of reactants on active catalyst sites.
4. Surface reaction on the active sites.
5. Diffusion of products to the exterior surface of the catalyst.
6. Mass transfer of the products to the bulk gas phase.

Any of these six steps could conceivably be rate determining. It is necessary to examine the effects of internal and external mass transport to determine their effect on the observed reaction rate. In addition, it is necessary to examine several other phenomena which are vital in the formulation of the kinetic model: the degree of isothermality along the catalyst bed, the fugacity coefficients of the reactants and products, and the nature of the flow in the reaction zone.
**Internal Mass Transport**

Since essentially all the reaction on the catalyst takes place within the catalyst particle, the reactants must diffuse into the particle and products must diffuse out. This mass transport occurs as the result of a concentration gradient between the bulk fluid phase and the interior of the catalyst. A gradient must exist for diffusion to occur. If the diffusion rate for the reactant and product species is very high compared to the surface reaction rate, then whenever even a small gradient occurs in the catalyst particle, diffusion of that species is rapid and the concentration within the catalyst is essentially constant. This is the case when surface reaction is rate controlling. If the diffusion rate is slow compared to the reaction rate, diffusion is rate controlling. Since the concentration at the interior catalyst surface is lower when diffusion is rate controlling, for first and higher order reactions a diffusion controlled rate will be lower than a surface controlled rate.

The catalyst effectiveness factor, $E$, is defined as the ratio of the actual overall reaction rate to the rate that would be observed if the reactant concentration in the entire catalyst were the same as the concentration at the catalyst surface. This effectiveness factor can be shown to be a function of a group of catalyst and kinetic parameters known as the Thiele modulus, $h_s$. For spherical particles, in which the simple reaction $A\rightarrow B$ is proceeding, as shown by Petersen (48),

$$h_s = R \frac{\rho S k_o}{D_e}$$

(1)
where \( \rho_p \) = catalyst density, g/cc  
\( R \) = catalyst particle radius, cm  
\( S_g \) = specific surface area, cm\(^2\)/g  
\( k_o \) = surface reaction rate constant, cm/sec  
\( D_e \) = effective diffusivity of reactant, cm\(^2\)/sec  

In order to investigate the effective diffusivity coefficient, the controlling diffusion regime must be defined. Diffusion within the catalyst pore usually occurs by either Fickian or Knudsen diffusion. Fickian diffusion is the predominant mechanism accounting for mass transfer in the catalyst when the pore diameter is much larger than the mean free path of the diffusing gas. In other words, Fickian diffusion is important when a given gas molecule collides with other gas molecules much more often than with the pore wall. Fickian diffusivities are of the order of \( 10^{-2} \) cm\(^2\)/sec. When the diameter of the pore is of the same order as the mean free path, collisions with the wall become important and Knudsen diffusion predominates. Knudsen diffusivities are of the order of \( 10^{-3} \rightarrow 10^{-4} \) cm\(^2\)/sec. When the diameter of the diffusing molecule approaches the pore diameter, a third form of diffusion may occur, configurational diffusion (49). In this regime, the size and shape of the diffusing molecules and the pores affect diffusion. Diffusivities in this regime are of the order of \( 10^{-5} \) cm\(^2\)/sec.

Spry and Sawyer (50) studied the configurational diffusion effects of large asphaltene molecules with molecule diameters, MD, of 25 to 100 Å in hydrotreating catalysts with pore diameters, PD, from 25 to over 1000 Å. They found that the molecular diffusivity could be multiplied by a correction factor accounting for the ratio MD/PD to yield a configurational diffusivity as follows,
\[ D_C = D_m \left(1 - \frac{MD}{PD}\right)^4 \]  

(2)

where \( D_C \) = configurational diffusivity

\( D_m \) = molecular or bulk diffusivity.

The results of Spry and Sawyer show that configurational diffusion becomes important when \( MD/PD \) is more than 0.1. Since the pores of the mordenite and faujalite catalysts used in this study are of the order of \( 6 \times 10^8 \) and the molecular diameters of \( n-C^5 \) and \( n-C^6 \) are \( \sim 5 \AA \), significant configurational diffusion resistance may be expected. To study this phenomenon, catalysts of various sized pores could be used at the same reaction conditions. Such catalysts have not been available. Thus, the effects of this diffusion were included in the overall rate expression. This procedure has been followed by others such as Voorhies and Hopper (63) and Braun, et al., (15).

To determine the effect of internal diffusion resistance, both molecular and Knudsen, a Thiele modulus can be calculated and correlated, as shown by Petersen (48), with the effectiveness factor. An effectiveness factor of 1.0 corresponds to insignificant diffusion resistance.

First, the diffusion regime in which the catalyst operates under conditions of this study, must be determined. Petersen states that the mean free path, \( \lambda \), must be compared to the pore diameter, \( D \). For \( D/\lambda << 1 \), molecular diffusion predominates. When \( D/\lambda + 1 \), Knudsen diffusion becomes important. The transition between these two regimes is called the slip region. A "slip" diffusivity, \( D_s \), can be calculated from the Knudsen and molecular diffusivities, \( D_k \) and \( D_m \), respectively, as will be shown below.

From the kinetic theory of gases, it can be shown that the mean free path is given by
\[ \lambda = \frac{kT}{\sqrt{2\pi} \sigma^2 P} \]  \hspace{1cm} (3)

where 
- \( k \) = Boltzman's constant, cm\(^2\)-atm/°K
- \( T \) = absolute temperature, °K
- \( \sigma \) = molecular diameter, cm
- \( P \) = absolute pressure, atm

The molecular diameters of the reacting species, \( n-C_5 \) and \( n-C_6 \), may be calculated from viscosity data as shown by Reid and Sherwood (64). This value represents the effective diameter of a molecule which corresponds to the hard sphere assumption upon which equation (3) is based. Reid and Sherwood list Lennard-Jones molecular radii for \( n-C_5 \) and \( n-C_6 \). Using these values, the mean free paths may be calculated at 465°F and 300 psig to be,

\[ \lambda_{C_5} = 23.0 \text{ Å} \]
\[ \lambda_{C_6} = 22.1 \text{ Å} \]

Since the pore diameters for the mordenite and faujasite catalysts used in this study are of the order of 8 Å, then by Petersen's criterion

\[ \frac{D}{\lambda_{C_5}} = \frac{D}{\lambda_{C_6}} = .36 \]

Thus, the diffusivities must be calculated based on the formula given by Bosanquet (51) for the slip region,

\[ \frac{1}{D_s} = \frac{1}{D_m} + \frac{1}{D_k} \]  \hspace{1cm} (4)
To calculate this effective diffusivity in the slip region, both the molecular and Knudsen diffusivities, \( D_m \) and \( D_K \), must be calculated. Using the equation of Wilke and Lee (52), it can be shown that at 465°F, 300 psig,

\[
D_m = 0.061 \text{ cm}^2/\text{sec} \quad \text{n-C}_5
\]

\[
D_m = 0.056 \text{ cm}^2/\text{sec} \quad \text{n-C}_6
\]

and from Peterson (48)

\[
D_k = 2.04 \times 10^{-3} \text{ cm}^2/\text{sec} \quad \text{n-C}_5
\]

\[
= 1.86 \times 10^{-3} \text{ cm}^2/\text{sec} \quad \text{n-C}_6
\]

and it can be seen that

\[
D_s = 1.97 \times 10^{-3} \quad \text{n-C}_5
\]

\[
= 1.80 \times 10^{-3} \text{ cm}^2/\text{sec} \quad \text{n-C}_6
\]

An alternate method of determining the true effective diffusivity is given by Petersen. He states that \( D_m \) must be multiplied by a geometric factor accounting for the tortuous paths of the true catalyst particle. Petersen summarizes several theoretical approaches to the problem of determining an accurate geometric factor, including electrical analogies. He states however that such methods fail in describing materials of relatively low porosity, such as a zeolite catalyst. In this case, experimental results are best. In general, the true effective diffusivity, \( D_e \), may be related to the geometric factor as shown

\[
\frac{D_e}{D_m} = \frac{\epsilon \alpha}{\tau} = f_1(\text{geometry}) \quad (5)
\]
Similarly

\[
\frac{D_e}{D_k} = \frac{\varepsilon \sigma}{\tau} = f_2(\text{geometry}) \tag{6}
\]

where \( \varepsilon \) = porosity of the catalyst

\( \sigma \) = constriction factor

\( \tau \) = totuosity factor

While there are wide ranges of results, in the worst cases, Petersen shows that \( D_e / D_m \) is approximately 0.04. In this case,

\[
D_e = 2.44 \times 10^{-3} \text{ cm}^2/\text{sec} \quad \text{n-C}_5
\]

\[
= 2.24 \times 10^{-3} \text{ cm}^2/\text{sec} \quad \text{n-C}_6
\]

Since these values approximate those calculated from Bosanquet's equation, it can be said that there is additional evidence for accepting the slip region values.

From equation (2), using the Lennard-Jones radii for n-C\(_5\) and n-C\(_6\) and the appropriate pore diameters for mordenite and faujasite, it can be shown that on the mordenite, \( D_{C_m} \mid C_5 \) = \( 4.6 \times 10^{-5} \text{ cm}^2/\text{sec} \) and \( D_{C_m} \mid C_6 \) = \( 2.9 \times 10^{-5} \text{ cm}^2/\text{sec} \) while on the faujasite \( D_{C_f} \mid C_5 \) = \( 9.7 \times 10^{-4} \text{ cm}^2/\text{sec} \) and \( D_{C_f} \mid C_6 \) = \( 7.9 \times 10^{-4} \text{ cm}^2/\text{sec} \). Using these values, it can be shown from equation (1) that on the mordenite \( h_s \mid C_5 \) = 3.3 and \( h_s \mid C_6 \) = 8.3 while on the faujasite \( h_s \mid C_5 \) = 0.72 and \( h_s \mid C_6 \) = 1.6. From Petersen (48), the effectiveness factors corresponding to these values of the Thiele modulus, \( h_s \), are

<table>
<thead>
<tr>
<th></th>
<th>Mordenite</th>
<th>Faujasite</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C(_5)</td>
<td>0.30</td>
<td>0.90</td>
</tr>
<tr>
<td>n-C(_6)</td>
<td>0.12</td>
<td>0.55</td>
</tr>
</tbody>
</table>

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Thus, configurational diffusion effects result in significant diffusion resistance. In order to study the effect of configurational diffusion, catalysts with varying pore sizes would be needed. Such catalysts have not been available and configurational diffusion resistance was not examined. The first order rate constant in this study includes configurational diffusion effects. As stated earlier, this is the procedure used by other investigators (15, 63).

To observe experimentally in this study the extent of internal mass transfer effects, the particle size of the catalyst could be decreased to decrease the resistance. If the rate constant increased with decreased particle size, internal mass transfer is important and must be accounted for. Bryant (33) and Hopper (53) observed no variation in the first order rate constant for n-C$_5$ isomerization on Pd-H-mordenite over a ten-fold change in catalyst particle size, 0.1 to 1.0 mm diameter. Since the catalyst particle size and reaction conditions in this study corresponded closely to those used by Bryant and Hopper, resistance was assumed to have an insignificant effect on the first order rate constant as defined by equations (26) and (27) and calculated from equation (15).

Flow Patterns

Another phenomenon that must be investigated is the bulk flow pattern of the reactants and products over the catalyst bed. Plug flow is desired since this results in higher conversions. Any significant backmixing would lower conversions and complicate modelling of the reaction. Bryant (33) studied the flow patterns in a reactor nearly identical to that used in this study. He related the extent of axial dispersion to the Peclet number. The Peclet number, $Pe$, is the ratio of the bulk stream flow to the random motion of eddies. A Peclet number of
zero corresponds to complete backmixing while \( \infty \) corresponds to plug flow. Bryant found that for \( Pe > 50 \) and conversions from 20\% to 70\% the effects of backmixing are negligible.

A Peclet number for typical conditions used in this study is calculated as follows. The particle Reynolds number, \( Re_p \), is found using the following relation:

\[
Re_p = \frac{d_p W}{\mu A} = 2.49
\]

where \( d_p \) = diameter of the catalyst particle, cm
\( \mu \) = viscosity of the fluid, gm/cm-sec.
\( A \) = cross sectional area, cm\(^2\)
\( w \) = mass flow rate, g/sec

Levenspiel and Bischoff have correlated a mixing intensity, \( M \), with \( Re_p \) (54). In this study

\[
M \cdot \frac{\varepsilon L}{Pe d_p} = 0.83
\]

from which a \( Pe \) of 63.2 is calculated. Since this is well above the value of 50 below which backmixing first becomes significant, plug flow is assumed in this study.

**External Mass Transport**

External mass transfer refers to the convective and diffusive processes by which reactant is transferred from the bulk gas phase to the catalyst surface and products from the surface back to the bulk phase. This process may be modelled as mass transfer through a thin gas film in laminar flow at the catalyst surface. The higher the gas flow rate across the catalyst particle, the thinner the laminar layer becomes and the...
higher the mass transfer rate. If external mass transfer were rate controlling, it would be expected that varying the gas velocity would affect the conversion.

Pure component studies have been carried out on Pd-H-mordenite at conditions nearly identical to those used in this study. Bryant (33) found no variation in the rate constant for n-C_5 isomerization at 550°F and 450 psig while varying the gas velocity by a factor of four. Luzarraga (55) showed no variation in rate constant over an eight-fold change in gas velocity. On Pd-H-faujasite, Hatcher (56) showed no change in rate constant for n-hexane hydrocracking over a factor of 3 change in gas velocity. It may be concluded that previous studies imply that there is no significant external mass transfer resistance in the catalysts and under the conditions of this study.

Temperature Gradient in the Reactor

In studying the isomerization of pentane and hexane mixtures, the model for the reaction is based either on an isothermal or non-isothermal assumption. If the heat of reaction and the reaction rate were large, there would be significant temperature gradients along the tubular reactor used in this study. If such gradients existed, the reaction rate would vary along the reactor and the model would have to account for this effect.

In this study, a thermocouple measuring the temperature at the end of the catalyst bed was monitored routinely during each run. If there had been significant heat of reaction effects, this thermocouple would have registered a temperature significantly different from the sand bath in which the reactor was located. A maximum temperature difference from the sand bath of 3°F was observed with the normal temperature difference.
within ± 1°F. Since this was well within experimental error, it was concluded that the isothermal model for the catalyst bed was adequate.

Reactant Fugacities

To formulate the model, the fugacity coefficients of each of the reactants in the reactor must be calculated. In order to calculate the fugacity coefficients of the components of the reaction, an equation of state must be selected. Since the Redlich-Kwong equation has been shown to be valid at conditions such as those involved in this study, it was used.

At constant temperature, it can be shown that (57),

\[ \ln \hat{\phi}_i = \int_v^\infty \left[ \left( \frac{3n_i Z}{3n_i V} \right) - 1 \right] \frac{dV}{V} - \ln Z \tag{8} \]

where \( \hat{\phi}_i \) = fugacity coefficient of component i in the mixture

\( V \) = molar volume of the mixture, cc/g-mole

\( Z \) = compressibility of the mixture

\( T \) = temperature, °R

\( n_i \) = moles of component j ≠ i, g-moles

\( n \) = mole of mixture, g-moles

the Redlich-Kwong equation of state is given by

\[ Z = \frac{1}{1-b/v} - \frac{a}{RT^{3/2} V(1+b/v)} \tag{9} \]

Where a and b are constants dependent on P and T but independent of composition.

Carrying out the indicated integration of equation (8) gives the result

\[ \ln \hat{\phi}_i = \frac{b_i}{b} (Z-1) - \ln(Z-Z_h) + \frac{a}{bRT^{3/2}} \left[ \frac{b_i}{b} - \frac{2}{a} \sum \limits_k Y_i a_{ik} \right] \ln(1+h) \tag{10} \]
where \( h = \frac{b}{v} \).

In order to use the above equation, certain interaction and mixture properties must be calculated as outlined by Prausnitz (58). The presence of hydrogen has a significant effect on this calculation, which is not detailed here. The results, calculated at 465°F, 300 psig, and 10/1 \( \text{H}_2/\text{HC} \) ratio, are

\[
\hat{\phi}_{\text{H}_2} = 1.00888 \\
\hat{\phi}_{\text{C}_5} = 1.00566 \\
\hat{\phi}_{\text{C}_6} = 1.00953
\]

Thus, the deviation from ideality at typical reaction conditions is <1%. The mixture will be assumed to be ideal in formulating the model.

Cracking

In studying hydroisomerization of \( \text{n-C}_5 \) and \( \text{n-C}_6 \), the extent of hydrocracking must be examined. If the extent of hydrocracking were large, it would have to be accounted for in the kinetic model. The products of hydrocracking of \( \text{n-C}_5 \) and \( \text{n-C}_6 \) would be \( \text{C}_1 \), \( \text{C}_2 \), and \( \text{C}_3 \) which are detectable even in small quantities (≥ 0.5 mole%) in the analysis of the reacting gas.

In the range of conditions used in this study, no hydrocracking was observed. Investigators using similar conditions and catalysts have not

Kinetic Model

The general Langmuir-Hinshelwood model describing reactions of gases on solid catalysts is given by:
The kinetic term includes both the true surface reaction rate constant, as well as constants characterizing the surface of the catalyst and in some cases adsorption constants. These constants may be lumped together to describe the dependence of the kinetic term on temperature as

$$k = A_o \exp \left( -\frac{E_{\text{app}}}{R T} \right)$$  \hspace{1cm} (12)

where $E_{\text{app}}$ = apparent activation energy, kcal/g-mole
$R$ = ideal gas constant, kcal/g-mole $\circ K$
$A_o$ = pre exponential term, cc/g/sec
$T$ = absolute temperature, $\circ K$.

The potential term for a first order elementary reaction $A \rightleftharpoons B$ has the form

$$\frac{K A_{PA} - K B P_B}{K}$$  \hspace{1cm} (13)

where $K_i$ = adsorption constant of species $i$, atm$^{-1}$
$P_i$ = partial pressure of species $i$, atm
$K$ = reaction equilibrium constant, dimensionless.

The adsorption term has the form

$$(1 + K A_{PA} + K B P_B)^n$$

where $n$ = number of active catalyst sites involved in the reaction.

The exponent $n$ usually has a value of 1 or 2. The exact form of the adsorption term may change depending on the rate-limiting step for a given reaction. Although this term is somewhat temperature
dependent, the exponential temperature dependence of the kinetic term makes the variation of the adsorption term with temperature relatively insignificant. However, the ratio $k' = \frac{\text{kinetic term}}{\text{adsorption term}}$ will vary depending on the nature of the catalyst, surface kinetics and the rate-determining step. Strickland (60) has developed the various forms that $k'$ can take depending on the rate controlling step for a catalyst with acidic and metallic sites for the reaction $A \not\to B$. These will be examined in discussing the statistical analysis of the data later in this chapter.

The overall rate constant expression must be developed to relate experimental results to the kinetic parameters of importance. The material balance equation for an integral reactor in plug flow is given by

$$r = \frac{dN_B}{dW} = k(C_A - C_B/K) \tag{14}$$

where $r =$ reaction rate, g-mole/gm/sec

$N_B =$ flow rate of product $B$, g-mole/sec

$W =$ weight of catalyst, gm

$k =$ first order rate constant, cc/gm/sec

$C_{A,B} =$ concentrations of $A$, $B$, g-mole/cc

$K =$ thermodynamic equilibrium constant, dimensionless.

The rate constant above, $k$, is a lumped term including both the adsorption term and the effectiveness factor.

Assuming first order kinetics, pure $A$ as feed, and fugacity coefficients of unity for all hydrocarbon species, the first order rate constant may be calculated from experimental data as shown by Livesay (65) to be,
\[ k = \frac{Y_B^i}{\rho_B t_H} \ln \left(1 - \frac{Y_B}{Y_B^i}\right) \]  

which is the integrated form of equation (14) assuming no B in the feed gas, where \( Y_B^i \) = equilibrium mole fraction of isomerized products

for \( A \neq B \)

\( t_H \) = catalyst volume/total volumetric flow rate or superficial holding time, sec.

\( Y_B \) = experimental mole fraction of isomers

\( \rho_B \) = bulk density of the catalyst, gm/cc.

The experiments are carried out to determine \( Y_B \) from analysis of the reactor effluent gas. Knowing \( t_H \) from the volumetric flow rates of reactants and products, \( \rho_B \) from measurement, and \( Y_B^i \) from literature data, it is possible to calculate \( k \) for a given set of conditions. In the case of \( n-C_5 \) and \( n-C_6 \) mixtures as feed, \( t_H \) accounts for both hydrocarbon feed rates and equation (15) is used to calculate the individual rate constants. For mixtures, the rate constant for \( n-C_5 \) or \( n-C_6 \) isomerization is found by

\[ Y_B = \frac{\Sigma \text{isomer concentrations}}{\Sigma (\text{isomers} + \text{normal}) \text{concentrations}} \]

\( Y_B \) was determined from analysis of the reactor effluent gas. Knowing \( t_H \) from the volumetric flow rates of reactants and products, \( \rho_B \) from measurement, and \( Y_B^i \) from literature data, it was possible to calculate \( k \) for a given set of conditions. In the case of \( n-C_5 \) and \( n-C_6 \) mixtures as feed, \( t_H \) accounts for both hydrocarbon feed rates and equation (15) is used to calculate the individual rate constants. For mixtures, the isomer concentration for \( n-C_5 \) or \( n-C_6 \) isomerization
was calculated by

\[
Y_B = \frac{\sum \text{isomer concentrations}}{\sum \text{(isomers + normal) concentrations}}
\]

as calculated from the reactor gas effluent. Appendices 1, 2, and 3 give details of this calculation.

Now, assuming that Langmuir adsorption isotherms may be applied to the simple first order reversible model for hydroisomerization (47), the first order rate constant may be expressed as

\[
k = \frac{k_0 \prod K_i}{(1 - \sum K_i P_i)^n}
\]

where \( n \) = number of catalyst sites involved in the reaction, usually 1 or 2

- \( k_0 \) = true surface reaction rate constant
- \( K_i \) = equilibrium adsorption constants for component \( i \)
- \( P_i \) = partial pressure of component \( i \), psia
- \( k \) = first order rate constant, cc/gm/sec

Since \( k_0 \) and \( K_i \) are functions of temperature only, then for a given isothermal set of runs, they may be considered constant. In the statistical analysis of the rate constant, we will then assume the following general form

\[
k = \frac{\bar{k}}{(1 + \sum K_i P_i)^n}
\]

From this general form, the dependence of \( k \) on pressure, temperature, \( H_2/HC \) ratio, space velocity, and a mixed hydrocarbon feed will be examined. By defining the relationship between \( k \) and these variables, important properties of the catalyst and the reaction kinetics can be determined.
Effect of Pressure

If the adsorption constants for the hydrocarbon species are approximately equal, it can be shown that

$$k^{-1/n} = \tilde{k}^{-1/n} \left[ 1 + P_{\text{tot}} \frac{(R_{\text{H}_2} + K_{\text{HC}})}{(1 + \tilde{R})} \right]$$

where \( \tilde{R} = \text{H}_2/\text{HC} \) ratio

\( K_{\text{H}_2} = \) hydrogen adsorption constant

\( K_{\text{HC}} = \) hydrocarbon adsorption constant

By plotting \( k^{-1/n} \) against \( P_{\text{tot}} \) at constant \( \tilde{R} \), a straight line should be obtained with a positive intercept corresponding to \( \tilde{k}^{-1/n} \).

In order to determine the value of \( n \), different values of \( n \) are assumed and the above plot is made. For a given \( n \), if a negative intercept is obtained, that value of \( n \) may be rejected since \( \tilde{k} > 0 \). Note that if the hydrocarbon adsorption constants are not equal, the same plot could be made for a given series of pure component, say \( n \)-\( C_5 \), runs to determine the value of \( n \) for \( C_5 \) isomerization.

Effect of Temperature

We assume that the temperature dependence of \( k_o \) may be represented by

$$k_o = A e^{-E'/RT}$$

where \( E' = \) true surface reaction activation energy.

The variation of the adsorption constants with temperature is given below where \( \Delta H_i \) is the heat of adsorption of species \( i \),

$$K_i = K_{oi} \exp \left[ \frac{\Delta H_i}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right] \quad i = C_5, C_6, \text{H}_2$$
The simplified rate constant defined by equation (16) includes the
temperature effects of the surface reaction as well as adsorption. If
(19) and (20) are substituted into (16) and the derivative of \( \ln k \) is
taken with respect to \( 1/T \), it can be shown that

\[
E_{\text{app}} = E' + \sum_{i=1}^{m} \Delta H_i + nR \frac{d}{d(1/T)} \left[ \ln \left( 1 + \sum_{i=1}^{m} K_i P_i \right) \right]
\]  

(21)

where \( E_{\text{app}} \) = apparent activation energy.

\( E \) is the value that would be obtained when a typical Arrhenius
plot of \( \ln k \) vs. \( 1/T \) is made. It includes both the true activation
energy, \( E' \), and the adsorption effects. Its value will thus depend on
the nature of the catalyst surface and the particular adsorbates. It
may be anticipated that \( E_{\text{app}} \) will vary substantially from catalyst to
catalyst. Levenspiel (61) has shown that if diffusion is rate-limiting,
then

\[
E_{\text{app}} = \frac{E' + E_d}{2}
\]

where \( E_d \) = activation energy for diffusion. Since \( E_d \) is typically
1 \( \rightarrow \) 4 kcal/g-mole and \( E' \) is of the order of 30 \( \rightarrow \) 60 kcal/g-mole, then

\[
E_{\text{app}} \approx \frac{E'}{2}
\]

for reactions influenced by strong pore resistance.

**Effect of Space Velocity**

From equation (15) it can be seen that since \( t_H \) is the ratio of
the catalyst volume to the total volumetric flow rate, \( V_T \), then

\[
t_H = \frac{W}{\rho_G V_T M_g}
\]

where \( \rho_G \) is the molar gas density and \( M_g \) is the gas molecular
weight. But \( V_T = \frac{RT}{P_{\text{tot}}} \left( N_{RO} + N_{H_2} \right) = \frac{N_{RO}}{\rho_G} \left( 1 + R \right) \). Substituting it

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can be seen that

\[
\ln\left(1 - \frac{Y_B}{Y_B^*}\right) = k \left[ \frac{\rho_G}{Y_B^* (1+R)} \frac{W_c}{N_{RO}} \right]
\]  

(22)

But \( \frac{N_{RO}}{W_c} \) = weight hourly space velocity, \( \tau_w \).

Thus

\[
\ln\left(1 - \frac{Y_B}{Y_B^*}\right) = k \left[ \frac{\rho_G}{Y_B^* (1+R)} \frac{1}{\tau_w} \right]
\]  

(23)

If the assumption that the hydroisomerization of \( n-C_5 \) and \( n-C_6 \) may be represented by a first order reversible reaction is valid, a plot of \( \ln(1 - Y_B/Y_B^*) \) versus \( 1/\tau_w \) should be a straight line with an intercept of 1.0 at any given temperature.

**Effect of H₂/HC Ratio**

From equation (18) it can be seen that at a given temperature and pressure, \( k \) will vary with \( R \) as

\[
k = k_R^{-1/n} + \frac{\rho_G \text{tot}}{1 + \frac{R}{1} \left[ \frac{K_H}{K_{HC}} \right]} \]

(24)

From this relationship, the relative values of the hydrocarbon and hydrogen adsorption constants may be determined as follows.

1. If \( K_{HC} >> K_{H_2} \), a plot of \( k^{-1/n} \) vs. \( 1/R + 1 \) should give a straight line with a negative abscissa intercept.
2. If $K_{H_2} \gg K_{HC}$, a plot of $k^{-1/n}$ vs. $R/(R+1)$ should give a straight line with a negative abscissa intercept.

3. If $K_{H_2} = K_{HC}$, $k$ will not vary with $R$.

Effect of a n-C₅/n-C₆ Mixture as Feed

From equation (17) it can be seen that if a mixture of hydrocarbons is used as feed, the adsorption term must include the $K_i P_i$ product for both hydrocarbons. If the two reactants have different adsorption constants, it can be seen that $k$ for the more strongly adsorbed species will increase on dilution with a more weakly adsorbed species. This can be reasoned as follows. For a C₅/C₆ feed:

$$k_i = \frac{k}{(1 + K_{C_5} P_{C_5} + K_{C_6} P_{C_6} + K_{H_2} P_{H_2})^n} \quad i = C_5, C_6$$

(25)

If $K_{C_6} \gg K_{C_5}$, as $P_{C_5}$ is increased, $P_{C_6}$ must decrease since all runs are made at a given $H_2/HC$ ratio. Since $K_{C_5}$ is small, the product $K_{C_5} P_{C_5}$ is also small and negligible to $K_{C_6} P_{C_6}$. However, $K_{C_6} P_{C_6}$ is getting smaller on dilution and thus $k_{C_6}$ must increase.

It should be noted that the pseudo first order rate constants are calculated for the reactions

$$n-C_5 \xrightarrow{k_{C_5}} i-C_5$$

(26)

$$n-C_6 \xrightarrow{k_{C_6}} \text{isomers of C}_6$$

(27)

using a model in which the rate constants are constant for a given $P_{tot}$, $T$, and $R$, i.e., for a given run.
Now, having established the experimental variation of $k$ with the important independent variables used in this study, it is necessary to examine the statistical methods to be used in analysis of the data. 

**Statistical Analysis of $k$**

The simplified rate constant may be subjected to statistical analysis to determine the rate controlling step and to some extent the nature of the surface kinetics. This is accomplished by analysis of the parameters of various postulated models of $k$ to decide not only the best model but the relationships among the parameters of a given model. By postulating various forms of $k(P_i)$ from different mechanisms and different rate limiting steps, it is possible to determine:

1. The apparent rate controlling step
2. The relative magnitude of the adsorption constants of the feed components
3. The number of sites involved in the surface reaction.

It is important to recognize that the information obtained by analyzing the rate constant as it varies with temperature, pressure, space velocity, and $H_2/HC$ ratio is independent of the information obtained through statistical work. For example, the fact that a plot of $k^{-1/2}$ vs. $P_{tot}$ indicates a dual site mechanism is independent of the fact that

$$k = \frac{k}{[1 + \Sigma K_i P_i]^2}$$

may give the best fit of the data, although equation (28) indicates a dual site mechanism also. However, it would be expected that results from statistical analysis and from other analysis would not be contradictory,
but complementary. If both types of analysis indicate, for example, that dehydrogenation was the rate controlling step for hydroisomerization of n-C₅ on the mordenite catalyst, this must be considered strong evidence that such is the case.

Strickland (60) has derived the various forms of the rate expression for the reaction A ⇌ B on a dual function catalyst such as those used in this study. Basically, they may be summarized as shown below:

<table>
<thead>
<tr>
<th>Rate Controlling Step</th>
<th>Single Site Mechanism</th>
<th>Dual Site Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerization</td>
<td>( k = \frac{k_1}{P_{H_2}(1 + \Sigma K_i P_i)} )</td>
<td>( k = \frac{k_1}{P_{H_2}(1 + \Sigma K_i P_i)^2} )</td>
</tr>
<tr>
<td>Dehydrogenation</td>
<td>( k = \frac{k_2}{(1 + \Sigma K_i P_i)^2} )</td>
<td></td>
</tr>
</tbody>
</table>
Daniel and Wood (62) have developed a non-linear least squares routine which can be used to test each model. Each model to be tested is of the form, for an \( m \) parameter model,

\[
k = k(P_i, B_j)
\]

\( i = C_5, C_6, H_2 \)

\( j = 1, \ldots, m \)

From the program (62), the following information is obtained for each model.

1. For each parameter; \( \sigma \), t-value, 95\% confidence limits, and the numerical value are given. This allows each parameter to be evaluated individually. For a given model, the confidence limits on each parameter are one measure of the validity of the model. The confidence limits are boundaries which, at a given confidence level, include the true value of the parameter. These limits represent a region in which the null hypothesis may be rejected at this given confidence level. The null hypothesis states that the variable in question, in this case a given parameter \( B_i \), is drawn from a population of mean zero and a standard deviation corresponding to that calculated for a given parameter. This is called the null population. The standard deviation is calculated for each parameter as described by Daniel and Wood. For example, 90\% confidence limits on \( B_i \) define two points symmetric to the mean at which there is a 10\% chance that the value of \( B_i \) was drawn from the null population. For a two parameter model, a plot of \( B_1 \) vs. \( B_2 \) would be an ellipsoid. Various confidence regions would then define concentric ellipsoids. The larger the confidence probability, the larger the
ellipsoids. For a three parameter model, the confidence region defines a response surface shaped as a hyperellipsoid, i.e., a roughly egg-shaped surface. The t-value for a given parameter defines, for the degrees of freedom corresponding to a given model, the probability that the value calculated for that parameter was not drawn from the null population. For example, for a t-value of 2.0 and 18 degrees of freedom, the probability that the null hypothesis can be rejected is .970. \( \sigma \) is the standard deviation for the given parameter corresponding.

2. The cross correlation matrix for the parameters is given. This matrix assigns a value from -1.00 to 1.00 to each set of parameters to describe the interdependence of those parameters. For example, a value of .98 to describe the relationship of \( B_1 \) to \( B_2 \) would indicate that \( B_1 \) and \( B_2 \) are "highly correlated" and one may be deleted from the model without significant effect on the fit of the experimental data being analyzed. This matrix is a valuable tool in distinguishing between say a 4 and 5 parameter model of basically the same functional form.

3. The residual root mean square (RRMS), residual sum of square (RSS), and residual mean square (RMS) are given. RSS is simply the sum of the squares of the residuals between the model and the data. It gives the total "variation" between the best fit the model can give and the actual data. When RSS is divided by the residual degrees of freedom, RMS is obtained. Then \( RRMS = (RMS)^{1/2} \). RRMS is a measure of the average experimental error.
4. A plot of the cumulative frequency of residuals, both positive and negative, is given. If the model results in a normal distribution of residuals this plot should be a straight line with a positive slope passing through the point (0, .5). This indicates that no statistical bias is present in the experimental errors.

5. A plot of residual values as a function of the fitted values of \( k \) is given. This plot enables one to visualize the distribution of the residuals around zero and determine if there are any particularly suspect data points. If, for example, one suspect point accounted for a large part of the error of a given model, this point would be quite far from the others on this plot. Also, the trend of the residuals with fitted \( k \)'s allows one to determine if the model is biased toward small or large values of \( k \) in determination of the parameters. For example, if all the large residuals were found at large values of \( k \), this may indicate that the model is biased toward low values of \( k \).

Variations of each of the models shown previously was used with the program described above to determine the statistically best one. For example, if the model derived from the assumption of dehydrogenation as the rate controlling step, a dual site mechanism, and \( K_{H_2} \ll K_{c_5}^0, K_{c_6}^0 \) was found to be clearly superior to any other, then this would constitute strong evidence in favor of such a model. Of course, it is possible to check these assumptions by the methods described earlier. Within each model there are several variations to be considered. For example, the relative values of the adsorption constants
may make it possible to delete $K_{H_2}$ from a model.

If the parameters represent true equilibrium adsorption constants, whose values do not change on dilution with another hydrocarbon, then $B_1$, $B_2$, and $B_3$ should be the same for both $k_{C_5}$ and $k_{C_6}$. Only the numerator, which contains the true surface reaction rate constant, should be different for $k_{C_5}$ and $k_{C_6}$. It is possible to "couple" the data for $k_{C_5}$ and $k_{C_6}$ in order to force the parameters corresponding to the adsorption constants, here $B_1$ and $B_2$, to be equal for $k_{C_5}$ and $k_{C_6}$. However, as noted previously, there is not always a relationship between equilibrium adsorption constants and those obtained on reacting systems (60). Thus, such coupling may not be valid. It is possible to determine from statistical analysis of various models whether or not coupling is valid. For example, if a coupled model resulted in a smaller residual root mean square than the corresponding models for the individual $k_{C_5}$ and $k_{C_6}$, then it could be said that coupling is valid. Mechanistically, this would imply that the adsorption parameter for each of the two reacting species, n-C$_5$ and n-C$_6$, were independent of dilution by the other. If the coupled model resulted in a higher RRMS than the individual models, it implies some interaction between the adsorption of C$_5$ and C$_6$.

Due to experimental error, it may not be possible to select one specific model as clearly superior to all others. However, it is anticipated that several general forms may be eliminated from consideration. Coupled with an analysis of the data as described previously, insight into the mechanism of the reaction and the interaction of n-C$_5$ and n-C$_6$ and their isomers on the catalyst surface may be obtained. In addition, the differences, if any, in Pd-H-faujasite and Pd-H-mordenite catalysis may be examined from a mechanistic viewpoint.
Mordenite Experimental Results

In order to establish baseline activity data for each catalyst, pure component runs were made using both n-C\textsubscript{5} and n-C\textsubscript{6}. Table 1 shows, the first order rate constants for pure n-C\textsubscript{5} hydroisomerization at 500°F, 350 psig over Pd-H-Mordenite and Table 2 shows similar results at 500°F, 450 psig. It can be seen that the mordenite catalyst used in this study had an activity for C\textsubscript{5} isomerization comparable to those used previously with 14/1 SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios at 10/1 H\textsubscript{2}/hydrocarbon. Note that the studies of Wallace (1) at 20/1 H\textsubscript{2}/HC ratios on a similar catalyst resulted in lower rate constants. This is consistent with previous findings of Bryant (33). Tables 1 and 2 also show that a 14/1 SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio resulted in a more active catalyst than a 10/1 ratio. This was due to decreased pore diffusion resistance resulting from larger pores resulting from the removal of Al atoms.

Since each study shown in Tables 1 and 2 was done on the same type catalyst but ones which were made in different batches, some scatter in the rate constants was to be expected. Activity is strongly dependent on the preparation procedures and batch to batch variation is inevitable. In addition, small temperature variations of +2-3°F which were typical in previous studies added to scatter of the data.

It may be concluded, then, that the catalyst used in this study was of a comparable activity to those used in the past.

In order to check the assumption of a first order reversible reaction, a plot of ln(1-Y\textsubscript{B}/Y\textsubscript{B}^\textsubscript{0}) versus (w/hrs/w)^{-1} for n-C\textsubscript{6} is shown in Figure 6. As shown previously, such a plot should be linear with an intercept of 1, if the reaction can be represented by a first order model. It can be seen that this assumption was valid. Previous studies
### TABLE 1

*n*-Pentane Hydroisomerization Over a Pd-H-Mordenite Catalyst  
500°F, 350 psig

<table>
<thead>
<tr>
<th>Investigator</th>
<th>(H_2/HC)</th>
<th>(SiO_2/Al_2O_3)</th>
<th>(k_{1ST})</th>
</tr>
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<td>14/1</td>
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<td>.1899</td>
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<td>.1606</td>
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<td>.1600</td>
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### TABLE 2

**n-Pentane Hydroisomerization Over a Pd-H-Mordenite Catalyst**

500°F, 450 psig

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<tr>
<th>Investigator</th>
<th>( \text{H}_2/\text{HC} )</th>
<th>( \text{SiO}_2/\text{Al}_2\text{O}_3 )</th>
<th>( k \text{IST} )</th>
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<td>14/1</td>
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<td>.0057</td>
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</table>
Figure 6. Test for first order reversible reaction, \( n-C_6 \).
have shown that similar results were obtained on this catalyst for n-C₅ hydroisomerization (65).

Now, having established the relative activity of this catalyst and the validity of first order reversible kinetics, the assumption of a dual site mechanism must be checked. As discussed earlier, a plot of $k^{-1/2}$ versus $P_{\text{tot}}$ should give a straight line with a positive intercept. This intercept corresponds to the true surface reaction rate constant. Figures 7 and 8 show plots of the C₅ and C₆ rate constants versus total pressure at 450°C and 465°C. In both cases, only the plot of $k^{-1/2}$ gave a positive intercept. This confirmed the assumption of a dual site mechanism for both C₅ and C₆ hydroisomerization.

Figure 9 shows the effect of temperature on $k_{C₆}$ and $k_{C₅}$. As expected, the Arrhenius relationship was observed. As noted previously, the apparent activation energy calculated from such a plot is given by

$$
E_{\text{app}} = E^\ast + \sum_{i=1}^{m} \Delta H_i + nR \frac{d}{d(i)} \ln(1 + \sum_{i=1}^{m} K_i P_i).
$$

As the nature of the catalyst surface changes, the surface adsorption energy, $\Delta H$, will change. Thus, some variation from catalyst to catalyst may be expected even if the true surface reaction activation energy, $E^\ast$, were the same. Previous studies on a mordenite of this type found $E_{\text{app}}$ to be between 30 and 50 kcal/g-mole for n-C₅ hydroisomerization (59). From Figure 9, it can be shown that $(E_{\text{app}})_{n-C₅}$ is 55 kcal/g-mole and $(E_{\text{app}})_{n-C₆}$ is 33 kcal/g-mole. These values were comparable to those...
Figure 7. Test for a dual site mechanism, n-C₅.
Figure 8. Test for a dual site mechanism, n-C₆.
Figure 9. Arrhenius plot of first-order rate constants, pure n-C\textsubscript{5} and C\textsubscript{6}.
obtained on previous studies which also showed $E_{\text{app}} n-C_5 < (E_{\text{app}}) n-C_5$ (59). The effect of the hydrogen to hydrocarbon mole ratio, $H_2/HC$, may be used to test the relative values of the adsorption constants of hydrogen and the hydrocarbon reactants. Figure 10 shows a plot of $k_{C_5}^{-1/2}$ and $k_{C_6}^{-1/2}$ versus $1/(R+1)$ at 200 and 300 psig total pressure. Since these lines had negative intercepts for both pressures, the data indicate that $K_{HC} > K_{H_2}$. Figure 11 shows a plot of $k_{C_5}^{-1/2}$ and $k_{C_6}^{-1/2}$ versus $R/(R+1)$. This line had a positive abscissa intercept, indicating that $K_{H_2} > K_{HC}$, confirming the results of Figure 9.

This knowledge was valuable in discriminating between two models for the reaction. For example, if the statistically determined adsorption parameters for the hydrocarbon species were much smaller than for hydrogen, such a model would be inconsistent even if the fit were good. In addition, if $K_{HC} > K_{H_2}$, $K_{H_2}$ may be neglected in some models as a valid simplification of the statistical analysis.

Figures 12 through 19 show the experimentally determined values of the first order rate constant for both $C_5$ and $C_6$ hydroisomerization at various conditions. Each figure represents one set of runs at a given temperature and pressure. The $H_2/HC$ ratio was 10/1 to 18/1 and w/hr/w was about 6.4 for all runs. For each set of runs, pure $n-C_5$ and $n-C_6$ and three mixtures were isomerized. The rate constants were calculated based on the conversion of normal reactant to isomerized products, as outlined previously.

The general trend of $k_{C_5}$ and $k_{C_6}$ with mixture concentration is constant at both 450° and 465°F. At both temperatures, $k_{C_5}$ decreased when the feed was diluted with $n-C_6$ while $k_{C_6}$ increased on
Figure 10. Rate constant versus H₂/HC ratio.
Figure 11. Rate constant versus $H_2$/HC ratio.
Figure 12. Rate constant versus feed composition.

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Figure 13. Rate constant versus feed composition.
Figure 14. Rate constant versus feed composition.
Figure 15. Rate constant versus feed composition.
Figure 16. Rate constant versus feed composition.
Figure 17. Rate constant versus feed composition.
Figure 18. Rate constant versus feed composition.
Figure 19. Rate constant versus feed composition.
dilution. As discussed previously, this would be the result if n-C₆ were more strongly adsorbed than n-C₅. The mean pore diameter of Pd-H-mordenite is 8-10 Å (50). While the molecular diameter of n-C₆ is slightly greater than n-C₅, both molecules are about 5 Å in diameter and pore sieve action would not exclude either species. Thus, pore resistance would not account for the differences in rate constants with dilution.

It can also be noted that the absolute values both \( k_{C_5} \) and \( k_{C_6} \) decreased with increasing total pressure. This result was consistent with the general Langmuir type model presented earlier, regardless of the rate determining step.

The values of \( k_{C_6} \) are greater than \( k_{C_5} \) at any given conditions. This phenomena can be explained by postulating that n-C₆ is more strongly adsorbed than n-C₅. Also, the first order rate constant is given by

\[
k = \frac{k_o \prod_{i=1}^{m} K_i}{(1 + \sum_{i} K_i P_i)^2}
\]

where \( k_o \) is the true surface reaction rate constant. As noted in equation (10), the value of \( k_o \) for n-C₆ may be obtained from the intercepts of Figures 7 and 8. From these figures, it can be seen that at 465°F, \( (k_o)_{C_5} = .6 \) and \( (k_o)_{C_6} = 1.0 \). Thus, the surface reaction rate of n-C₆ appeared to be greater than that of n-C₅.

It can also be seen that the absolute values of both \( k_{C_6} \) and \( k_{C_5} \) decreased with increasing H₂/HC ratio = \( \tilde{R} \). This may be
explained by considering the equation
\[ k^{-1/2} = k_0^{-1/2} \left( 1 + \frac{P_{\text{tot}} R K_H^2 + K_{HC}}{1 + R} \right) \]

At constant total pressure, increasing \( R \) will decrease the value of \( k \), provided \( K_H^2 \neq K_{HC} \).

The experimental results as analyzed thus far are consistent with the following:

1. First order reversible kinetics, Figure 6.
2. A dual site mechanism for both \( n-C_5 \) and \( n-C_6 \) hydroisomerization, Figures 7,8.
3. \( (k_o)_{C_6} > (k_o)_{C_5} \), Figures 7,8.
4. \( K_{C_6} > K_{C_5} \), Figures 10,11.

This information was used in the formulation of various kinetic models, and in analyzing the results of statistical programs.

The statistical analysis was carried out as follows: The rate constants, \( k_{C_5} \) and \( k_{C_6} \), were expressed as functions of partial pressures and parameters to be determined. For example,
\[ k_i = \frac{B_i}{(1 + B_1 P_{C_5} + B_2 P_{C_6} + B_3 P_{H_2})^2} \quad i = C_5, C_6 \]

is the model expected from Langmuir adsorption, a dual site mechanism, and dehydrogenation as the rate controlling step. This model may then be subjected to non-linear regression analysis to determine the least-squares values of the parameters, \( B_i \). In this particular model, \( B_1 \) corresponds to \( K_{C_5} \), \( B_2 \) to \( K_{C_6} \), \( B_3 \) to \( K_{H_2} \). Tables 4 through 6
show the results obtained on the mordenite catalyst for both coupled
and individual $C_5$ and $C_6$ models. For each of the individual models
20 data points were used, while 40 data points were used in each
coupled model.

Table 3 shows the models that were used for individual
and coupled modeling. These models were based on both theoretical
forms derivable from the kinetic models developed in the previous
section (Models 1-6,9-12) and more empirical forms (Models 7,8). Models
7,8 contained Langmuir adsorption denominators with $P_i$ in the numerator.
As can be seen from Tables 4-6, the coefficient of $P_i$ in some models
became essentially zero. The nature of the statistical program of
Daniel and Wood was such that when a coefficient in a denominator
approached zero, it indicated that this parameter and corresponding
independent variable, if placed in the numerator, may result in a
better fit. For this reason, Models 7,8 were tested.

Tables 4-6 show the statistical results obtained on the
eight models tested for the data obtained on Pd-H-mordenite.

For the individual ($k_{C_5}$ and $k_{C_6}$) models, it can be seen by
examining the RMS and RRMS that for both $k_{C_5}$ and $k_{C_6}$, Models 2, 4,
5, 7, 9, and 10 had the lower error terms. For Model 2 in both
cases, however, the value of $B_1$ approached zero while $B_3 > 0$. Since
$B_1$ corresponded to $K_{C_5}$ and $B_3$ to $K_{C_6}$, and since it has been shown
that $K_{HC} >> K_{H_2}$, this Model was rejected as unrealistic.

Model 7, although its error term was small, had no certainty
in any of the parameters, as shown by the low t-values. In addition,
it can be seen from the correlation matrix that, for $k_{C_5}$, the parameters

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TABLE 3

INDIVIDUAL MODELS

<table>
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<th>MODEL NUMBER</th>
<th>MODEL</th>
<th>ASSUMPTIONS LEADING TO THE MODEL</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>$k = \frac{B_4}{(1 + B_1 P_{C_5} + B_2 P_{C_6})^3}$</td>
<td>Dehydrogenation rate controlling, $K_{HC} \gg K_{H_2}$, $B_3$ represents the number of sites.</td>
</tr>
<tr>
<td>2</td>
<td>$k = \frac{B_4}{(1 + B_1 P_{C_5} + B_2 P_{C_6} + B_3 P_{H_2})^2}$</td>
<td>Hydrogen rate constant significant, dual site mechanism, dehydrogenation rate controlling.</td>
</tr>
<tr>
<td>3</td>
<td>$k = \frac{B_3}{(1 + B_1 P_{C_5} + B_2 P_{C_6})^2}$</td>
<td>Dehydrogenation rate controlling, $K_{HC} \gg K_{H_2}$, dual site mechanism.</td>
</tr>
<tr>
<td>4</td>
<td>$k = \frac{B_3}{P_{H_2} (1 + B_1 P_{C_5} + B_2 P_{C_6})^2}$</td>
<td>Isomerization rate controlling, $K_{HC} \gg K_{H_2}$, dual site mechanism.</td>
</tr>
<tr>
<td>5</td>
<td>$k = \frac{B_3}{P_{H_2} (1 + B_1 P_{C_5} + B_2 P_{C_6})}$</td>
<td>Same as 4 but single site mechanism.</td>
</tr>
<tr>
<td>6</td>
<td>$k = \frac{B_4}{(1 + B_1 P_{C_5} + B_2 P_{C_6} + B_3 P_{H_2})^{B_5}}$</td>
<td>$B_5$ defines number of sites, $K_{H_2}$ significant, dehydrogenation rate controlling.</td>
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<td>MODEL</td>
<td>ASSUMPTIONS LEADING TO THE MODEL</td>
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<tr>
<td>7</td>
<td>[ k = \frac{B_7 P_i B_4}{(1 + B_2 P_{C_5} + B_3 P_{C_6})^2} ]</td>
<td>( i = C_5 ) for ( k_{C_5} = C_6 ) for ( k_{C_6}, K_{H_2} ). Significant ( P_i ) in numerator is semi-empirical.</td>
</tr>
<tr>
<td>8</td>
<td>[ k = \frac{B_7 P_i B_4}{(1 + B_2 P_{C_5} + B_3 P_{C_6})^2} ]</td>
<td>Same as 7 but with variable exponent.</td>
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<tr>
<td>9</td>
<td>[ k = \frac{B_2}{(1 + B_1 P_{C_6}) P_{H_2}} ]</td>
<td>Single site mechanism, isomerization rate controlling, ( K_{C_6} \gg K_{H_2}, K_{C_5} ).</td>
</tr>
<tr>
<td>10</td>
<td>[ k = \frac{B_2}{(1 + B_1 P_{C_6})^2 P_{H_2}} ]</td>
<td>Same as 9 with a dual site mechanism.</td>
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<tr>
<td>11</td>
<td>[ k = \frac{B_2}{(1 + B_1 P_{C_5}) P_{H_2}} ]</td>
<td>Same as 9 with ( K_{C_5} \gg K_{C_6}, K_{H_2} ).</td>
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<tr>
<td>12</td>
<td>[ k = \frac{B_2}{(1 + B_1 P_{C_5})^2 P_{H_2}} ]</td>
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### COUPLED MODELS

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<td>1</td>
<td>[ k = \frac{B_{4,5}}{(1 + B_1 P_{c5} + B_2 P_{c6})^3} ]</td>
<td>Dehydrogenation rate controlling, $K_{HC} \gg K_{H2}$ B_3 represents the number of sites.</td>
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<td>2</td>
<td>[ k = \frac{B_{4,5}}{(1 + B_1 P_{c5} + B_2 P_{c6} + B_3 P_{H2})^2} ]</td>
<td>Dehydrogenation rate controlling, $K_{HC}$ significant, dual site mechanism.</td>
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<td>[ k = \frac{B_{3,4}}{(1 + B_1 P_{c5} + B_2 P_{c6})^2} ]</td>
<td>Dehydrogenation rate controlling, $K_{HC} \gg K_{H2}$ dual site mechanism.</td>
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<td>[ k = \frac{B_{3,4}}{(1 + B_1 P_{c5} + B_2 P_{c6})^2 P_{H2}} ]</td>
<td>Isomerization rate controlling, dual site mechanism, $K_{HC} \gg K_{H2}$.</td>
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<tr>
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<td>[ k = \frac{B_{3,4}}{(1 + B_1 P_{c5} + B_2 P_{c6}) P_{H2}} ]</td>
<td>Same as 4 but single site mechanism.</td>
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<td>6</td>
<td>[ k = \frac{B_{4,5}}{(1 + B_1 P_{c5} + B_2 P_{c6} + B_3 P_{H2})^3} ]</td>
<td>Dehydrogenation rate controlling, $B_6$ defines number of sites, $K_{H2}$ significant.</td>
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<td>$k = \frac{B_{4,5}}{(1 + B_1 P_{C_5} + B_2 P_{C_6} + B_3 P_{H_2})}$</td>
<td>Same as 6 but single site mechanism.</td>
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<td>$k = \frac{B_{4,5}}{(1 + B_1 P_{C_5} + B_2 P_{C_6} + B_3 P_{H_2})^2 P_{H_2}}$</td>
<td>Isomerization rate controlling, dual site mechanism, $K_{H_2}$ significant.</td>
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<td>$k = \frac{B_{2,3}}{(1 + B_1 P_{C_6}) P_{H_2}}$</td>
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<thead>
<tr>
<th>Model Number</th>
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<th>T-Value</th>
<th>RMS</th>
<th>RSS</th>
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<th>95% Confidence Limits</th>
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<th>σ</th>
<th>RMS</th>
<th>RRMS</th>
<th>RSS</th>
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<td></td>
</tr>
<tr>
<td>B₄ = 59.7 0.827 0.932 0.771 1.00</td>
<td>42. → 78.</td>
<td>6.8</td>
<td>8.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₁ = 7.0×10⁻¹³ 1.00</td>
<td>-0.38 → 0.38</td>
<td>0.0</td>
<td>0.185</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₂ = 0.358 0.644 1.00</td>
<td>-5.8 → 6.5</td>
<td>0.1</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₃ = 0.0686 0.601 0.998 1.00</td>
<td>-1.1 → 1.2</td>
<td>0.1</td>
<td>0.575</td>
<td>0.0013 0.036 0.044</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₄ = 5.15 0.637 0.999 0.999 1.00</td>
<td>-97. → 108.</td>
<td>0.1</td>
<td>50.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₅ = 16.7 0.636 0.999 0.999 1.00 1.00</td>
<td>-316. → 349.</td>
<td>0.1</td>
<td>163.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₆ = 1.57 -0.530 0.984 -0.990 -0.982 0.983 1.00 -0.301 → 3.4</td>
<td>1.7</td>
<td>918</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MODEL NUMBER</td>
<td>COEFFICIENT VALUES</td>
<td>CORRELATION MATRIX</td>
<td>95% CONFIDENCE LIMITS</td>
<td>t-VALUE</td>
<td>α</td>
<td>RMS</td>
<td>RRMS</td>
<td>RSS</td>
</tr>
<tr>
<td>--------------</td>
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<td>---</td>
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<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>7</td>
<td>(B_1 = 7.7 \times 10^{-13}) 1.00</td>
<td></td>
<td>-1.2 \rightarrow 1.2</td>
<td>0.0</td>
<td>0.571</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_2 = 1.34) .703 1.00</td>
<td></td>
<td>-11. \rightarrow 14.</td>
<td>.2</td>
<td>6.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_3 = .137) .623 .991 1.00</td>
<td></td>
<td>-1.1 \rightarrow 1.4</td>
<td>.2</td>
<td>6.02</td>
<td>.0022</td>
<td>.047</td>
<td>.076</td>
</tr>
<tr>
<td></td>
<td>(B_4 = 2.68) .668 .997 .998 1.00</td>
<td></td>
<td>-21. \rightarrow 26.</td>
<td>.2</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_5 = 8.56) .665 .997 .998 1.00 1.00</td>
<td></td>
<td>-67. \rightarrow 84.</td>
<td>.2</td>
<td>37.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_1 = 5.7 \times 10^{-14}) 1.00</td>
<td></td>
<td>-.04 \rightarrow .04</td>
<td>0.0</td>
<td>0.0197</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_2 = .0385) .882 1.00</td>
<td></td>
<td>-.0094 \rightarrow .087</td>
<td>1.6</td>
<td>0.236</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(B_3 = .00297) -.428 -.289 1.00</td>
<td></td>
<td>.00041 \rightarrow .0055</td>
<td>2.4</td>
<td>.00126</td>
<td>.0021</td>
<td>.045</td>
<td>.073</td>
</tr>
<tr>
<td></td>
<td>(B_4 = 36.0) .682 .725 .265 1.00</td>
<td></td>
<td>12. \rightarrow 60.</td>
<td>3.1</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_5 = 115.8) .695 .804 .288 .911 1.00</td>
<td></td>
<td>46. \rightarrow 186.</td>
<td>3.4</td>
<td>34.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_1 = .0511) 1.00</td>
<td></td>
<td>.022 \rightarrow .081</td>
<td>3.5</td>
<td>0.0145</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(B_2 = 17.5) .371 1.00</td>
<td></td>
<td>14. \rightarrow 21.</td>
<td>9.3</td>
<td>1.88</td>
<td>.0014</td>
<td>.0373</td>
<td>.051</td>
</tr>
<tr>
<td></td>
<td>(B_3 = 56.5) .896 .333 1.00</td>
<td></td>
<td>47. \rightarrow 66.</td>
<td>12.6</td>
<td>4.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MODEL NUMBER</td>
<td>COEFFICIENT VALUES</td>
<td>CORRELATION MATRIX</td>
<td>95% CONFIDENCE LIMITS</td>
<td>t-VALUE</td>
<td>σ</td>
<td>RMS</td>
<td>RRMS</td>
<td>RSS</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>10</td>
<td>B_1 = 0.0205</td>
<td>1.00</td>
<td>0.0101 → 0.031</td>
<td>4.0</td>
<td>0.00514</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B_2 = 17.1</td>
<td>0.328 1.00</td>
<td>13. → 21.</td>
<td>9.3</td>
<td>1.84</td>
<td>0.0014</td>
<td>0.0376</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>B_3 = 54.8</td>
<td>0.868 0.285 1.00</td>
<td>47. → 63.</td>
<td>13.9</td>
<td>3.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B_1 = 9.14×10^{-14} 1.00</td>
<td>-0.018 → 0.018</td>
<td>0.0</td>
<td>0.00907</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>B_2 = 14.4</td>
<td>0.491 1.00</td>
<td>10. → 19.</td>
<td>6.5</td>
<td>2.21</td>
<td>0.0025</td>
<td>0.0500</td>
<td>0.0925</td>
</tr>
<tr>
<td></td>
<td>B_3 = 43.3</td>
<td>0.700 0.344 1.00</td>
<td>38. → 49.</td>
<td>16.1</td>
<td>2.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B_1 = 1.51×10^{-13} 1.00</td>
<td>-0.0094 → 0.0094</td>
<td>0.0</td>
<td>0.00462</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>B_2 = 13.5</td>
<td>0.488 1.00</td>
<td>9.2 → 18.</td>
<td>6.4</td>
<td>2.12</td>
<td>0.0023</td>
<td>0.0481</td>
<td>0.0857</td>
</tr>
<tr>
<td></td>
<td>B_3 = 40.8</td>
<td>0.703 0.344 1.00</td>
<td>36. → 46.</td>
<td>15.7</td>
<td>2.60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
were not independent. For the $k_{C_6}$ case, the parameters showed independence with the exception that $B_3$ and $B_4$ were related to $B_2$. However, t-values for all parameters were less than .6 indicating a very low degree of confidence in the parameter values. On the basis of statistical uncertainty, Model 7 was rejected.

Models 4 and 5 were identical with the exception of the exponent of the adsorption term. Models 9 and 10 were also related in the same way. Both of these sets of models were derivable from the assumptions of isomerization rate controlling and $K_{HC} \gg K_{H_2}$. Model 4 indicated a dual site mechanism while Model 5 indicated a single site mechanism. Similarly, Model 9 was a single and model 10 a dual site mechanism. Models 9 and 10 further assumed $K_{C_6} \gg K_{C_5}$, as shown from qualitative considerations discussed earlier. While it has been shown earlier in this section that the data indicated a dual site mechanism, it would be expected that statistical analysis of these sets of models would yield the same result.

For $k_{C_5}$, Model 4 resulted in a higher t-value for all three parameters than Model 5. Although the RMS and RRMS were higher for model 4, it can be seen that the differences were very small, especially when compared to the values obtained on other models. The correlation matrix for Model 4 showed that no parameter was correlated above the .95 level while Model 5 resulted in $B_3$ correlated with $B_1$ and $B_2$ at .95 or above. This indicated that in Model 4 the parameters are more independent. It is important to note that both Models 4 and 5 were consistent with the qualitative observation made earlier that $K_{C_5} < K_{C_6}$. That is, to the extent that $B_1$ and $B_2$ correspond to $K_{C_5}$ and $K_{C_6},$ Models 4 and 5 result in valid values for $B_1$ and $B_2,$

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namely $B_1 < B_2$. Based on the higher t-values of the Model 4 parameters and the relative independence of the parameters, it is judged that Model 4 is superior.

Models 9 and 10 would be expected to demonstrate the same relationship as Models 4 and 5. It can be seen that the error terms of Models 9 and 10 were essentially equal to each other and to those of Models 4 and 5. However, as with Models 4 and 5, the dual site Model, 10, had a higher t-value for $B_1$, with the t-values for $B_2$ being equal. In addition, the $B_1$-$B_2$ correlation was less, .658 versus .675, for Model 10. On the basis of more certainty and independence of the parameters, Model 10 was superior.

Now, for $k_{C_5}$, Models 4 and 10 must be compared. It can be seen that if it is assumed that $K_{C_6} > K_{C_5}$, Model 4 becomes Model 10. The two models are thus not contradictory but complementary, both being derivable from the same assumptions with only the above mentioned difference. It can be seen that $B_1$ in Model 4, corresponding to $K_{C_5}$, had a low t-value and includes zero in the 95% confidence limits. On this basis, it was impossible to reject the hypothesis that $B_1$ was zero at the .95 level. Thus, statistically, Model 10 was superior.

The t-values for both $B_1$ and $B_2$ of Model 10 are 3.9 and 14.6, indicating that the null hypothesis may be rejected well above the .99 confidence level. Thus, for $k_{C_5}$ models, it can be seen that Model 10 was both statistically superior and was consistent with the qualitative and quantitative conclusions presented earlier in this section, namely $K_{C_6} > K_{C_5}$ or $K_{H_2}$, dual site mechanism, and isomerization rate controlling.
For \( k_c \), Models 4, 5, 9, and 10 must also be compared, other models being ruled out as indicated earlier. For example, it can be seen that for Model 8, \( B_4 \to 0 \) which reduced Model 8 to the same form as Model 3. However, the RMS and RRMS for Model 3 were much higher than for Models 4, 5, 9, and 10. Models 8 and 3 were thus rejected. Models 1, 2, 6, 7, and 12 may be rejected on the basis of higher error terms. Models 4 and 5 both implied that \( B_1 \to 0 \). Note that this resulted in a low t-value for \( B_1 \). Thus Models 4 and 5 were inadequate. However, they indicated that a better fit may be obtained by deleting \( B_1 \) from the model altogether. Models 9 and 10 resulted from the assumption that \( K_{c_6} >> K_{c_5} \), as indicated by the results of Models 4 and 5. Models 9 and 10 for \( k_{c_6} \) were derived assuming single and dual site kinetics, respectively, with isomerization rate controlling, as stated earlier. Even though both these models had only two parameters, which is fewer than any of the others, the error term was smaller than for any other proposed model for \( k_{c_6} \) except Model 8, which had four parameters. Model 8 had been ruled out previously on the basis of low t-values for all parameters. Thus, Models 9 and 10 were the best realistic representations of the data. It should also be noted that zero was not included in the 95% confidence limits of the parameters for both Models 9 and 10 as was the case for \( k_{c_5} \). In order to distinguish between Models 9 and 10, examine first the correlation matrix. Model 10 showed the \( B_1 - B_2 \) correlation to be less than for Model 9, .879 to .905. Model 10 had higher t-values for both \( B_1 \) and \( B_2 \). Since the RRMS and RMS were essentially the same for Models 9 and 10, Model 10 was seen as the superior statistical representation of the data. Note that Model 10 was derivable from a dual site mechanism whereas Model 9
resulted from a single site mechanism. Model 10 being a better fit was thus consistent with the results indicated earlier in this section.

It was concluded that for both $k_{C_5}$ and $k_{C_6}$, Model 10 was the superior model.

For the coupled models as shown in Table 6, it can be seen that Models 1, 2, 6, and 7 may be rejected based on the t-values of the parameters. Of the remaining models, Model 3 had a RMS and RRMS more than twice that of Model 4, 5, or 8. It was rejected on the basis of a less adequate fit of the data. Of Models 4, 5, 8, 11, and 12 it can be seen in each case, $B_1 \to 0$. This indicated that $K_{C_5} \ll K_{C_6}$ for the coupled models as was the case for $k_{C_6}$ alone. Models 9 and 10 had the lowest RRMS and RMS of any model except the model which had been rejected above. The error terms of Models 9 and 10 were essentially equal and cannot be distinguished on that basis. However, as was the case with the individual models, Model 10, corresponding to a dual site mechanism, had higher t-values for $B_1$ and $B_3$ ($B_2$ t-value being equal) than Model 9. In addition, the correlation matrix showed greater independence among all of the parameter relationships. Thus, the statistical analysis indicated that Model 10 was superior. This was to be expected since a dual site mechanism was also consistent with results presented earlier in this section.

Now, the individual and coupled Model 10 results must be compared. Such a comparison should reveal the validity of the coupling procedure. From Tables 4, 5, and 6, it can be seen that for Model 10 the values of the parameters $B_1 \to B_3$ were of the same order. The results
are shown below for convenience.

<table>
<thead>
<tr>
<th></th>
<th>From $k_{C_5}$ Data</th>
<th>From $k_{C_6}$ Data</th>
<th>From Coupled Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>0.0427</td>
<td>0.0180</td>
<td>0.0205</td>
</tr>
<tr>
<td>$B_2$</td>
<td>19.5</td>
<td>53.1</td>
<td>17.5</td>
</tr>
<tr>
<td>$B_3$</td>
<td></td>
<td></td>
<td>54.8</td>
</tr>
</tbody>
</table>

Note that $B_2$ for $k_{C_5}$ data corresponds to $B_2$ for the coupled data while $B_2$ for $k_{C_6}$ data corresponds to $B_3$ for the coupled data. It can be seen that $B_1$ for the coupled data lies between the other two values as expected. In addition, note the close correspondence of $B_2$ for $k_{C_5}$, 19.5, and $B_2$ for the coupled data, 17.5. The same was true for $B_2$ for $k_{C_6}$ data and $B_3$ for the coupled data, 53.1 versus 54.8. This indicated that the coupling procedure was valid and did not contradict results obtained by individual analysis.
Faujasite Experimental Results

As with the mordenite catalyst, pure component runs were carried out on the Pd-H-faujasite to establish the baseline activity of this particular catalyst. Table 7 shows the comparison of the Pd-H-faujasite used in this study with similar catalysts. It can be seen that the catalyst used in this study had an activity comparable to those used in previous studies. It should be noted that the isomerization activity of this Pd-H-faujasite, as with the mordenite discussed earlier, was strongly dependent on the preparation technique. Thus, some scatter in rate constant values from batch to batch was inevitable.

Table 8 and Figure 20 show a comparison of the activation energy indicated by this study for the isomerization of \( n-C_5 \) compared with results obtained on similar catalysts studied at LSU. It can be seen that the catalyst used in this study had an activation energy for \( n-C_5 \) isomerization of 44 kcal/g-mole which is comparable to that obtained on similar catalysts in previous studies.

The relative magnitudes of the hydrocarbon and hydrogen adsorption constants may be evaluated by examining the effect of the hydrogen to hydrocarbon ratio, \( H_2/HC \), as discussed earlier. Figure 21 shows a plot of \( k_{C_5}^{-1/2} \) and \( k_{C_6}^{-1/2} \) versus \( 1/(R+1) \) at 200 and 300 psig total pressure. Figure 22 shows a plot of \( k_{C_5}^{-1/2} \) and \( k_{C_6}^{-1/2} \) versus \( R/(R+1) \) at 200 psig and 300 psig. As discussed earlier, if \( K_{HC} \gg K_{H_2} \), then Figure 21 should yield a straight line with a negative abscissa intercept and Figure 22 should not. This was the case. These results were
TABLE 7

\( n-c_5 \) rate constants, Pd-H-Faujasite

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>PRESSURE, ( \text{psia} )</th>
<th>TEMP., ( ^\circ\text{F} )</th>
<th>w/hr/w, ( \text{hr}^{-1} )</th>
<th>H(_2)/HC</th>
<th>( k_{c_5} ), ( \text{cc/gm/sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habibe</td>
<td>465</td>
<td>555</td>
<td>8.5</td>
<td>6.2</td>
<td>.156</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.5</td>
<td>6.0</td>
<td></td>
<td>.0119</td>
</tr>
<tr>
<td>This Study</td>
<td>465</td>
<td>500</td>
<td>6.2</td>
<td>10.1</td>
<td>.014</td>
</tr>
<tr>
<td>Strickland</td>
<td>465</td>
<td>550</td>
<td>7.7</td>
<td>10.1</td>
<td>.0691</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.2</td>
<td>10.4</td>
<td></td>
<td>.0171</td>
</tr>
</tbody>
</table>
**TABLE 8**

Activation energies for \( n-c_5 \) hydroisomerization on Pd-H-Faujasite

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>TEMPERATURE RANGE, °F</th>
<th>ACTIVATION ENERGY, kcal/g-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habibe</td>
<td>500-550</td>
<td>53</td>
</tr>
<tr>
<td>Strickland</td>
<td>450-600</td>
<td>40</td>
</tr>
<tr>
<td>This Study</td>
<td>450-500</td>
<td>44</td>
</tr>
</tbody>
</table>

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Figure 20. Arrhenius plot of first-order rate constants
Figure 21. Rate constant versus $H_2$/HC ratio

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Figure 22. Rate constant versus $\text{H}_2$/HC ratio.
consistent with those obtained on the mordenite catalyst as shown in Figures 21 and 22 and indicated that the relative magnitudes of the hydrogen and hydrocarbon adsorption parameters was the same on both catalysts.

Under the simplifying assumptions discussed earlier, a plot of $k^{-1/n}$ vs $P_{tot}$ should give a straight line with a positive intercept for the correct value of $n$, where $n$ is the number of sites involved in the surface reaction. Figures 23 and 24 show the results of such a plot for an $n$ of 1 and 2. The plot of both $(k_{C_5}^{-2})$ and $(k_{C_6}^{-2})$ both have positive intercepts whereas $(k_{C_5}^{-1})$ and $(k_{C_6}^{-1})$ both had negative intercepts. The data were thus consistent with the assumption of a dual site mechanism.

Previous studies (44,56) had shown that Pd-H-mordenite and Pd-H-faujasite may both be considered to isomerize through a dual site mechanism, and that the assumption of first order reversible kinetics is valid. Thus this study did not duplicate the experiments to verify first order kinetics on the faujasite catalyst but concentrated on examining the mechanism of isomerization of mixtures and comparing these results to Pd-H-mordenite.

Figures 25 through 30 show the results obtained on mixtures of n-C$_5$ and n-C$_6$ at 465°F, 6.4 w/hr/w, pressures from 100 to 300 psig, and $H_2/HC$ ratios from 10/1 to 18/1. These runs were carried out in the same manner as those over the mordenite catalyst, i.e., a pure n-C$_5$ and n-C$_6$ run and three mixture runs were done at each temperature and pressure. Several general trends may be noted.
Figure 23. Test for a dual site mechanism, \( n-C_5 \).
Figure 24. Test for a dual site mechanism, \( n-C_6 \).
Figure 25. Rate constant versus feed concentration.
Figure 26. Rate constant versus feed concentration.
Figure 27. Rate constant versus feed concentration.
Figure 28. Rate constant versus feed concentration.
Figure 29. Rate constant versus feed concentration.
Figure 30. Rate constant versus feed concentration.
Both $k_{c5}$ and $k_{c6}$ decreased on dilution. This was in contrast to the mordenite catalyst on which $k_{c6}$ increased on dilution while $k_{c5}$ decreased. On the Pd-H-faujasite catalyst, the results thus indicated a competitive interaction between $C_5$ and $C_6$ on the catalysts surface. It may be said that $n$-$C_5$ and $n$-$C_6$ had approximately the same adsorption affinity on the faujasite catalyst. Otherwise, the rate constant of the preferentially adsorbed hydrocarbon would increase on dilution. The pore diameter of the faujasite was 8Å, comparable to that of the mordenite. Thus, differences in adsorption between the mordenite and faujasite must be due to another cause, perhaps differences in the types of active centers involved in surface reaction.

The results also show that the values of both $k_{c5}$ and $k_{c6}$ decrease with increasing total pressure. This same result was observed on the mordenite. This was expected from the Langmuir form of rate constant:

$$k_j = \frac{k}{[1 + \sum K_i P_i]^n}$$

j = $c_5, c_6$

i = $c_5, c_6, H_2$

since, as the $P_i$'s are increased, the denominator gets larger and $k_j$ gets smaller.

As with the mordenite catalyst, the absolute values of $k_{c6}$ were greater than for $k_{c5}$. This may be due to a larger true surface reaction rate constant for $n$-$C_6$ than $n$-$C_5$. i.e., $(k_0)_{c6} > (k_0)_{c5}$. From equation (18) the value of $k_0$ may be obtained from the intercepts of Figures 23 and 24. From these Figures, it can be seen that $(k_0)_{c5} = 1.0$ whereas $(k_0)_{c6} = 4.9$. Thus, the data indicated that indeed the inherent surface reaction rate constant for $n$-$C_6$ was greater than that for $n$-$C_5$. The same result was
obtained on the mordenite catalyst.

Finally, it can be seen that the absolute value of both \( k_{c_5} \) and \( k_{c_6} \) decreased with increasing \( H_2/HC \) ratio, \( \tilde{R} \). This was consistent with equation (18) developed earlier showing the functional dependence of the rate constant on \( \tilde{R} \) at a given \( P_{tot} \)

\[
k^{-\frac{1}{2}} = \bar{k}^{-\frac{1}{2}} \left[ 1 + \frac{P_{tot} (\tilde{R} K_{H_2} + K_{HC})}{1 + \tilde{R}} \right].
\]

As \( \tilde{R} \) increases at constant \( P_{tot} \), \( k \) must decrease unless \( K_{H_2} = K_{HC} \). It has been shown that \( K_{HC} \gg K_{H_2} \) and thus \( k \) must decrease with increasing \( \tilde{R} \).

In summary, it can be said that the data on the Pd-H faujasite are consistent with the following:

1. First order reversible kinetics (44,56).
2. Dual site mechanism for both \( n-C_5 \) and \( n-C_6 \) hydroisomerization, Figures 23,24.
3. \( (k_0)_{c_6} > (k_0)_{c_5} \), Figures 23,24.
4. \( K_{c_5} = K_{c_6} \), Figures 25-30.
5. \( K_{HC} \gg K_{H_2} \), Figures 21,22.

These results were identical to those obtained on the mordenite catalyst with the exception of the relative magnitudes of the \( n-C_5 \) and \( n-C_6 \) adsorption constants. On the mordenite, \( K_{c_6} \gg K_{c_5} \) while \( K_{c_6} \approx K_{c_5} \) on the faujasite.

The information obtained from the statistical analysis of the experimental results may be used to formulate and judge the rate constant and partial pressure relationships. The statistical analysis was carried out in the same manner as described earlier for the mordenite.
catalyst. Various models, shown in Table 3, were postulated as functional forms for \( k \) (\( P_i \)) based on assumptions about the number of sites involved in the mechanism, the relative values of the adsorption parameters, and the rate controlling step. Both individual and coupled models were used.

Tables 9-11 show the results for the Pd-H-faujasite catalyst. On each individual model, twenty-four data points were used and the coupled models thus used forty-eight points.

On the individual n-C_5 models, Table 9, examination of the RMS and RRMS showed that Models 2, 4, 5, and 6 resulted in substantially better representations of the data than the remaining models. Of these four models, only Model 4 did not include zero in the 95% confidence limits of any of the coefficients. In addition, even though Model 2 had four parameters and Model 6 had five, neither resulted in a significantly better fit than Model 4 which has only three parameters. Model 6 may be ruled out by virtue of the low t-values for four of the five coefficients. Low t-values result from parameter values which approach zero, since the t-value is equal to the parameter value divided by \( \sigma \). For Model 5, while the t-values were non-zero, zero is within the \( B_1 \) confidence limits. There was also a .98 correlation between \( B_1 \) and \( B_3 \). On this basis, Model 5 was rejected. For Model 2, zero was within 3 of 4 parameter confidence limits. Also, there were low t-values for \( B_1 \) and \( B_2 \). Thus Model 2 was rejected in favor of Model 4.

While Model 4 may be judged to be the best of the twelve models in describing the relationship between the simplified pentane rate constant and the partial pressures of the reactants, it was noted that \( B_1 \) and \( B_3 \) were correlated at the .948 level. However, the \( B_1-B_2 \) and
<table>
<thead>
<tr>
<th>MODEL NUMBER</th>
<th>COEFFICIENT VALUES</th>
<th>CORRELATION MATRIX</th>
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<th>t-VALUE</th>
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<th>RMS</th>
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<th>RSS</th>
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<td>.009 .005 1.00</td>
<td>.895 → 1.7</td>
<td>7.0</td>
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<td>9</td>
<td>$B_1 = 2.16 \times 10^{-12}$, $-0.459$, $0.862$, $0.288$, $1.00$</td>
<td>$B_2 = 0.254$, $1.00$</td>
<td>$-0.61$ to $0.61$</td>
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<td>$B_1 = 19.8$, $0.617$, $1.00$</td>
<td>$B_2 = 0.0971$, $1.00$</td>
<td>$0.15$ to $0.36$</td>
<td>5.3</td>
<td>0.0483</td>
<td>0.000378</td>
<td>0.0194</td>
<td>0.00830</td>
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<td>$B_1 = 19.4$, $0.606$, $1.00$</td>
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<td>0.0347</td>
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### TABLE 10

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<td>6.26</td>
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<td>.992</td>
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<th>B_2</th>
<th>B_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>1.33</td>
<td>18.2</td>
<td>44.2</td>
</tr>
<tr>
<td>12</td>
<td>0.0539</td>
<td>17.7</td>
<td>43.6</td>
</tr>
</tbody>
</table>
$B_3 - B_2$ correlations were only .736 and .831, respectively, indicating relative independence among these parameters. Also note that zero is not included in the 95% confidence limits of any of the coefficients of Model 4. In addition, the t-values of the coefficients were $\leq 2.2$, indicating a $\geq .961$ probability of rejecting the null hypothesis i.e., the hypothesis that the coefficients are different from zero. Model 4 was thus considered to be the best representation of the data for $k_{c5}$.

For the individual $k_{c6}$ models, shown in Table 10, it can be seen that Models 4, 6, 11, and 12 have RMS and RRMS values which were significantly lower than those for the remaining models. In discriminating among these four models, it was noted that the t-values for Model 6 were $\leq 1.7$ with the exception of $B_4$, that zero was in the 95% confidence limits of each coefficient, and that all five parameters were highly correlated. Model 6 was thus rejected.

Models 11 and 12 both have RMS and RRMS values which were 19 and 23% respectively, higher than for Model 4, indicating a poorer fit of the data.

In addition, the t-values for $B_1$, corresponding to the $C_5$ adsorption parameter for Models 4, 11, and 12 were higher for Model 4 (9.7) than for Models 11 (3.4) or 12 (4.0). It should be noted, however, that the t-values for the numerator, proportional to $(k_o)_{c6}$, were higher in Models 11 (13.0) and 12 (13.6) than for Model 4 (8.8). On the basis of the lower error values for Model 4, although the remaining bases of comparison are equivalent on balance, Model 4 was judged to be the representation of the $k_{c6}$ rate constant.
The coupled model results are shown in Table 11. On the basis of RMS and RRMS, models 2, 4, 5, 6, and 8 were superior to the remaining models. Further discrimination can be made by examining the t-values of these models. Models 2, 5, and 6 each had both low t-values for the parameters and a very high degree of correlation among all the parameters. These models are thus rejected. Model 8 shows that B₃, corresponding to the n-C₆ adsorption parameter, approached zero, and thus had a low t-value. Since earlier qualitative results indicate the approximate equivalence of K₅ and K₆, Model 8 was rejected as unrealistic.

Thus, Model 4 was the most accurate representation of the coupled data, as it is for the individual models. The 95% confidence limits for this model did not include zero for any of the four coefficients. Although B₂ and B₄ were correlated at the .981 level, the remaining correlations were satisfactory. The t-values for the parameters were all ≥ 3.2, indicating a ≥ .997 probability of rejecting the null hypothesis. Thus, not only was Model 4 the best of the models, it was also an acceptable fit of the data.

Comparison of the individual and coupled models showed the following for Model 4:

<table>
<thead>
<tr>
<th></th>
<th>From k₅ Data</th>
<th>From k₆ Data</th>
<th>From Coupled Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>.0273</td>
<td>.181</td>
<td>.155</td>
</tr>
<tr>
<td>B₂</td>
<td>.143</td>
<td>.0732</td>
<td>.0744</td>
</tr>
<tr>
<td>B₃</td>
<td>28.7</td>
<td>132.</td>
<td>48.3</td>
</tr>
<tr>
<td>B₄</td>
<td></td>
<td></td>
<td>127.</td>
</tr>
</tbody>
</table>
$B_4$ for the coupled model corresponds to $B_3$ for the $k_{C_6}$ data while $B_3$ for the coupled model corresponds to $B_3$ for the $k_{C_5}$ data. Note that the values of $B_1$ and $B_2$ from the coupled model lie between those of the $k_{C_5}$ and $k_{C_6}$ data as expected. However, these values were much closer to the $k_{C_6}$ model values than to the $k_{C_5}$ values. Since the relative values of $B_1$ and $B_2$, corresponding to $k_{C_5}$ and $k_{C_6}$ respectively, were reversed in the two individual models, the fact that the coupled data showed that $B_1 > B_2$, as do the $k_{C_6}$ data, indicated that the data were best represented by $B_1 > B_2$. The difference in $B_1$ and $B_2$, namely $B_1 = 2.1 B_2$, was not as great as on the mordenite catalyst. There, $B_1 \neq B_2$ and $B_2$ could be deleted from the model.

It may thus be concluded that the faujasite data may be modelled by assuming a dual site mechanism, $K_{H_2} \ll K_{HC}$, $K_{C_5}$ of the same order as $K_{C_6}$, and surface reaction rate controlling. Further, the data indicate that $B_1$, corresponding to $k_{C_5}$, was approximately twice the value of $B_2$, corresponding to $k_{C_6}$.
Comparison of the Mordenite and Faujasite Catalysts

Having modelled the results on both the mordenite and faujasite catalysts, a comparison was made of the reaction and adsorption phenomena as indicated by both the models and the additional analysis discussed earlier.

First, the results showed that at 465°F, 6.4 w/hr/w and at pressures of 100, 200, and 300 psig, Pd-H-mordenite was a more active catalyst for hydroisomerization of n-C5, n-C6, and mixtures of the two. Table 12 shows a comparison of the results on each catalyst. For the pure component runs on both n-C5 and n-C6, there were no distinct trends of the mordenite and faujasite rate constants with pressure or H2/HC ratio. However, for 3 out of 5 n-C5 runs and 3 of 5 n-C6 runs, the mordenite catalyst was more active.

For the mixture runs, Table 12 showed that the mordenite catalyst was more active over the entire range of conditions of total pressure and H2/HC used in this study. However, it can be seen that there was no general trend of the rate constants on the mordenite versus the faujasite with total pressure or H2/HC ratio. It may thus be concluded that the Pd-H-mordenite catalyst used in this study was more active for hydroisomerization of n-C5, n-C6, and mixtures of the two than was the Pd-H-faujasite.

Comparison of the statistical models which describe the reactions on each catalyst showed that the mordenite exhibits preferential adsorption of n-C6 such that the adsorption parameter of n-C5 can be neglected. On the faujasite catalyst, both n-C5 and n-C6 adsorption parameters must be included in the model. The models for the hydroisomerization reactions on each catalyst are shown below for convenience.
TABLE 12

Comparison of the Results of Pd-H-Mordenite and Pd-H Faujasite Hydroisomerization at 465°F

<table>
<thead>
<tr>
<th>Total Pressure, psig</th>
<th>C₅/C₆ Volume Ratio</th>
<th>H₂/HC</th>
<th>k_C₅</th>
<th>k_C₆</th>
<th>k_C₅</th>
<th>k_C₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Pure C₅</td>
<td>10/1</td>
<td>.241</td>
<td>-</td>
<td>.187</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200 Pure C₅</td>
<td>10/1</td>
<td>.061</td>
<td>-</td>
<td>.091</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>192 Pure C₅</td>
<td>17.8/1</td>
<td>.073</td>
<td>-</td>
<td>.079</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300 Pure C₅</td>
<td>10/1</td>
<td>.071</td>
<td>-</td>
<td>.046</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>291 Pure C₅</td>
<td>14.7/1</td>
<td>.058</td>
<td>-</td>
<td>.053</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Pressure, psig</th>
<th>C₅/C₆ Volume Ratio</th>
<th>H₂/HC</th>
<th>k_C₅</th>
<th>k_C₆</th>
<th>k_C₅</th>
<th>k_C₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Pure C₆</td>
<td>10/1</td>
<td>-</td>
<td>.337</td>
<td>-</td>
<td>.431</td>
<td>-</td>
</tr>
<tr>
<td>200 Pure C₆</td>
<td>10/1</td>
<td>-</td>
<td>.143</td>
<td>-</td>
<td>.125</td>
<td>-</td>
</tr>
<tr>
<td>192 Pure C₆</td>
<td>17.8/1</td>
<td>-</td>
<td>.127</td>
<td>-</td>
<td>.246</td>
<td>-</td>
</tr>
<tr>
<td>300 Pure C₆</td>
<td>10/1</td>
<td>-</td>
<td>.100</td>
<td>-</td>
<td>.047</td>
<td>-</td>
</tr>
<tr>
<td>291 Pure C₆</td>
<td>14.7/1</td>
<td>-</td>
<td>.133</td>
<td>-</td>
<td>.083</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Pressure, psig</th>
<th>C₅/C₆ Volume Ratio</th>
<th>H₂/HC</th>
<th>k_C₅</th>
<th>k_C₆</th>
<th>k_C₅</th>
<th>k_C₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 15/85</td>
<td>10/1</td>
<td>.101</td>
<td>.374</td>
<td>.042</td>
<td>.293</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>10/1</td>
<td>.137</td>
<td>.519</td>
<td>.095</td>
<td>.208</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>10/1</td>
<td>.143</td>
<td>.507</td>
<td>.081</td>
<td>.183</td>
<td>-</td>
</tr>
<tr>
<td>200 15/85</td>
<td>10/1</td>
<td>.046</td>
<td>.171</td>
<td>.020</td>
<td>.078</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>10/1</td>
<td>.048</td>
<td>.179</td>
<td>.021</td>
<td>.043</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>10/1</td>
<td>-</td>
<td>.024</td>
<td>-</td>
<td>.038</td>
<td>-</td>
</tr>
<tr>
<td>192 15/85</td>
<td>17.8/1</td>
<td>.045</td>
<td>.125</td>
<td>.042</td>
<td>.156</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>17.8/1</td>
<td>.050</td>
<td>.152</td>
<td>.045</td>
<td>.118</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>17.8/1</td>
<td>.058</td>
<td>.144</td>
<td>.055</td>
<td>.080</td>
<td>-</td>
</tr>
<tr>
<td>300 15/85</td>
<td>10/1</td>
<td>.029</td>
<td>.115</td>
<td>.026</td>
<td>.029</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>10/1</td>
<td>.032</td>
<td>.125</td>
<td>.024</td>
<td>.017</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>10/1</td>
<td>.038</td>
<td>.162</td>
<td>.030</td>
<td>.018</td>
<td>-</td>
</tr>
<tr>
<td>292 15/85</td>
<td>14.8/1</td>
<td>.030</td>
<td>.150</td>
<td>.025</td>
<td>.053</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>14.8/1</td>
<td>.033</td>
<td>.165</td>
<td>.027</td>
<td>.031</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>14.8/1</td>
<td>.043</td>
<td>.205</td>
<td>.024</td>
<td>.032</td>
<td>-</td>
</tr>
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</table>

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<table>
<thead>
<tr>
<th>Model Number</th>
<th>Mordenite</th>
<th>Model Number</th>
<th>Faujasite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{c_5} )</td>
<td>( 10 )</td>
<td>( k_{c_5} )</td>
<td>( 4 )</td>
</tr>
<tr>
<td>( 19.5 )</td>
<td>( (1 + 0.0427 P_{c_6})^2 )</td>
<td>( 28.7 )</td>
<td>( (1 + 0.0273 P_{c_5} + 0.143 P_{c_6})^2 )</td>
</tr>
<tr>
<td>( k_{c_6} )</td>
<td>( 10 )</td>
<td>( k_{c_6} )</td>
<td>( 4 )</td>
</tr>
<tr>
<td>( 53.1 )</td>
<td>( (1 + 0.0180 P_{c_6})^2 )</td>
<td>( 132. )</td>
<td>( (1 + 0.181 P_{c_5} + 0.0732 P_{c_6})^2 )</td>
</tr>
</tbody>
</table>

**Coupled Models**

| \( k_{c_5} \) | \( 10 \) | \( k_{c_5} \) | \( 4 \) |
| \( 17.1 \) | \( (1 + 0.0205 P_{c_6})^2 \) | \( 48.3 \) | \( (1 + 0.155 P_{c_5} + 0.0744 P_{c_6})^2 \) |
| \( k_{c_6} \) | \( 10 \) | \( k_{c_6} \) | \( 4 \) |
| \( 54.8 \) | \( (1 + 0.0205 P_{c_6})^2 \) | \( 127. \) | \( (1 + 0.155 P_{c_5} + 0.0744 P_{c_6})^2 \) |

On the mordenite catalyst, both qualitative considerations and the statistical analysis, as shown and discussed earlier, indicated that \( K_{c_6} \gg K_{c_5} \). On the faujasite, both \( K_{c_5} \) and \( K_{c_6} \) must be included in the model. This may account for the anomalous effects observed on both catalysts. On the mordenite, the increase in \( k_{c_6} \) on dilution of n-C_6 with n-C_5 may be explained by the preferential adsorption of n-C_6, i.e., the predominance of n-C_6 in competing for active sites. This hypothesis was strengthened by the statistical analysis which showed that the model corresponding to the predominance of n-C_6 adsorption was the most accurate. Interestingly, the faujasite data required that both adsorption parameters be included, which indicated both n-C_5 and n-C_6 adsorption were
important with neither species predominating. This competition for active sites may cause the observed decrease in the rate constant for both adsorbing species on dilution. It has been shown that this observed decrease occurred at each pressure and H₂/HC ratio examined in this study.

On both catalysts, the individual results indicate that the numerator, which was proportional to the surface reaction rate constant, was greater for n-C⁶ than for n-C⁵ isomerization. Comparison of the coupled models indicated that while the true surface reaction rate constants for both n-C⁵ and n-C⁶, proportional to the numerators of the models, were greater on the faujasite than the mordenite, the larger adsorption terms, i.e. the denominators, caused the simplified rate constants on the faujasite to be lower at a given set of conditions.

Thus, the differences in the performance of the two catalysts may be explained by qualitative considerations and statistically determined models. The results of these two methods of analysis were consistent and complementary.
Conclusions

Based on the results of the analysis discussed in this study, the following conclusions may be made.

1. The data obtained in the hydroisomerization of n-C_5 and n-C_6 mixtures and pure components on both the Pd-H-mordenite and Pd-H-faujasite used in this study are consistent with a model derived assuming a dual site mechanism, with isomerization rate-controlling, and hydrocarbon adsorption parameters much greater than hydrogen adsorption parameters.

2. Further, the results indicate that on the mordenite, the hexane adsorption parameter is much greater than that of pentane, while on the faujasite the hexane adsorption parameter is of the same order as that of pentane.

3. The Pd-H-mordenite catalyst is more active for hydroisomerization of n-C_5 and n-C_6 mixtures than the Pd-H-faujasite catalyst over the entire range of pressures and H_2/HC ratios used in this study.

4. Both catalysts exhibit anomalous effects in hydroisomerization of n-C_5 and n-C_6 mixtures. On the mordenite catalyst, the simplified hexane isomerization rate constant increases while that of pentane decreases on dilution. On the faujasite, both rate constants decrease. On the mordenite, the anomaly is attributed to the preferential adsorption of n-C_6. On the faujasite, competition between the adsorbents appears to result in a decrease in both the hexane and pentane rate constants on dilution.

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Recommendations

The following recommendations for further work may be made based on the results of this study.

1. Investigate the adsorption of the n-C₅ and n-C₆ on both Pd-H-mordenite and Pd-H-faujasite on zeolites with varying pore geometry to relate adsorption more generally to structure. Since adsorption appears to affect the rate constants on both catalysts used in this study a more detailed examination of the effects of structural parameters and reaction conditions on the adsorption mechanism would be illustrative. Part of such a study could be the relationship between the equilibrium adsorption constants and values obtained in a kinetic study.

2. Study the effect of aromatics on hydroisomerization of n-paraffins on mordenite and faujasite catalysts. Since typical feedstocks for isomerization in a refinery would contain aromatics, the effect of various concentrations of aromatics on adsorption and reaction at low molecular weight n-paraffins is appropriate.

3. Further examine the effect of structural parameters such as pore geometry and configuration, parameters, and surface activity especially as related to the acidity of the zeolite on the reaction of n-C₅ and n-C₆. The negative interaction seen in this study may be related to effects of catalyst preparation on the strength and distribution of active sites, both metallic and acidic.

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4. Examine the reactions of n-C₅ and n-C₆ using isomers of these paraffins as feeds. Since the data were consistent with isomerization being rate controlling on both the mordenite and faujasite, interaction between isomers of the two feeds may be important in explaining the observed synergism. Such interaction as well as a more detailed mechanism of reaction, may be described more fully by such a study, with conversions of each isomer held to differential levels in order to understand the mechanism of isomerization.
References


31. Kouwenhoven, H. W., and Van Zijll Langhout, W. C., Petrol. and


APPENDIX 1

SAMPLE CALCULATIONS

A. Experimental Conditions

Run Number MI-37
Catalyst volume, cc 4.26
Catalyst weight, gm 2.0012
Barometric pressure, in. Hg 30.08
Room temperature, °F 74
Reactor temperature, °F 465
Reactor pressure, psig 97

H₂ flow rate data

Average WTM reading, sec/o.05 ft³ 87.4
Average WTM temperature, °F 74.3
Normal Pentane flow rate, cc/hr 20.0
Normal Hexane flow rate, cc/hr 20.0
Average gas flow rate, sec/o.05 ft³ 82.4
Average WTM temperature, °F 74.4

B. Analytical Data (Gas Chromatograph)

<table>
<thead>
<tr>
<th>Component</th>
<th>Hydrogen Free Mole % (from Gas Chromatograph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopentane</td>
<td>2.09</td>
</tr>
<tr>
<td>Normal Pentane</td>
<td>36.69</td>
</tr>
<tr>
<td>2,2 Dimethyl Butane</td>
<td>0.0</td>
</tr>
<tr>
<td>2 Methyl Pentane</td>
<td>10.23</td>
</tr>
<tr>
<td>3 Methyl Pentane</td>
<td>2.79</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>45.70</td>
</tr>
</tbody>
</table>

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C. Calculated Process Conditions

1. Hydrocarbon feed rates

- Normal Pentane = \( \frac{(20.0 \text{ cc/hr}) (0.6262 \text{ gm/cc})}{(72.15 \text{ gm/g-mole})} = 0.1736 \text{ g-mole/hr} \)

- Normal Hexane = \( \frac{(20.0 \text{ cc/hr}) (0.6601 \text{ gm/cc})}{(84.16 \text{ gm/g-mole})} = 0.1569 \text{ g-mole/hr} \)

2. Corrected barometric pressure

- Temperature of barometer: \((74-32.0)/1.8 = 23.3^\circ \text{C}\)

- Corrected pressure = \(30.38 \left[ 1 - \frac{0.000164(23.3)}{1+0.000182(23.3)} \right] = 29.97 \text{ in Hg} \)

3. Hydrogen flow rate

\[ \text{H}_2 = \frac{(14.72 \text{ psia}) (453.6 \text{ g-mole/lb mole})(3600 \text{ sec/hr}) (29.97-0.875) \text{ in Hg}}{(29.92 \text{ in Hg})(10.73 \text{ psia ft}^2/\text{lb mole}^\circ \text{R})(20-0.05 \text{ ft}^3/\text{ft}^3)(87.46 \text{ sec}/0.05 \text{ ft}^3) \]

\[ = 2.335 \text{ g-mole/hr} \]

4. Hydrogen/hydrocarbon molar ratio

\[ 2.335/(0.1736 + 0.1569) = 14.89 \]

5. Feed \( w/hr/w \) and \( v/hr/v \)

\[ w/hr/w = \frac{[(20.0) (0.6262) + (20.0) (0.6601)] \text{ gm/hr}}{(2.0012 \text{ gm})} = 6.55 \text{ gm/hr/gm cat} \]

\[ v/hr/v = (20.0 + 20.0)/4.26 = 9.39 \text{ cc/hr/cc cat} \]

6. Molar gas density in reactor

\[ \frac{(97 + 14.7) \text{ psia} (10.73 \text{ psia ft}^3/\text{lb mole}^\circ \text{R})(28312.6 \text{ cc/ft}^3)}{(460+465)^\circ \text{R}} = 1.803 \times 10^{-4} \text{ g-mole/cc} \]

7. Superficial residence time

\[ \frac{(1.803 \times 10^{-4} \text{ g-mole/cc})(4.26 \text{ cc})(3600 \text{ sec/hr})}{(2.335 + 0.1736 + 0.1569) \text{ g-mole/hr}} = 1.11 \text{ sec} \]

8. Superficial gas velocity

\[ \frac{4.26 \text{ cc}}{(1.96 \text{ cm}^2)(1.11 \text{ sec})} = 1.96 \text{ cm/sec} \]
D. Material Balance Calculations

Basis: 1 hour

1. Hydrocarbon atoms in hydrocarbon feed
   \[12(0.1736) + 14(0.1569) = 4.280 \text{ gm atoms H}\]

2. Carbon atoms in hydrocarbon feed
   \[5(0.1736) + 6(0.1569) = 1.809 \text{ gm atoms C}\]

3. Gm atoms C per mole of hydrocarbon product
   \[
   \begin{array}{ccc}
   \text{Component} & \text{Average Mole Fraction} & \text{Gm atoms C/g mole} \\
   1\text{C5} & 0.0209 & 5 \\
   \text{NC5} & 0.3669 & 5 \\
   22\text{DMB} & 0.0000 & 6 \\
   \text{2MP} & 0.1023 & 6 \\
   \text{3MP} & 0.0279 & 6 \\
   \text{NC6} & 0.4570 & 6 \\
   \end{array}
   \]

4. Calculated g-moles of hydrocarbon product
   \[1.809 \text{ gm atom C/5.4622 gm atom C/g mole = .3312 g-moles}\]

5. Gram atoms H per g-mole of hydrocarbon product
   \[
   \begin{array}{ccc}
   \text{Component} & \text{Average Mole Fraction} & \text{Gm atoms H/g mole} \\
   1\text{C5} & 0.0209 & 12 \\
   \text{NC5} & 0.3669 & 12 \\
   22\text{DMB} & 0.0000 & 14 \\
   \text{2MP} & 0.1023 & 14 \\
   \text{3MP} & 0.0279 & 14 \\
   \text{NC6} & 0.4570 & 14 \\
   \end{array}
   \]

6. Calculated \(H_2\) in product streams
   \[2.335 [4.280-.3312(12.0)] = 2.4878 \text{ g-mole } H_2\]

7. Calculated g-moles of product gas
   \[2.4878+.3312 = 2.8190 = \text{g-moles}\]

8. Observed g-moles of product gas
   \[
   \frac{(14.7)(453.6)(3600)}{(29.92)(10.73)(20)} \times \left[\frac{(29.97-.876)}{(82.4)(460+74.4)}\right] = 2.4701 \text{ g-moles/hr}
   \]
E. Reaction Rate Constants

\[ k = \frac{-Y_i \cdot V}{W_{cH}} \ln(1 - \frac{Y_i}{Y_i^*}) \]

1. Normal pentane

\[ k = \frac{(-.807)}{(.475)(1.11)} \ln(1 - \frac{.0539}{.807}) = .107 \text{ cc/gm/sec} \]

2. Normal Hexane

\[ k = \frac{(-.840)}{(.47)(1.11)} \ln(1 - \frac{.2217}{.840}) = .492 \text{ cc/gm/sec} \]

F. GC Factors

<table>
<thead>
<tr>
<th>Component</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopentane</td>
<td>1.580</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1.495</td>
</tr>
<tr>
<td>2,2-DMButane</td>
<td>1.352</td>
</tr>
<tr>
<td>2-MPentane</td>
<td>1.308</td>
</tr>
<tr>
<td>3-MPentane</td>
<td>1.318</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.278</td>
</tr>
</tbody>
</table>
APPENDIX 2

List of Computer Program for
Calculation of \( n-C_6 \) and Mixture Runs
// EXEC EYFORT3,PARM,=FORT=(NOSOURCE,NOMAP),PARM,LKED=LET
//FORT,SYSPRINT DD DUMMY.
DIMENSION XIC5(7),XNC5(7),X22DMB(7),X2MP(7),X3MP(7),
XNC6(7)
DIMENSION RUNN0(2)
DIMENSION CATYP(2)
DATA STP/* */
666 CONTINUE
READ(5,999)RUNN0
IF(RUNN0(1).EQ.STP)CALL EXIT
READ(5,999)CATYP
999 FORMAT(2A4)
READ(5,999)XC5R,XC6R
998 FORMAT(8F10.0)
READ(5,1)XN
1 FORMAT(5F10.0)
XNC6(6)=XN
READ(5,2)PRES,CATWT,DCAT,HFL0MI,AVGAS
2 FORMAT(5F10.0)
CVOL=CATWT/DCAT
READ(5,3)TTEMP,YC5,YC6,C5VFR,C6VFR
3 FORMAT(5F10.0)
READ(5,4)PBAR,TBAR,TWTMA,TWTM3
4 FORMAT(4F10.0)
TWTMAK=273.16+5.*((TWTMA-32.)/9.
TAR5=647.27-TWTMAK
ARG=TARG*(3.2433*TARG*0.00587*(TARG+3.)*1.17E-8)/
1(TWTMAK*(1.+TARG*.0219))
PTMA=213.17*(1.+(-ARG))*29.92
TWTMAK=273.16+5.*((TWTM3-32.)/9.
TAR3=647.27-TWTMAK
ARG=TARG*(3.2433*TARG*0.00587*(TARG+3.)*1.17E-8)/
1(TWTMAK*(1.+TARG*.0219))
PTMA=213.17*(1.+(-ARG))*29.92
READ(5,5)(XIC5(I),I=1,N)
READ(5,5)(XNC5(I),I=1,N)
READ(5,5)(X22DMB(I),I=1,N)
READ(5,6)(X2MP(I),I=1,N)
READ(5,6)(X3MP(I),I=1,N)
READ(5,6)(XNC6(I),I=1,N)
5 FORMAT(3F10.0)
TPRES=PRES+14.7
GMNC5=(C5VFR*.6262)/72.15
GMNC6=(C6VFR*.661)/36.18
TM0LE=GMNC5+GMNC6
PENT=GMNC5/TM0LE
H2X=GMNC6/TM0LE
TEMPC=(TBAR-32.)/1.8
PSARC=PBAR*(1.-(.00164*TEMPC)/(1.+0.000182*TEMPC))
HRATE=5732.1*(PSARC-PTMA)/HFL0MI/1.460*TWTMA
H2CR=HRATE/(GMNC5+GMNC6)
PPH2=H2CR/(H2CR+1.)*TPRES

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$P_{25} = P_{WV}/(H2CR+1.) * TPRES$

$P_{26} = P_{HEX}/(H2CR+1.) * TPRES$

$WHSV = (C5VFR * 62.62 * C5VFR * 6601) / CATWT$

$VHSV = (C5GFR * C6GFR) / CTVOI$

$GDEN = TPRES * 653.6 / 10.73 / 28452.6 / (460. + TTEMP)$

$THOLD = GDEN * CTVOI * 3600. / (GMNC5 + GMNC6 + HRATE)$

$AIC5 = 0.$

$ANC5 = 0.$

$A22DMB = 0.$

$A2MP = 0.$

$A3MP = 0.$

$ANC6 = 0.$

$50$ $CONTINUE$

$AIC5 = AIC5 + XIC5(1)$

$ANC5 = ANC5 + XNC5(1)$

$A22DMB = A22DMB + X22DMB(I)$

$A2MP = A2MP + X2MP(I)$

$A3MP = A3MP + X3MP(I)$

$ANC6 = ANC6 + XNC6(I)$

$50$ $CONTINUE$

$AIC5 = AIC5 / XM$

$ANC5 = ANC5 / XM$

$A22DMB = A22DMB / XM$

$A2MP = A2MP / XM$

$A3MP = A3MP / XM$

$ANC6 = ANC6 / XM$


$CATOM = 5. * GMNC5 + 6. * GMNC6$


$1/100$

$GMHCP = CATOM / TCATOM$

$GMH2P = HRATE + 0.5 * (HATOM - GMHCP * THATOM)$

$CMOP = GMH2P / GMHCP$

$AGMP = SQRT(3732.1 * (PBARC - PMTB) / AVGAS / (460. + TTEMP))$

$XHAT3 = AGMP / GMMP * 100.$

$SUMIC5 = AIC5 / (AIC5 + ANC5)$

$XC5 = (YC5 / (THOLD + CAT)) * ALOG(1. - SUMIC5 / YC5) * (-1.) * XCR$

$SUMIC6 = (A22DMB * A2MP * A3MP) / (ANC6 + A22DMB * A2MP + A3MP)$

$XC6 = (YC6 / (THOLD + CAT)) * ALOG(1. - SUMIC6 / YC6) * (-1.) * XCR$

$WRITE(6, 777)$

$777$ $FORMAT(1HI1)$

$WRITE(6, 199) RUNNO$

$199$ $FORMAT(50X, 'RUN', 2A4)$

$WRITE(6, 1001)$

$WRITE(6, 1001)$

$WRITE(6, 1001)$

$WRITE(6, 1001)$

$1001$ $FORMAT(1X)$

$WRITE(6, 102) TTEMP$

$102$ $FORMAT(20X, 'TEMPERATURE', 17X, F10.0, 7X, 'DEG F')$
WRITE(6,103) PRESS
103 FORMAT(20X,'PRESSURE',20X,F10.3,7X,'PSI')
WRITE(6,104) CATWT
104 FORMAT(20X,'CATALYST WEIGHT',16X,F10.3,4X,'GRAMS')
WRITE(6,105) CATYP
980 FORMAT(20X,'CATALYST TYPE',21X,2A4)
WRITE(6,106) WRITE(6,105)
106 FORMAT(20X,'HYDROCARBON FEED COMPOSITION*')
WRITE(6,101)
WRITE(6,116)
116 FORMAT(51X,'MOLE FRACTION',4X,'PARTIAL PRESSURE*')
WRITE(6,107) PENT,PPC5
107 FORMAT(20X,'NORMAL PENTANE',15X,F10.2,4X,F10.2,2X,'PSIA*)
WRITE(6,108) HEX,PPC6
108 FORMAT(20X,'NORMAL HEXANE',16X,F10.2,4X,F10.2,2X,'PSIA*')
WRITE(6,109) H2CR
109 FORMAT(20X,'HYDROGEN PRESSURE',11X,F10.1,3X,'PSIA*')
WRITE(6,110) THOLO
110 FORMAT(20X,'SOLUTION KEPT TIME',3X,F10.2,2X,'SEC*')
WRITE(6,111) XMATB
111 FORMAT(20X,'MATERIAL BALANCE',13X,F10.2,2X,'PERCENT*')
WRITE(6,112) WRITE(6,111)
WRITE(6,113) WRITE(6,112)
WRITE(6,114) WRITE(6,113)
114 FORMAT(20X,'MOLES PRODUCT/100 MOLES FEED*')
WRITE(6,115) WRITE(6,114)
WRITE(6,116) WRITE(6,115)
WRITE(6,117) WRITE(6,116)
WRITE(6,118) WRITE(6,117)
118 FORMAT(20X,'ISO C5',F10.2)
WRITE(6,119) WRITE(6,118)
119 FORMAT(20X,'N C5',2X,F10.2)
WRITE(6,120) WRITE(6,119)
120 FORMAT(20X,'22DMB',1X,F10.2)
WRITE(6,121) WRITE(6,120)
121 FORMAT(20X,'2MP',3X,F10.2)
WRITE(6,122) WRITE(6,121)
122 FORMAT(20X,'3MP',3X,F10.2)
WRITE(6,123) WRITE(6,122)
123 FORMAT(20X,'NC6',3X,F10.2)
WRITE(6,124) WRITE(6,123)
124 FORMAT(20X,'C5 RATE CONSTANT',15X,F10.3,2X,'CC/GM/SEC*')
WRITE(6,125) WRITE(6,124)
125 FORMAT(20X,'C6 RATE CONSTANT',15X,F10.3,2X,'CC/GM/SEC*')
GO TO 566
END
APPENDIX 3

List of Computer Program for Calculation of n-C$_5$ Runs

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// EXEC EYFORT3,PARM1=Fort=(NOSOURCE,NOMAP),PARM2=LET
// FORT=SYSPRINT DO DUMMY
DIMENSION XIC5(7),XNC5(7),X22DMB(7),X2MP(7),X3MP(7),
XNC6(7)
DIMENSION CATYF(2)
DIMENSION RUNNO(2)
DATA STF/* •/
CONTINUE
READ(5,999)RUNNO
IF (RUNNO(1).EQ.10) CALL EXIT
READ(5,999)STFP
999 FORMAT(3A4)
READ(5,998)XC5R,XC6R
998 FORMAT(8F10.0)
READ(5,1)XM
1 FORMAT(5F10.0)
N=XM
READ(5,2)PRES,CATWT,DCAT,HFLOWI,AVGAS
2 FORMAT(5F10.0)
CTVOL=CATWT/DCAT
READ(5,3)TEMP,YC5,YC6,C5VFR,C6VFR
3 FORMAT(5F10.0)
READ(5,4)PBAR,TBAR,TWTMA,TWTMB
4 FORMAT(4F10.0)
TWTMAK=273.16+5.*(TWTMA-32.)/9.
ARG=TEMP*(3.2439+TEMP*.00567+(TEMP**3)*1.17E-08)/
1(TWTMAK*(1.+TEMP*.00219))
PWMA=218.17*(10.**(-ARG))**0.52
TWTMBK=273.16+5.*(TWTMB-32.)/9.
TARG=647.27-TWTMBK
PRG=TEMP*(3.2439+TEMP*.00567+(TEMP**3)*1.17E-08)/
1(TWTMBK*(1.+TEMP*.00219))
PWMB=218.17*(10.**(-ARG))**0.52
RE=10.(Xi,5)(XIC5(I),I=1,N)
READ(5,5)XNC5(I),I=1,N
6 FORMAT(8F10.0)
TPRES=PRRES*14.7
GMNC5=C5VFR*.66*6262/72.15
GMNC6=C6VFR*6501/86.1*
TMOLE=GMNC5+GMNC6
PENT=GMNC5/TMOLE
HEX=GMNC6/TMOLE
TEMPC=(TBAR-32.)/1.8
PBARC=PBAR*(1.-0.000164*TEMPC)/(1.+0.000182*TEMPC))
HRATE=3732.1*(PBARC-PWMA)/HFLOWI/(460.+TWTMA)
H2CR=HRATE/(GMNC5+GMNC6)
PPH2=H2CR/(H2CR+1.)*TPRES
PPC5=PENT/(H2CR+1.)*TPRES
PPC6=HEX/(H2CR+1.)*TPRES
WHSV=(C5VFR*.66*6262+C6VFR*6501)/CATWT
VHSV=(C5VFR+C6VFR)/CTVOL

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GDEN = TPRES * 453.6 / (10.73 / 28312.6 / (460 + TTEMP))
THOLD = GDEN * CTVOL * 36 / 0.73 / 28312.6 / (440 + TTEMP)
AIC5 = 0.
ANC5 = 0.
DO 50 I = 1, N
AIC5 = AIC5 + XIC5(I)
ANC5 = ANC5 + XNC5(I)
50 CONTINUE
AIC5 = AIC5 / XM
ANC5 = ANC5 / XM
HATOM = 12.*GMNC5
CATOM = 5.*GMNC5
TCATOM = (5.*AIC5 + 5.*ANC5) / 100.
THATOM = (12.*AIC5 + 12.*ANC5) / 100.
GMHCP = CATOM / TCATOM
GMH2P = THRATE + 0.5*(HATOM - GMHCP*THATOM)
AGMPG = 3732.1*(PBARC - PWTMB) / AVGAS / (460 + TWTMS)
XMATB = AGMPG / CGMPG * 100.
SUMIC5 = AIC5 / 100.
XC5 = (YC5 / (THOLD * DCAT) * ALOG(1 - SUMIC5 / YC5)) * (-1) * YC5
WRITE(6, 777)
777 FORMAT(1H1)
WRITE(6, 199) RUNNO
199 FORMAT(50X, 'RUN ', 3A4)
WRITE(6, 1001)
WRITE(6, 1001)
WRITE(6, 1001)
WRITE(6, 1001)
1001 FORMAT(*)
WRITE(6, 102) TTEMP
102 FORMAT(20X, 'TEMPERATURE', 17X, F10.4, 7X, 'FEC ') WRITE(6, 103) PRES
103 FORMAT(20X, 'PRESSURE', 20X, F10.4, 7X, 'PSIG ')
WRITE(6, 104) CATWT
104 FORMAT(20X, 'CATALYST WEIGHT', 16X, F10.4, 6X, 'GAM ')
WRITE(6, 880) CATYP
880 FORMAT(20X, 'CATALYST TYPE', 21X, 2A4)
WRITE(6, 1001)
WRITE(6, 106)
106 FORMAT(20X, 'HYDROCARBON FEED COMPOSITION ')
WRITE(6, 1001)
WRITE(6, 116)
116 FORMAT(51X, 'MOLE FRACTION', 4X, 'PARTIAL PRESSURE ')
WRITE(6, 107) PENT, PPC5
107 FORMAT(20X, 'NORMAL PENTANE', 15X, F10.2, 4X, F10.2, 2X, 'PSIA ')
WRITE(6, 108) HEX, PPC6
WRITE(6, 1001)
WRITE(6, 110) H2CR
110 FORMAT(20X, 'H2/HYDROCARBON MOLE RATIO', 4X, F10.2)
WRITE(6, 115) PPH2
115 FORMAT(20X, 'HYDROGEN PRESSURE', 11X, F10.4, 7X, 'PSIA ')

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WRITE(6,111) WHSV
111 FORMAT(20X, 'WEIGHT HOURLY SPACE VELOCITY*, 1X, F10.2, 
  2X, 'WHSV')
WRITE(6,113) THOLD
113 FORMAT(20X, 'SUPERFICIAL RESIDENCE TIME*, 3X, F10.2, 2X, 
  *SEC*')
WRITE(6,114) XMATS
114 FORMAT(20X, 'MATERIAL BALANCE*, 13X, F10.2, 2X, *PERCENT*')
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,120)
120 FORMAT(20X, 'MOLES PRODUCT/100 MOLES FEED')
WRITE(6,1001)
WRITE(6,1001)
WRITE(6,121) AIC5
121 FORMAT(20X, 'ISO C5*, F10.2')
WRITE(6,122) ANC5
122 FORMAT(20X, 'NON C5*, 2X, F10.2')
WRITE(6,1001)
WRITE(6,130) XKC5
WRITE(6,1001)
GO TO 666
END
//LKED.SYSPRINT DD DUMMY
//GO.SYSIN DD *
APPENDIX 4

Detailed Run Data and Results
### Run C61-5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465</td>
<td>DEG F</td>
</tr>
<tr>
<td>Pressure</td>
<td>200</td>
<td>PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.000</td>
<td>GRAMS</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 289</td>
<td></td>
</tr>
</tbody>
</table>

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>19.28 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon MOLE RATIO</td>
<td>10.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>195.4</td>
<td>PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.60</td>
<td>WHR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>2.44</td>
<td>SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>99.40</td>
<td>PERCENT</td>
</tr>
</tbody>
</table>

### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>0.14</td>
</tr>
<tr>
<td>N C5</td>
<td>2.15</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.63</td>
</tr>
<tr>
<td>2MP</td>
<td>12.03</td>
</tr>
<tr>
<td>3MP</td>
<td>5.39</td>
</tr>
<tr>
<td>NC6</td>
<td>79.65</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.0</td>
<td>CC/GM/STC</td>
</tr>
<tr>
<td>C6</td>
<td>0.143</td>
<td>CC/GM/SEC</td>
</tr>
</tbody>
</table>
RUN C6I-7

TEMPERATURE 465° DEG F
PRESSURE 300° PSIG
CATALYST WEIGHT 2.000 GRAMS
CATALYST TYPE LJJ 289

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
<th>PARTIAL PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.0</td>
<td>0.0 PSIA</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>1.00</td>
<td>27.98 PSIA</td>
<td>27.98 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO 10.25
HYDROGEN PRESSURE 296.7 PSIA
WEIGHT HOURLY SPACE VELOCITY 6.60 W/HP/W
SUPERFICIAL RESIDENCE TIME 3.54 SEC
MATERIAL BALANCE 98.62 PERCENT

MOLES PRODUCT/100 MOLES FEED

| ISO C5 | 0.19    |
| N C5   | 3.03    |
| 22DMB  | 0.48    |
| 2M     | 12.24   |
| 3M     | 5.42    |
| NC6    | 78.63   |

C5 RATE CONSTANT 2.2 CC/GM/SEC
C6 RATE CONSTANT 0.100 CC/GM/SEC

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**RUN C61-8**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465.0°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>100.0 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.000 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJ9 289</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>10.61 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>9.91</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>104.1 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.60 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.34 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>99.38 PERCENT</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso C5</td>
<td>0.11</td>
</tr>
<tr>
<td>N C5</td>
<td>0.90</td>
</tr>
<tr>
<td>22DMS</td>
<td>1.19</td>
</tr>
<tr>
<td>2MP</td>
<td>16.95</td>
</tr>
<tr>
<td>3MP</td>
<td>4.81</td>
</tr>
<tr>
<td>NC6</td>
<td>76.15</td>
</tr>
</tbody>
</table>

**C5 Rate Constant**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.0 CC/GM/SEC</td>
</tr>
</tbody>
</table>

**C6 Rate Constant**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>0.337 CC/GM/SEC</td>
</tr>
</tbody>
</table>
### RUN C61-14

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>465°F</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>192 psig</td>
</tr>
<tr>
<td><strong>Catalyst Weight</strong></td>
<td>2.002 grams</td>
</tr>
<tr>
<td><strong>Catalyst Type</strong></td>
<td>LuJ 289</td>
</tr>
</tbody>
</table>

#### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.0</td>
<td>0.0 psia</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>10.99 psia</td>
</tr>
</tbody>
</table>

| H2/Hydrocarbon Mole Ratio | 17.82 |
| Hydrogen Pressure        | 195.7 psia |
| Weight Hourly Space Velocity | 6.60 W/HR/W |
| Superficial Residence Time | 1.39 sec |
| Material Balance         | 99.68 percent |

#### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>0.0</td>
</tr>
<tr>
<td>N C5</td>
<td>1.82</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.80</td>
</tr>
<tr>
<td>2MP</td>
<td>6.46</td>
</tr>
<tr>
<td>3MP</td>
<td>2.51</td>
</tr>
<tr>
<td>NC6</td>
<td>98.42</td>
</tr>
</tbody>
</table>

| C5 Rate Constant | 0.0 CC/G^°/SEC |
| C6 Rate Constant | 0.127 CC/G^°/SEC |

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RUN C61-15

TEMPERATURE 465.1 DEG F
PRESSURE 291.2 PSIG
CATALYST WEIGHT 2.007 GRAMS
CATALYST TYPE LJ 289

HYDROCARBON FEED COMPOSITION

NORMAL PENTANE MOLE FRACTION 0.0
NORMAL HEXANE 1.00

H2/HYDROCARBON MOLE RATIO 14.8
HYDROGEN PRESSURE 286.5 PSIA
WEIGHT HOURLY SPACE VELOCITY 6.58 W/Hr/W
SUPERFICIAL RESIDENCE TIME 2.44 SEC
MATERIAL BALANCE 111.95 PERCENT

MOLES PRODUCT/100 MOLES FEED

ISO C5 0.0
N C5 2.81
22DMB 0.30
2MP 11.63
3MP 4.97
NC6 80.28

C5 RATE CONSTANT 0.0 CC/GM/SEC
C6 RATE CONSTANT 0.133 CC/GM/SEC
## RUN C6I-16

<table>
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<th>Value</th>
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<tbody>
<tr>
<td>Temperature</td>
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<tr>
<td>Pressure</td>
<td>291 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.013 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>19.29 PSIA</td>
</tr>
</tbody>
</table>

| Hydrogen Pressure  | 286.4 PSIA    |
| Weight Hourly Space Velocity | 6.56 W/HR/W  |
| Superficial Residence Time  | 3.13 sec    |
| Material Balance          | 102.03 Percent |

### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Product</th>
<th>Moles</th>
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<td>ISO C5</td>
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<td>N C5</td>
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<td>22DMB</td>
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<td>2MP</td>
<td>7.16</td>
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<td>3MP</td>
<td>3.73</td>
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<tr>
<td>NC6</td>
<td>86.75</td>
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<tr>
<td>C5</td>
<td>0.0 CC/GM/SEC</td>
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<tr>
<td>C6</td>
<td>0.083 CC/GM/SEC</td>
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**RUN C61-17**

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</tr>
<tr>
<td>PRESSURE</td>
<td>300.0 PSIG</td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.013 GRAMS</td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>HJE 243</td>
</tr>
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</table>

**HYDROCARBON FEED COMPOSITION**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>1.00</td>
<td>22.51 PSIA</td>
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</tbody>
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<table>
<thead>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>10.04</td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>286.2 PSIA</td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.56 W/HR/W</td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>4.63 SEC</td>
</tr>
<tr>
<td>MATERIAL BALANCE</td>
<td>105.30 PERCENT</td>
</tr>
</tbody>
</table>

**MOLES PRODUCT/100 MOLES FEED**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
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</tr>
<tr>
<td>N C5</td>
<td>2.59</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.21</td>
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<tr>
<td>2MP</td>
<td>6.05</td>
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<tr>
<td>3MP</td>
<td>3.11</td>
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<tr>
<td>NC6</td>
<td>88.05</td>
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<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
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</tr>
<tr>
<td>C6 RATE</td>
<td>0.047</td>
</tr>
</tbody>
</table>

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RUN C61-19

TEMPERATURE
PRESSURE
CATALYST WEIGHT
CATALYST TYPE

HYDROCARBON FEED COMPOSITION

NORMAL PENTANE
NORMAL HEXANE

H2/HYDROCARBON MOLE RATIO
HYDROGEN PRESSURE
WEIGHT HOURLY SPACE VELOCITY
SUPERFICIAL RESIDENCE TIME
MATERIAL BALANCE

MOLE FRACTION
PARTIAL PRESS

0.0
0.0
PSIA
1.00
19.74
PSIA

195.0
PSIA
6.58
W/HR/W
3.20
SEC
105.84
PERCENT

MOLES PRODUCT/100 MOLES FEED

ISO C5
N C5
22DMB
2MP
3MP
NC6

4.70
19.36
5.43
5.02
2.33
63.15

C5 RATE CONSTANT
C6 RATE CONSTANT

0.0
0.125
CC/GM/SEC

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### Run C61-18

**Temperature** | 465.0°F
---|---
**Pressure** | 100.0 PSIG
**Catalyst Weight** | 2.003 Grams
**Catalyst Type** | HJE 243

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.00</td>
<td>0.00 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>10.43 PSIA</td>
</tr>
</tbody>
</table>

**H₂/Hydrocarbon Mole Ratio**: 10.00
**Hydrogen Pressure**: 104.3 PSIA
**Weight Hourly Space Velocity**: 6.59 W/HR/W
**Superficial Residence Time**: 1.69 SEC

### Material Balance

<table>
<thead>
<tr>
<th></th>
<th>103.03 Percent</th>
</tr>
</thead>
</table>

### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Compound</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>7.88</td>
</tr>
<tr>
<td>N C5</td>
<td>17.77</td>
</tr>
<tr>
<td>22DMP</td>
<td>9.37</td>
</tr>
<tr>
<td>2MP</td>
<td>10.24</td>
</tr>
<tr>
<td>3MP</td>
<td>1.25</td>
</tr>
<tr>
<td>NC6</td>
<td>53.48</td>
</tr>
</tbody>
</table>

**C5 Rate Constant**: 0.0 CC/GM/SEC
**C6 Rate Constant**: 0.431 CC/GM/SEC
RUN C6I-20

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>TEMPERATURE</td>
<td>465°F</td>
<td></td>
</tr>
<tr>
<td>PRESSURE</td>
<td>97°F</td>
<td>PSIG</td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.001 GRAMS</td>
<td></td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>HJE 243</td>
<td></td>
</tr>
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</table>

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th></th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>1.00</td>
<td>7.07 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO | 14.79
HYDROGEN PRESSURE        | 104.6 PSIA
WEIGHT HOURLY SPACE VELOCITY | 6.60 W/HR/W
SUPERFICIAL RESIDENCE TIME | 1.14 SEC
MATERIAL BALANCE          | 6.14 PERCENT

MOLES PRODUCT/100 MOLES FEED

| ISO C5 | 3.73 |
| N C5   | 13.41 |
| 22DMS  | 8.26 |
| 2MP    | 9.16 |
| 3MP    | 2.51 |
| NC6    | 62.93 |

C5 RATE CONSTANT | 0.0 CC/GM/SEC
C6 RATE CONSTANT | 0.528 CC/GM/SEC

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RUN C61-22

<table>
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<th>Value</th>
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<td>Temperature</td>
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</tr>
<tr>
<td>Pressure</td>
<td>192.002</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.002</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJF 243</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>1.00</td>
<td>10.97 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>17.85</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.7 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.60 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.77 SEC</td>
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</table>

**Material Balance**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOles Product/100 MOles Feed</td>
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</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
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<td>0.0</td>
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<tr>
<td>N C5</td>
<td>1.04</td>
</tr>
<tr>
<td>22DMP</td>
<td>0.13</td>
</tr>
<tr>
<td>2MP</td>
<td>12.92</td>
</tr>
<tr>
<td>3MP</td>
<td>4.92</td>
</tr>
<tr>
<td>NC6</td>
<td>80.99</td>
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</tbody>
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<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>C5 Rate Constant</td>
<td>0.0 CC/GM/SEC</td>
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<tr>
<td>C6 Rate Constant</td>
<td>0.246 CC/GM/SEC</td>
</tr>
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RUN MI-4

<p>| | | |</p>
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<tbody>
<tr>
<td>TEMPERATURE</td>
<td>465°F</td>
<td></td>
</tr>
<tr>
<td>PRESSURE</td>
<td>200 psig</td>
<td></td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.000 grams</td>
<td></td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>LUJ 289</td>
<td></td>
</tr>
</tbody>
</table>

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th></th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.17</td>
<td>3.16 psia</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>0.83</td>
<td>15.80 psia</td>
</tr>
</tbody>
</table>

H₂/HYDROCARBON MOLE RATIO | 10.33
HYDROGEN PRESSURE        | 195.7 psia
WEIGHT HOURLY SPACE VELOCITY | 6.55 W/HR/W
SUPERFICIAL RESIDENCE TIME  | 2.35 sec
MATERIAL BALANCE         | 99.36 percent

MOLES PRODUCT/100 MOLES FEED

| ISO C₅  | 1.26  |
| N C₅   | 19.01 |
| 22DM₅  | 0.22  |
| 2MP    | 11.09 |
| 3MP    | 5.36  |
| NC₆    | 63.04 |
| C₅ RATE CONSTANT | 0.046 CC/GM/SEC |
| C₆ RATE CONSTANT | 0.171 CC/GM/SEC |

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**RUN MI-5**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>TEMPERATURE</td>
<td>465°F</td>
</tr>
<tr>
<td>PRESSURE</td>
<td>200°PSIG</td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.000 GRAMS</td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>LJJ 289</td>
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**HYDROCARBON FEED COMPOSITION**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.38</td>
<td>7.62 PSIA</td>
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<td>NORMAL HEXANE</td>
<td>0.52</td>
<td>12.49 PSIA</td>
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>9.68</td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>194.6 PSIA</td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.49 W/HR/4</td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>2.43 SEC</td>
</tr>
<tr>
<td>MATERIAL BALANCE</td>
<td>99.35 PERCENT</td>
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**MOLES PRODUCT/100 MOLES FEED**

<table>
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<tr>
<th>Component</th>
<th>Moles</th>
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<tbody>
<tr>
<td>ISO C5</td>
<td>2.55</td>
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<tr>
<td>NC5</td>
<td>36.75</td>
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<tr>
<td>22DMB</td>
<td>0.17</td>
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<td>2MP</td>
<td>10.48</td>
</tr>
<tr>
<td>3MP</td>
<td>4.35</td>
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<tr>
<td>NC6</td>
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<table>
<thead>
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<tbody>
<tr>
<td>C5</td>
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<td>C6</td>
<td>0.201 CC/G'/SEC</td>
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### RUN MI-6

<table>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465° F</td>
</tr>
<tr>
<td>Pressure</td>
<td>200 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.000 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 285</td>
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</table>

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press (PSIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>10.00</td>
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<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>8.82</td>
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</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press (PSIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>10.41</td>
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>195.9 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.43 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>2.23 SEC</td>
</tr>
</tbody>
</table>

### Material Balance

<table>
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<tr>
<th>Component</th>
<th>Moles Product/100 Moles Feed</th>
</tr>
</thead>
<tbody>
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<td>ISO C5</td>
<td>3.62</td>
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<tr>
<td>n C5</td>
<td>54.37</td>
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<tr>
<td>22DMB</td>
<td>0.19</td>
</tr>
<tr>
<td>2MP</td>
<td>6.22</td>
</tr>
<tr>
<td>3MP</td>
<td>2.39</td>
</tr>
<tr>
<td>NC6</td>
<td>33.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Rate Constant (CC/GM/SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
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<tr>
<td>C6</td>
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</tbody>
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**RUN MI-10**

<table>
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<tr>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465° DEG F</td>
</tr>
<tr>
<td>Pressure</td>
<td>300 PSIG</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>2.000 Grams</td>
</tr>
<tr>
<td>Catalyst type</td>
<td>LJ 289</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.17</td>
<td>4.68 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.83</td>
<td>23.40 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>10.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>286.6 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Velocity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.55 W/HR/W</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superficial Residence Time</td>
<td>3.48 SEC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Balance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Balance</td>
<td>99.86 PERCENT</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>1.41</td>
</tr>
<tr>
<td>N C5</td>
<td>2.97</td>
</tr>
<tr>
<td>22DM9</td>
<td>0.10</td>
</tr>
<tr>
<td>2MP</td>
<td>0.91</td>
</tr>
<tr>
<td>3MP</td>
<td>0.84</td>
</tr>
<tr>
<td>NC6</td>
<td>59.77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.02 CC/GM/SEC</td>
</tr>
<tr>
<td>C6</td>
<td>0.115 CC/GM/SEC</td>
</tr>
</tbody>
</table>

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**RUN M1-11**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>465°F</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>300 PSIG</td>
</tr>
<tr>
<td><strong>Catalyst Weight</strong></td>
<td>2.000 Grams</td>
</tr>
<tr>
<td><strong>Catalyst Type</strong></td>
<td>LJJ 299</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Commodity</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>15.07 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>13.30 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂/Hydrocarbon Mole Ratio</strong></td>
<td>10.09</td>
</tr>
<tr>
<td><strong>Hydrogen Pressure</strong></td>
<td>286.3  PSIA</td>
</tr>
<tr>
<td><strong>Weight Hourly Space Velocity</strong></td>
<td>6.43 WHP/W</td>
</tr>
<tr>
<td><strong>Superficial Residence Time</strong></td>
<td>3.36 SEC</td>
</tr>
<tr>
<td><strong>Material Balance</strong></td>
<td>100.32 PERCENT</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Comp</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C₅</td>
<td>3.22</td>
</tr>
<tr>
<td>N C₅</td>
<td>48.22</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.01</td>
</tr>
<tr>
<td>2MP</td>
<td>7.37</td>
</tr>
<tr>
<td>3MP</td>
<td>3.21</td>
</tr>
<tr>
<td>NC6</td>
<td>37.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅</td>
<td>0.032 CC/GM/SEC</td>
</tr>
<tr>
<td>C₆</td>
<td>0.125 CC/GM/SEC</td>
</tr>
</tbody>
</table>
**RUN MI-12**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>300 psig</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2,000 grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJ 280</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.77</td>
<td>21.90 psia</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>6.44 psia</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>10.10</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>286.4 psia</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.35 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>3.26 sec</td>
</tr>
<tr>
<td>Material Balance</td>
<td>99.64 percent</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso C5</td>
<td>5.50</td>
</tr>
<tr>
<td>N C5</td>
<td>72.31</td>
</tr>
<tr>
<td>22D4M9</td>
<td>0.0</td>
</tr>
<tr>
<td>2M2P</td>
<td>4.02</td>
</tr>
<tr>
<td>3M2P</td>
<td>1.84</td>
</tr>
<tr>
<td>NC6</td>
<td>16.34</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 Rate Constant</td>
<td>0.035 cc/gm/sec</td>
</tr>
<tr>
<td>C6 Rate Constant</td>
<td>0.162 cc/gm/sec</td>
</tr>
<tr>
<td><strong>RUN MI-13</strong></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td><strong>TEMPERATURE</strong></td>
<td>465° DEG F</td>
</tr>
<tr>
<td><strong>PRESSURE</strong></td>
<td>100 PSIG</td>
</tr>
<tr>
<td><strong>CATALYST WEIGHT</strong></td>
<td>2,000 GRAMS</td>
</tr>
<tr>
<td><strong>CATALYST TYPE</strong></td>
<td>LJJ 289</td>
</tr>
</tbody>
</table>

**HYDROCARBON FEED COMPOSITION**

<table>
<thead>
<tr>
<th><strong>NORMAL PENTANE</strong></th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
<th><strong>NORMAL HEXANE</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.17</td>
<td>1.77 PSIA</td>
<td>0.83</td>
</tr>
</tbody>
</table>

**H2/HYDROCARBON MOLE RATIO** 9.82

**HYDROGEN PRESSURE** 104.1 PSIA

**WEIGHT HOURLY SPACE VELOCITY** 6.55 W/Ha/Y

**SUPERFICIAL RESIDENCE TIME** 1.31 SEC

**MATERIAL BALANCE** 99.26 PERCENT

**MOLES PRODUCT/100 MOLES FEED**

| **ISO C5** | 1.56 |
| **N C5**   | 18.97 |
| **220MB**  | 0.52 |
| **2MP**    | 14.32 |
| **3MP**    | 4.93 |
| **NC6**    | 59.70 |

**C5 RATE CONSTANT** 0.101 CC/GM/SEC

**C6 RATE CONSTANT** 0.374 CC/GM/SEC
RUN MI-14

TEMPERATURE 465° F
PRESSURE 100. Psig
CATALYST WEIGHT 2.000 Grams
CATALYST TYPE LJJ 289

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
<th>NORMAL PENTANE</th>
<th>0.53</th>
<th>5.66 Psia</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL HEXANE</td>
<td>0.47</td>
<td></td>
<td>5.00</td>
<td>Psia</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO 9.76
HYDROGEN PRESSURE 104.0 Psia
WEIGHT HOURLY SPACE VELOCITY 6.43 W/HP/H
SUPERFICIAL RESIDENCE TIME 1.26 Sec
MATERIAL BALANCE 99.33 Percent

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>ISOC5</th>
<th>5.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>N C5</td>
<td>53.26</td>
</tr>
<tr>
<td>22DM</td>
<td>0.13</td>
</tr>
<tr>
<td>2MP</td>
<td>0.97</td>
</tr>
<tr>
<td>3MP</td>
<td>2.79</td>
</tr>
<tr>
<td>NCS5</td>
<td>28.14</td>
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</tbody>
</table>

C5 RATE CONSTANT 0.137 CC/GM/SEC
C6 RATE CONSTANT 0.519 CC/GM/SEC

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RUN MI-15

TEMPERATURE 465° DEG F
PRESSURE 100 PSIG
CATALYST WEIGHT 2,000 GRAMS
CATALYST TYPE LJL 289

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.77</td>
<td>8.23 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>2.42 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO 9.76
HYDROGEN PRESSURE 104.0 PSIA
WEIGHT HOURLY SPACE VELOCITY 6.35 W/HR/W
SUPERFICIAL RESIDENCE TIME 1.23 SEC
MATERIAL BALANCE 103.22 PERCENT

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>6.37</td>
</tr>
<tr>
<td>N C5</td>
<td>59.95</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.05</td>
</tr>
<tr>
<td>2MP</td>
<td>8.01</td>
</tr>
<tr>
<td>3MP</td>
<td>2.36</td>
</tr>
<tr>
<td>NC6</td>
<td>24.26</td>
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</tbody>
</table>

C5 RATE CONSTANT 0.143 CC/GM/SEC
C6 RATE CONSTANT 0.567 CC/GM/SEC
## RUN MI-19

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465.0°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>192.0 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.002 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 289</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.17</td>
<td>1.81 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.93</td>
<td>9.05 PSIA</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>18.04</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.8 PSIA</td>
<td></td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.54 W/Hr/W</td>
<td></td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.35 SEC</td>
<td></td>
</tr>
<tr>
<td>Material Balance</td>
<td>100.26 Percent</td>
<td></td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>0.85</td>
</tr>
<tr>
<td>N C5</td>
<td>23.08</td>
</tr>
<tr>
<td>220MB</td>
<td>0.37</td>
</tr>
<tr>
<td>2MP</td>
<td>4.87</td>
</tr>
<tr>
<td>3MP</td>
<td>1.95</td>
</tr>
<tr>
<td>NC6</td>
<td>68.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 Rate Constant</td>
<td>0.045 CC/GM/SEC</td>
</tr>
<tr>
<td>C6 Rate Constant</td>
<td>0.124 CC/GM/SEC</td>
</tr>
</tbody>
</table>
### RUN MI-20

**Temperature** 465°F  
**Pressure** 192 OSIG  
**Catalyst Weight** 2.002 Grams  
**Catalyst Type** LJ 289  

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>5.79 PSI</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>5.11 PSI</td>
</tr>
</tbody>
</table>

**H₂/Hydrocarbon Mole Ratio** 17.97  
**Hydrogen Pressure** 195.8 PSI  
**Weight Hourly Space Velocity** 6.43 W/Hr/W  
**Superficial Residence Time** 1.20 SEC  
**Material Balance** 99.99 Percent  

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>1.99</td>
</tr>
<tr>
<td>N C5</td>
<td>50.20</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.10</td>
</tr>
<tr>
<td>2MP</td>
<td>3.71</td>
</tr>
<tr>
<td>3MP</td>
<td>1.46</td>
</tr>
<tr>
<td>NC6</td>
<td>42.54</td>
</tr>
</tbody>
</table>

**C5 Rate Constant** 0.050 CC/GM/SEC  
**C6 Rate Constant** 0.152 CC/GM/SEC  

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RUN MI-21

TEMPERATURE 465° DEG F
PRESSURE 192 PSIG
CATALYST WEIGHT 2.002 GRAMS
CATALYST TYPE LJJ 239

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.77</td>
<td>8.47 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>0.23</td>
<td>2.49 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO 17.86
HYDROGEN PRESSURE 195.7 PSIA
WEIGHT HOURLY SPACE VELOCITY 6.34 W/HR/W
SUPERFICIAL RESIDENCE TIME 1.26 SEC
MATERIAL BALANCE 98.65 PERCENT

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>3.33</td>
</tr>
<tr>
<td>N C5</td>
<td>74.39</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.0</td>
</tr>
<tr>
<td>2MP</td>
<td>1.84</td>
</tr>
<tr>
<td>3MP</td>
<td>0.44</td>
</tr>
<tr>
<td>NC6</td>
<td>20.01</td>
</tr>
</tbody>
</table>

C5 RATE CONSTANT 0.059 CC/GM/SEC
C6 RATE CONSTANT 0.144 CC/GM/SEC
Run MI-22

**Temperature** 465° Deg F
**Pressure** 299 PSIG
**Catalyst Weight** 2.007 Grams
**Catalyst Type** LJJI

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Normal Pentane</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
<th>Normal Hexane</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.17</td>
<td>3.19 PSIA</td>
<td></td>
<td>0.83</td>
<td>15.95 PSIA</td>
</tr>
</tbody>
</table>

**H₂/Hydrocarbon Mole Ratio** 14.87
**Hydrogen Pressure** 284.6 PSIA
**Weight Hourly Space Velocity** 6.33 W/HR/W
**Superficial Residence Time** 2.36 SEC
**Material Balance** 113.09 Percent

**Moles Product/100 Moles Feed**

| ISO C₅  | 1.52  |
| N C₅   | 35.03 |
| 22DMB  | 0.09  |
| 2MP    | 8.27  |
| 3MP    | 3.63  |
| NC₆    | 51.45 |

**C₅ Rate Constant** 0.030 CC/GM/SEC
**C₆ Rate Constant** 0.150 CC/GM/SEC
**RUN MI-23**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465.0°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>291.0 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.007 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 289</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>10.25 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>9.05 PSIA</td>
</tr>
</tbody>
</table>

| Mole Ratio         | 14.84         |
| Hydrogen Pressure  | 286.4 PSIA    |
| Weight Hourly Space Velocity | 6.41 WHR/W |
| Superficial Residence Time | 2.30 SEC |

**Material Balance**

<table>
<thead>
<tr>
<th>Moles Product/100 Moles Feed</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>2.32</td>
</tr>
<tr>
<td>N C5</td>
<td>50.95</td>
</tr>
<tr>
<td>22DMB</td>
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<td>3MP</td>
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<tr>
<td>NC6</td>
<td>37.44</td>
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<table>
<thead>
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<th>Rate Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>C5</td>
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<tr>
<td>C6</td>
<td>0.165 CC/GM/SEC</td>
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**Run MI-24**

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</tr>
<tr>
<td>Pressure</td>
<td>291 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.007 GRAMS</td>
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<tr>
<td>Catalyst Type</td>
<td>LJJ 259</td>
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**Hydrocarbon Feed Composition**

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<thead>
<tr>
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<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.77</td>
<td>14.88 PSIA</td>
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<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>4.38 PSIA</td>
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<table>
<thead>
<tr>
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<tbody>
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</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>286.4 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.33 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>2.22 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
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**Moles Product/100 Moles Feed**

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<th>Component</th>
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<td>n C5</td>
<td>69.55</td>
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<td>22DM</td>
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<tr>
<td>2MP</td>
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<td>3MP</td>
<td>1.95</td>
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C5 Rate Constant: 0.043 CC/GM/SEC

C6 Rate Constant: 0.205 CC/GM/SEC
### Run MI-25

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<td>Pressure</td>
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<tr>
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<td>2.013 Grams</td>
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<td>Catalyst Type</td>
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### Hydrocarbon Feed Composition

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<tr>
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<th>Partial Pressure</th>
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<td>Normal Pentane</td>
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<tr>
<td>Normal Hexane</td>
<td>0.83</td>
<td>16.09 PSIA</td>
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<table>
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<tr>
<td>Hydrogen Pressure</td>
<td>286.4 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.51 WHR/W</td>
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<tr>
<td>Superficial Residence Time</td>
<td>3.08 SEC</td>
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<td>Material Balance</td>
<td>105.53 Percent</td>
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### Moles Product/100 Moles Feed

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<td>N C₅</td>
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<td>22DMB</td>
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<td>2MP</td>
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<td>3MP</td>
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<td>NC₆</td>
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### RUN M1-26

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<td>Temperature</td>
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<tr>
<td>Pressure</td>
<td>291 PSIG</td>
</tr>
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<td>2.013 GRAMS</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
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#### Hydrocarbon Feed Composition

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<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
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<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>10.27 PSIA</td>
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<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>9.06 PSIA</td>
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<th>MOLE RATIO</th>
<th>PARTIAL PRESS</th>
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<tr>
<td>H2/HYDROCARBON</td>
<td>14.82</td>
</tr>
<tr>
<td>HYDROGEN PRESS</td>
<td>286.4 PSIA</td>
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<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.39 W/HR/W</td>
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<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>2.94 SEC</td>
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<tr>
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#### Moles Product/100 Moles Feed

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<td>N C5</td>
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<td>22DMB</td>
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<td>2MP</td>
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<td>3MP</td>
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<td>NC6</td>
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<table>
<thead>
<tr>
<th>RATE CONSTANT</th>
<th>CC/GM/SEC</th>
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<tr>
<td>C5</td>
<td>0.027</td>
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<td>C6</td>
<td>0.031</td>
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**RUN MI-27**

<table>
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<tbody>
<tr>
<td>PRESSURE</td>
<td>PSIG</td>
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<td>CATALYST WEIGHT</td>
<td>GRAMS</td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>HJF 243</td>
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**HYDROCARBON FEED COMPOSITION**

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<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
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<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.77</td>
<td>15.13 PSIA</td>
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<tr>
<td>NORMAL HEXANE</td>
<td>0.23</td>
<td>4.45 PSIA</td>
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<table>
<thead>
<tr>
<th>H2/HYDROCARBON MOLE RATIO</th>
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</tr>
</thead>
<tbody>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>286.1 PSIA</td>
<td></td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.31 WHR/W</td>
<td></td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>2.89 SEC</td>
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<tr>
<td>MATERIAL BALANCE</td>
<td>105.42 PERCENT</td>
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**MOLES PRODUCT/100 MOLES FEED**

| IS0 C5  | 2.44 |
| N C5    | 74.12 |
| 22CMB   | 0.0  |
| 2MP     | 0.67 |
| 3MP     | 0.32 |
| NC6     | 22.45 |

| C5 RATE CONSTANT | 0.024 CC/GM/SEC |
| C6 RATE CONSTANT | 0.032 CC/GM/SEC |
RUN MI-28

<p>| | | |</p>
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<tr>
<td>PRESSURE</td>
<td>300 PSIG</td>
<td></td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.013 GRAMS</td>
<td></td>
</tr>
<tr>
<td>CATALYST TYPE</td>
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**HYDROCARBON FEED COMPOSITION**

<table>
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<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.17</td>
<td>4.70 PSIA</td>
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<td>NORMAL HEXANE</td>
<td>0.83</td>
<td>23.51 PSIA</td>
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</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
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<td></td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>286.5 PSIA</td>
<td></td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.51 W/HR/W</td>
<td></td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>4.49 SEC</td>
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<td>MATERIAL BALANCE</td>
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**MOLES PRODUCT/100 MOLES FEED**

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<thead>
<tr>
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<tbody>
<tr>
<td>ISO C5</td>
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<tr>
<td>N C5</td>
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<td>22DMB</td>
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<td>2MP</td>
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<tr>
<td>3MP</td>
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<td>NCS</td>
<td>30.41</td>
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<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>C5 RATE CONSTANT</td>
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<td>C6 RATE CONSTANT</td>
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### RUN MI-29

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<tr>
<td>Pressure</td>
<td>300 psig</td>
</tr>
<tr>
<td>Catalyst Weight</td>
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<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
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#### Hydrocarbon Feed Composition

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<tr>
<th>Component</th>
<th>Mol Fraction</th>
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<tbody>
<tr>
<td>Normal Pentane</td>
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<tr>
<td>Normal Hexane</td>
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<td>13.38 psia</td>
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<table>
<thead>
<tr>
<th>Ratio</th>
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<tbody>
<tr>
<td>H2/Hydrocarbon</td>
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<table>
<thead>
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<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>286.2 psia</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.39 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>4.35 sec</td>
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<td>Material Balance</td>
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#### Moles Product/100 Moles Feed

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<table>
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<td>C6</td>
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RUN MI-30

<table>
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<tr>
<td>Pressure</td>
<td>300 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.013 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
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<tbody>
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<td>Normal Pentane</td>
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**Other Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>286.1 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.31 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>4.23 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>103.72 PERCENT</td>
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**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso C₅</td>
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<tr>
<td>N C₅</td>
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<td>3MP</td>
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<tr>
<td>N C₆</td>
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<tr>
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<td>100</td>
<td>PSIG</td>
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<td>CATALYST WEIGHT</td>
<td>2.003</td>
<td>GRAMS</td>
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<tr>
<td>CATALYST TYPE</td>
<td>HJE 243</td>
<td></td>
</tr>
<tr>
<td>HYDROCARBON FEED COMPOSITION</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NORMAL PENTANE</td>
<td>0.17</td>
<td>MOLE FRACTION</td>
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<td>NORMAL HEXANE</td>
<td>0.83</td>
<td>PARTIAL PRESS</td>
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<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>9.96</td>
<td>PSIA</td>
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<td>HYDROGEN PRESSURE</td>
<td>104.2</td>
<td>W/HR/W</td>
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<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
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<td>SEC</td>
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<td>SUPERFICIAL RESIDENCE TIME</td>
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<td>MATERIAL BALANCE</td>
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<td>PERCENT</td>
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<th>FEED</th>
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<td>3MP</td>
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<tr>
<td>NC6</td>
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<tr>
<td>C5 RATE CONSTANT</td>
<td>0.042</td>
<td>CC/GM/SEC</td>
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<td>C6 RATE CONSTANT</td>
<td>0.203</td>
<td>CC/GM/SEC</td>
</tr>
</tbody>
</table>

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## RUN MI-32

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>465°F</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>100 PSIG</td>
</tr>
<tr>
<td><strong>Catalyst Weight</strong></td>
<td>2.003 Grams</td>
</tr>
<tr>
<td><strong>Catalyst Type</strong></td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

## Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure (PSIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>5.44</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>4.89</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon mole ratio</td>
<td>10.00</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>104.3 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.42 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.58 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>103.52 Percent</td>
</tr>
</tbody>
</table>

## Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>3.45</td>
</tr>
<tr>
<td>N C5</td>
<td>47.52</td>
</tr>
<tr>
<td>220MB</td>
<td>0.32</td>
</tr>
<tr>
<td>2MP</td>
<td>6.50</td>
</tr>
<tr>
<td>3MP</td>
<td>0.3</td>
</tr>
<tr>
<td>NC6</td>
<td>42.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 Rate Constant</td>
<td>0.095 CC/GM/SEC</td>
</tr>
<tr>
<td>C6 Rate Constant</td>
<td>0.209 CC/GM/SEC</td>
</tr>
</tbody>
</table>

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RUN MI-33

TEMPERATURE: 465° DEG F
PRESSURE: 100 PSIG
CATALYST WEIGHT: 2.003 GRAMS
CATALYST TYPE: HJE 243

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.77</td>
<td>8.16 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>0.23</td>
<td>2.40 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO: 9.86
HYDROGEN PRESSURE: 104.1 PSIA
WEIGHT HOURLY SPACE VELOCITY: 6.34 W/HR/W
SUPERFICIAL RESIDENCE TIME: 1.55 SEC
MATERIAL BALANCE: 103.78 PERCENT

MOLES PRODUCT/100 MOLES FEED

| ISO C5   | 4.36 |
| N C5     | 72.29 |
| 220MB    | 0.10 |
| 2MP      | 2.78 |
| 3MP      | 0.0  |
| NC6      | 20.49 |

C5 RATE CONSTANT: 0.081 CC/GM/SEC
C6 RATE CONSTANT: 0.183 CC/GM/SEC
RUN MI-34

<table>
<thead>
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<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465. DEG F</td>
</tr>
<tr>
<td>Pressure</td>
<td>200. PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.007 GRAMS</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.17</td>
<td>3.26 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>16.25 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO | 9.98
HYDROGEN PRESSURE       | 155.2 PSIA
WEIGHT HOURLY SPACE VELOCITY | 6.53 W/HR/W
SUPERFICIAL RESIDENCE TIME | 3.10 SEC
MATERIAL BALANCE         | 109.41 PERCENT

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>1.47</td>
</tr>
<tr>
<td>N C5</td>
<td>49.91</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.0</td>
</tr>
<tr>
<td>2MP</td>
<td>3.53</td>
</tr>
<tr>
<td>3MP</td>
<td>1.64</td>
</tr>
<tr>
<td>NC6</td>
<td>43.45</td>
</tr>
</tbody>
</table>

C5 RATE CONSTANT | 0.020 CC/GM/SEC
C6 RATE CONSTANT | 0.079 CC/GM/SEC
### RUN MI-35

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465</td>
<td>DEG F</td>
</tr>
<tr>
<td>Pressure</td>
<td>200</td>
<td>PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.007</td>
<td>Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
<td></td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>10.47 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>9.24 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.0</td>
<td>PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.41</td>
<td>W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>2.99</td>
<td>SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>104.76</td>
<td>Percent</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>1.84</td>
</tr>
<tr>
<td>N C5</td>
<td>61.82</td>
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<tr>
<td>22DMB</td>
<td>0.03</td>
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<tr>
<td>2MP</td>
<td>1.68</td>
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<tr>
<td>3MP</td>
<td>0.40</td>
</tr>
<tr>
<td>NC6</td>
<td>34.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
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<td>CC/GM/SEC</td>
</tr>
<tr>
<td>C6</td>
<td>0.043</td>
<td>CC/GM/SEC</td>
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### RUN MI-36

<table>
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</thead>
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<td>TEMPERATURE</td>
<td>465.0 °F</td>
</tr>
<tr>
<td>PRESSURE</td>
<td>200.0 PSIG</td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.007 GRAMS</td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

### HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>0.77</td>
<td>15.15 PSIA</td>
</tr>
<tr>
<td>NORMAL HEXANE</td>
<td>0.23</td>
<td>4.46 PSIA</td>
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<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>9.95</td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>195.1 PSIA</td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.33 W/HR/W</td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>2.99 SEC</td>
</tr>
<tr>
<td>MATERIAL BALANCE</td>
<td>102.00 PERCENT</td>
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</tbody>
</table>

### MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>2.56</td>
</tr>
<tr>
<td>N C5</td>
<td>78.59</td>
</tr>
<tr>
<td>22D MB</td>
<td>0.0</td>
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<tr>
<td>2M P</td>
<td>0.83</td>
</tr>
<tr>
<td>3M P</td>
<td>0.12</td>
</tr>
<tr>
<td>NC6</td>
<td>17.90</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.024 CC/GM/SEC</td>
</tr>
<tr>
<td>C6</td>
<td>0.039 CC/GM/SEC</td>
</tr>
</tbody>
</table>

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**RUN MI-37**

<table>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465.4 °F</td>
</tr>
<tr>
<td>Pressure</td>
<td>97.1 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.001 g</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.17</td>
<td>1.17 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.93</td>
<td>5.86 PSIA</td>
</tr>
</tbody>
</table>

| Hydrogen (H2)        | 14.89 PSIA    |
| Hydrocarbon Mole Ratio| 104.7 PSIA   |

| Feed Mole Ratio      | 6.55 WHP/WH |
| Superficial Residence Time | 1.11 sec   |

**Material Balance**

<table>
<thead>
<tr>
<th>Mole Balance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>2.09</td>
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<tr>
<td>N C5</td>
<td>39.69</td>
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<td>22DMB</td>
<td>0.00</td>
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<tr>
<td>2MP</td>
<td>10.24</td>
</tr>
<tr>
<td>3MP</td>
<td>2.30</td>
</tr>
<tr>
<td>NC6</td>
<td>45.68</td>
</tr>
</tbody>
</table>

| C5 Rate Constant  | 0.099 CC/GM/SEC |
| C6 Rate Constant  | 0.476 CC/GM/SEC |

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### RUN M1-38

<table>
<thead>
<tr>
<th>Property</th>
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<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Pressure</td>
<td>97* PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.001 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>3.74 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>3.30 PSIA</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon</td>
<td>14.85</td>
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<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Pressure</td>
<td>104.7 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.43 W/HP/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.07 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>97.90 Percent</td>
</tr>
</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>3.00</td>
</tr>
<tr>
<td>N C5</td>
<td>44.04</td>
</tr>
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<td>225MB</td>
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<td>2°P</td>
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<tr>
<td>3°P</td>
<td>1.78</td>
</tr>
<tr>
<td>N C6</td>
<td>44.07</td>
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</table>

<table>
<thead>
<tr>
<th>Rate Constant C5</th>
<th>Value</th>
<th>0.130 CC/GM/SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Constant C6</td>
<td></td>
<td>0.342 CC/GM/SEC</td>
</tr>
</tbody>
</table>

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RUN MI-39

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465°</td>
<td>F</td>
</tr>
<tr>
<td>Pressure</td>
<td>97</td>
<td>PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.001</td>
<td>Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
<td></td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.77</td>
<td>5.44 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>1.60 PSIA</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 Rate Constant</td>
<td>0.129 CC/GM/SEC</td>
</tr>
<tr>
<td>C6 Rate Constant</td>
<td>0.321 CC/GM/SEC</td>
</tr>
</tbody>
</table>

Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>4.07</td>
</tr>
<tr>
<td>N C5</td>
<td>63.64</td>
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<tr>
<td>22DMB</td>
<td>0.0</td>
</tr>
<tr>
<td>2'MP</td>
<td>3.70</td>
</tr>
<tr>
<td>3'MP</td>
<td>0.90</td>
</tr>
<tr>
<td>NC6</td>
<td>27.70</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465° F</td>
</tr>
<tr>
<td>Pressure</td>
<td>192 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.002 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.17</td>
<td>1.81 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.83</td>
<td>9.05 PSIA</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/Hydrocarbon Mole Ratio</td>
<td>18.02</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.8 PSIA</td>
<td></td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>5.54 W/HR/W</td>
<td></td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.72 SEC</td>
<td></td>
</tr>
<tr>
<td>Material Balance</td>
<td>120.87 Percent</td>
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</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles/100 Moles Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>0.86</td>
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<tr>
<td>N C5</td>
<td>25.16</td>
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<td>22DMB</td>
<td>0.90</td>
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<td>2MP</td>
<td>5.68</td>
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<td>3MP</td>
<td>2.19</td>
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<tr>
<td>NC6</td>
<td>65.32</td>
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</table>

<table>
<thead>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>C6</td>
<td>0.156 CC/GM/SEC</td>
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</tbody>
</table>
RUN MI-44

TEMPERATURE: 465° DEG F
PRESSURE: 192 PSIG
CATALYST WEIGHT: 2.002 GRAMS
CATALYST TYPE: HJE 243

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.53</td>
<td>5.85 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.47</td>
<td>5.16 PSIA</td>
</tr>
</tbody>
</table>

H2/HYDROCARBON MOLE RATIO: 17.78
HYDROGEN PRESSURE: 195.7 PSIA
WEIGHT HOURLY SPACE VELOCITY: 6.43 W/HR/W
SUPERFICIAL RESIDENCE TIME: 1.67 SEC
MATERIAL BALANCE: 101.70 PERCENT

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Moles/100 Mols Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>1.09</td>
</tr>
<tr>
<td>N C5</td>
<td>52.70</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.0</td>
</tr>
<tr>
<td>2MP</td>
<td>0.0</td>
</tr>
<tr>
<td>3MP</td>
<td>0.20</td>
</tr>
<tr>
<td>NC6</td>
<td>41.43</td>
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</table>

C5 RATE CONSTANT: 0.045 CC/GM/SEC
C6 RATE CONSTANT: 0.118 CC/GM/SEC
**RUN MI-45**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>465°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>192 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.002 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>4JE 243</td>
</tr>
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</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>0.77</td>
<td>8.42 PSIA</td>
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<tr>
<td>Normal Hexane</td>
<td>0.23</td>
<td>2.48 PSIA</td>
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<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
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<tbody>
<tr>
<td>H2/Hydrocarbon</td>
<td>17.96</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.8 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Velocity</th>
<th>Value</th>
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<tbody>
<tr>
<td>Weight Hourly Space</td>
<td>6.34 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence</td>
<td>1.60 SEC</td>
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</table>

**Material Balance**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Balance</th>
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<tbody>
<tr>
<td></td>
<td>99.82 Percent</td>
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**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
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<tbody>
<tr>
<td>ISO C5</td>
<td>2.76</td>
</tr>
<tr>
<td>N C5</td>
<td>65.12</td>
</tr>
<tr>
<td>22DMB</td>
<td>0.1</td>
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<tr>
<td>2MP</td>
<td>1.68</td>
</tr>
<tr>
<td>3MP</td>
<td>0.14</td>
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<tr>
<td>NC6</td>
<td>29.5</td>
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<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.055 CC/GM/SEC</td>
</tr>
<tr>
<td>C6</td>
<td>0.080 CC/GM/SEC</td>
</tr>
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RUN C5I-6

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>DEG F</th>
<th>PRESSURE</th>
<th>PSIG</th>
<th>CATALYST WEIGHT</th>
<th>GRAMS</th>
<th>CATALYST TYPE</th>
<th>LJJ 289</th>
</tr>
</thead>
<tbody>
<tr>
<td>465</td>
<td></td>
<td>200</td>
<td></td>
<td>2.012</td>
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HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
<th>PARTIAL PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-PENTANE</td>
<td>1.00</td>
<td>15.34 PSIA</td>
<td>0.0 PSIA</td>
</tr>
<tr>
<td>N-H ExANE</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MOLE RATIO</th>
<th>PARTIAL PRESS</th>
<th>PARTIAL PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2/HC</td>
<td>195.4 PSIA</td>
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</table>

WEIGHT HOURLY SPACE VELOCITY 6.22 W/HR/WEIGHT HOURLY SPACE VELOCITY 2.17 SEC

SUPERFICIAL RESIDENCE TIME 2.17 SEC

MATERIAL BALANCE 92.92 PERCENT

MOLES PRODUCT/100 MOLES FEED

| C5            | 7.60         |
| C6            | 92.40        |

C5 RATE CONSTANT 0.061 CC/SEC
RUN C51-10

<table>
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<tr>
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<th>Value</th>
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<tbody>
<tr>
<td>TEMPERATURE</td>
<td>465 °F</td>
</tr>
<tr>
<td>PRESSURE</td>
<td>300 PSIG</td>
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<tr>
<td>CATALYST WEIGHT</td>
<td>2,030 GRAMS</td>
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<tr>
<td>CATALYST TYPE</td>
<td>LJ229</td>
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HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>1.00</td>
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<tr>
<td>Normal Hexane</td>
<td>0.00</td>
<td>3.00 PSIA</td>
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>10.07</td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>256.3 PSIA</td>
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<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.26 W/HR/W</td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>3.17 SEC</td>
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<tr>
<td>MATERIAL BALANCE</td>
<td>98.79 PERCENT</td>
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MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
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</thead>
<tbody>
<tr>
<td>Iso C5</td>
<td>12.42</td>
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<tr>
<td>N C5</td>
<td>87.58</td>
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</table>

C5 RATE CONSTANT 3.071 CC/MM/SEC
RUN C51-12

TEMPERATURE  465.  DEG F
PRESSURE  100.  PSIG
CATALYST WEIGHT  2.000  GRAMS
CATALYST TYPE  LJ 289

HYDROCARBON FEED COMPOSITION

NORMAL PENTANE  MOLE FRACTION  PARTIAL PRESS
NORMAL HEXANE  1.00  10.43  PSIA

H2/HYDROCARBON MOLE RATIO  10.00
HYDROGEN PRESSURE  104.3  PSIA
WEIGHT HOURLY SPACE VELOCITY  6.26  W/HR/W
SUPERFICIAL RESIDENCE TIME  1.16  SEC
MATERIAL BALANCE  97.66  PERCENT

MOLES PRODUCT/100 MOLES FEED

ISO C5  15.19
n C5  84.91

CAT RATE CONSTANT  0.241  CC/GM/SEC
RUN C5I-15

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
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<tr>
<td>Pressure</td>
<td>192 PSI</td>
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<tr>
<td>Catalyst Weight</td>
<td>2.002 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 289</td>
</tr>
</tbody>
</table>

**Hydrocarbon Feed Composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>1.00</td>
<td>10.97 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>17.95</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>195.7 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.26 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.22 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>101.12 PERCENT</td>
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</tbody>
</table>

**Moles Product/100 Moles Feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>5.20</td>
</tr>
<tr>
<td>N C5</td>
<td>4.50</td>
</tr>
<tr>
<td>C5 Rate Constant</td>
<td>0.073 CC/3H/SEC</td>
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</tbody>
</table>

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### RUN C51-16

<table>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>465° F</td>
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<tr>
<td>Pressure</td>
<td>290 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.007 Grams</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>LJJ 289</td>
</tr>
</tbody>
</table>

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
<td>1.00</td>
<td>19.13 PSIA</td>
</tr>
<tr>
<td>Normal Hexane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>14.39</td>
</tr>
<tr>
<td>Hydrogen Pressure</td>
<td>235.5 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.24 W/HR/W</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>2.15 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>103.68 Percent</td>
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<table>
<thead>
<tr>
<th>Component</th>
<th>Moles Product/100 Moles Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso C5</td>
<td>7.11</td>
</tr>
<tr>
<td>N C5</td>
<td>92.89</td>
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</table>

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.059 CC/GM/SEC</td>
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</table>
### RUN C5I-17

<table>
<thead>
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<th>Value</th>
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<td>465 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>291 PSIG</td>
</tr>
<tr>
<td>Catalyst Weight</td>
<td>2.013 GRAMS</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>HJE 243</td>
</tr>
</tbody>
</table>

### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
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</tr>
<tr>
<td>Normal Hexane</td>
<td>0.0</td>
<td>0.0 PSIA</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/Hydrocarbon Mole Ratio</td>
<td>14.66</td>
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<tr>
<td>Hydrogen Pressure</td>
<td>296.2 PSIA</td>
</tr>
<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.22 w/HR/W</td>
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<tr>
<td>Superficial Residence Time</td>
<td>2.30 SEC</td>
</tr>
<tr>
<td>Material Balance</td>
<td>103.51 PERCENT</td>
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### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles Product/100 Moles Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>6.69</td>
</tr>
<tr>
<td>ν C5</td>
<td>93.32</td>
</tr>
</tbody>
</table>

**Rate Constant**: 0.053 CC/gm/sec
RUN C51-18

TEMPERATURE 465° DEG F
PRESSURE 300* PSIG
CATALYST WEIGHT 2.013 GRAMS
CATALYST TYPE HUE 243

HYDROCARBON FEED COMPOSITION

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
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</thead>
<tbody>
<tr>
<td>NORMAL PENTANE</td>
<td>1.00</td>
<td>23.46 PSIA</td>
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<tr>
<td>NORMAL HEXANE</td>
<td>0.0</td>
<td>0.0 PSIA</td>
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</table>

H2/HYDROCARBON MOLE RATIO 10.06
HYDROGEN PRESSURE 286.2 PSIA
WEIGHT HOURLY SPACE VELOCITY 6.22 W/HR/W
SUPERFICIAL RESIDENCE TIME 4.03 SEC
MATERIAL BALANCE 100.86 PERCENT

MOLES PRODUCT/100 MOLES FEED

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>MOLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 25</td>
<td>8.36</td>
</tr>
<tr>
<td>4 C0</td>
<td>91.64</td>
</tr>
</tbody>
</table>

C0 RATE CONSTANT 6.04E-6 CC/CM/SEC

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Run C5I-19

| TEMPERATURE | 465 °C | DEG F |
| PRESSURE | 100 PSIG |
| CATALYST WEIGHT | 2.003 GRAMS |
| CATALYST TYPE | HJE 243 |

**HYDROCARBON FEED COMPOSITION**

| HYDROCARBON | MOLE FRACTION | PARTIAL PRESSURE |
| N-PENTANE | 1.00 | 10.54 PSIA |
| N-Hexane | 0.0 | 0.0 PSIA |

- $n_2$/HYDROCARBON MOLE RATIO = 9.68
- HYDROGEN PRESSURE = 104.2 PSIA
- WEIGHT HOURLY SPACE VELOCITY = 6.25 W/HR/W
- SUPERFICIAL RESIDENCE TIME = 1.50 SEC
- MATERIAL BALANCE = 119.75 PERCENT

**MOLES PRODUCT/100 MOLES FEED**

| ISO C5 | 12.16 |
| N C5 | 57.54 |

C5 RATE CONSTANT = 1.167 CC/MM^3/SEC
RUN C51-20

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>TEMPERATURE</td>
<td>465. DEG F</td>
<td></td>
</tr>
<tr>
<td>PRESSURE</td>
<td>200. PSIG</td>
<td></td>
</tr>
<tr>
<td>CATALYST WEIGHT</td>
<td>2.007 GRAMS</td>
<td></td>
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<tr>
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<td>HJE 243</td>
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**HYDROCARBON FEED COMPOSITION**

<table>
<thead>
<tr>
<th></th>
<th>MOLE FRACTION</th>
<th>PARTIAL PRESS</th>
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<tbody>
<tr>
<td>NORMAL PENTANE</td>
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<td>19.61 PSIA</td>
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<tr>
<td>NORMAL HexANE</td>
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<td>0.0 PSIA</td>
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<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>9.95</td>
<td></td>
</tr>
<tr>
<td>HYDROGEN PRESSURE</td>
<td>195.1 PSIA</td>
<td></td>
</tr>
<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>6.24 W/HR/ft</td>
<td></td>
</tr>
<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>2.80 SEC</td>
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</tr>
<tr>
<td>MATERIAL BALANCE</td>
<td>99.71 PERCENT</td>
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</table>

**MOLES PRODUCT/100 MOLES FEED**

| ISO C5   | 11.13 |
| V C5     | 96.97 |
| C5 RATE CONSTANT | 0.391 CC/GM/SEC |

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### RUN C5I-21

<table>
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<tr>
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<th>Value</th>
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</thead>
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<tr>
<td>Pressure</td>
<td>675 psig</td>
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<tr>
<td>Catalyst Weight</td>
<td>2.001 lbs</td>
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<tr>
<td>Catalyst Type</td>
<td>HFe 24.3</td>
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### Hydrocarbon Feed Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Partial Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Pentane</td>
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<td>7.04 psia</td>
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<tr>
<td>Normal Hexane</td>
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<td>0.00 psia</td>
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/Hydrocarbon Mole Ratio</td>
<td>1.87</td>
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<tr>
<td>Hydrogen Pressure</td>
<td>104.7 psia</td>
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<tr>
<td>Weight Hourly Space Velocity</td>
<td>6.26 W/HR/H</td>
</tr>
<tr>
<td>Superficial Residence Time</td>
<td>1.00 sec</td>
</tr>
<tr>
<td>Material Balance</td>
<td>99.13 percent</td>
</tr>
</tbody>
</table>

### Moles Product/100 Moles Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO C5</td>
<td>10.17</td>
</tr>
<tr>
<td>N C5</td>
<td>89.83</td>
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### CR Rate Constant

<table>
<thead>
<tr>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>0.231</td>
<td>cc/gm/Sec</td>
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**RUN C5I-22**

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<td>TEMPERATURE</td>
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<tr>
<td>PRESSURE</td>
<td>192PSIG</td>
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<tr>
<td>CATALYST WEIGHT</td>
<td>2.001</td>
</tr>
<tr>
<td>CATALYST TYPE</td>
<td>HJE 243</td>
</tr>
<tr>
<td>HYDROCARBON FEED COMPOSITION</td>
<td></td>
</tr>
<tr>
<td>NORMAL PENTANE</td>
<td>1.00 MOL FRACTION</td>
</tr>
<tr>
<td>NORMAL HFXANE</td>
<td>0.0 MOL FRACTION</td>
</tr>
<tr>
<td>H2/HYDROCARBON MOLE RATIO</td>
<td>17.58</td>
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<tr>
<td>HYDROGEN PRESSURE</td>
<td>195.6 PSIA</td>
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<tr>
<td>WEIGHT HOURLY SPACE VELOCITY</td>
<td>5.26 WHR/W</td>
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<tr>
<td>SUPERFICIAL RESIDENCE TIME</td>
<td>1.59 SEC</td>
</tr>
<tr>
<td>MATERIAL BALANCE</td>
<td>104.96 PERCENT</td>
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**MOLES PRODUCT/100 MOLES FEED**

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<tr>
<th>Product</th>
<th>Moles</th>
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<tr>
<td>ISO C5</td>
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<tr>
<td>N C5</td>
<td>94.31</td>
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**C5 RATE CONSTANT**

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<th>Value</th>
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<tr>
<td>0.079</td>
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APPENDIX 5

Nomenclature
Nomenclature

A Cross Sectional Area
A_j Deactivation Time Constant
a Redlich Kwong Constant
B_j Adsorption Parameter of Component j
b Redlich Kwong Constant
C_i Concentration of Component i
d_p Catalyst Particle Diameter
D Total Diffusivity
D_c Configurational Diffusity
D_e Effective Diffusivity
D_k Knudsen Diffusivity
D_m Molecular Diffusivity
D_s "Slip" Region Diffusivity
E' True Reaction Activation Energy
E_app Apparent Reaction Activation Energy
\Delta H_m Heat of Adsorption of Component m
h Redlich Kwong Constant
h_s Thiele Modulus for Spherical Catalyst Particles
k General Reaction Rate Constant
k General Surface Reaction Rate Constant
k_i Boltzman's Constant Reaction Rate Constant for Reactant i
k_o Surface Reaction Rate Constant Pre-exponential Term
K General Equilibrium Constant
K_i Adsorption Constant for Species i
### Nomenclature (Cont'd.)

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<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>M</td>
<td>Mixing Intensity</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Diameter</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Molar Flow Rate of Component $i$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of Catalyst Active Sites</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Moles of Component $i$</td>
</tr>
<tr>
<td>PD</td>
<td>Catalyst Pore Diameter</td>
</tr>
<tr>
<td>Pe</td>
<td>Peclet Number</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Partial Pressure of Species $i$</td>
</tr>
<tr>
<td>$P_{tot}$</td>
<td>Total Pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Overall Reaction Rate, Catalyst Pore Radius</td>
</tr>
<tr>
<td>$\tilde{R}$</td>
<td>Hydrogen/Hydrocarbon Mole Ratio</td>
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<tr>
<td>$R$</td>
<td>Ideal Gas Constant</td>
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<tr>
<td>$Re_P$</td>
<td>Particle Reynolds Number</td>
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<tr>
<td>S</td>
<td>Specific Surface Area of the Catalyst</td>
</tr>
<tr>
<td>T</td>
<td>Absolute Temperature</td>
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<tr>
<td>$t_H$</td>
<td>Holding Time</td>
</tr>
<tr>
<td>V</td>
<td>Molar Volume</td>
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<tr>
<td>$V_T$</td>
<td>Total Volumetric Molar Flow Rate</td>
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<tr>
<td>$w$</td>
<td>Relative number of Water Molecules in the General Zeolite Structure</td>
</tr>
<tr>
<td>W</td>
<td>Mass Flow Rate Weight of Catalyst</td>
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<tr>
<td>X</td>
<td>Relative Number of Alumina Molecules in the General Zeolite Structure</td>
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<tr>
<td>Y</td>
<td>Relative Number of Silica Molecules in the General Zeolite Structure</td>
</tr>
<tr>
<td>$Y^*_i$</td>
<td>Hydrogen-free Mole Fraction of Species $i$ at Equilibrium</td>
</tr>
<tr>
<td>Z</td>
<td>Compressibility</td>
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### Greek Symbols

<table>
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<th>Symbol</th>
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<tr>
<td>$\epsilon$</td>
<td>Porosity of Catalyst Particle</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Mean Free Path of Molecule $i$</td>
</tr>
<tr>
<td>$\hat{\phi_i}$</td>
<td>Fugacity of Component $i$ in a Mixture</td>
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<tr>
<td>$\rho_i$</td>
<td>Density of Species $i$</td>
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<tr>
<td>$\rho_B$</td>
<td>Bulk Density of the Catalyst</td>
</tr>
<tr>
<td>$\rho_G$</td>
<td>Molar Gas Density</td>
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<tr>
<td>$\rho_P$</td>
<td>True Catalyst Particle Density</td>
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<tr>
<td>$\sigma$</td>
<td>Molecular Diameter, equation (3)</td>
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<tr>
<td>$\tau$</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>Constriction Factor, equation (6)</td>
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<tr>
<td>$\mu$</td>
<td>Tortuosity Factor</td>
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<td></td>
<td>Weight Hourly Space Velocity</td>
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<tr>
<td></td>
<td>Fluid Viscosity</td>
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VITA

James Jerome Spivey was born July 26, 1950 in Gastonia, North Carolina. He attended Grimsley Senior High School in Greensboro, North Carolina and graduated in 1968.

He attended North Carolina State University in Raleigh, North Carolina on an athletic scholarship in track and was co-captain of the track team in 1971 and 1972. He received his B.S. degree in Chemical Engineering in May, 1972. Work toward an M.S. degree in the same field was begun after graduation and completed in February, 1974. He accepted employment at Ethyl Corporation in Baton Rouge, Louisiana in February 1974. Part-time class and experimental work was begun toward a Ph.D. degree in 1975. He spent a year in residence at LSU in 1978 with a leave of absence from Ethyl Corporation. Work toward the Ph.D. degree was completed in 1980. He is currently employed as a Process Design Engineer at Ethyl Corporation.
Candidate: James Jerome Spivey

Major Field: Chemical Engineering

Title of Thesis: Hydroisomerization of Pentane and Hexane Mixtures on Zeolite Catalysts

Date of Examination: July 14, 1980

EXAMINING COMMITTEE:

Approved:

[Signatures]

Dean of the Graduate School

Date of Examination: July 14, 1980

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