

Benzene Production over the Catforming Catalyst

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PREVIOUS papers (1, 2, 4) have dealt with the development and use of the Atlantic Catforming catalyst for the octane improvement of straight-run naphthas. Platinum on silica-alumina is an active catalyst for dehydrogenation of naphthenes, isomerization of paraffins and naphthenes, dehydrocyclization of paraffins, and the hydrocracking reactions. By deactivating the silica-alumina base, these reactions can be properly balanced to improve octane number with a minimum loss in volume of the naphtha being reformed.

The production of benzene from a C₆ naphtha fraction requires a catalyst of similar balanced activity. In this case, the two most important reactions that must be promoted are the dehydrogenation of cyclohexane (CH) and the dehydroisomerization of methylcyclopentane (MCP). The dehydroisomerization of methylcyclopentane is the more difficult to achieve, but because about 50% of the naphthenic hydrocarbons in most naphthas are of the cyclopentane type (3), the catalyst used for making benzene must be very active in catalyzing this reaction. Dehydroisomerization involves an isomerization action of the catalyst. This must be done without appreciable hydrocracking, or benzene will be lost through the formation of hexanes and paraffins of lower molecular weight. The problem is again one of selectivity or balancing the various reactions that the catalyst promotes.

This paper presents the results of an experimental program carried out to investigate the conditions under which the highest conversions of methylcyclopentane and cyclohexane to benzene are obtained using the Atlantic Catforming catalyst. The work consists of two parts: an investigation of the effect of operating variables on the reactions of a given mixture of hydrocarbons, and a study of the effect of the composition of the mixture, when these optimum operating variables are used.

STUDY OF OPERATING VARIABLES

For this investigation, a synthetic blend consisting of 40% hexane, 30% methylcyclopentane, and 30% cyclohexane was used. This was chosen because it is similar to a typical C₆ naphtha cut but is more easily analyzed by mass spectrometry. Three variables—pressure, liquid space velocity, and temperature—were studied. At each condition of pressure and space velocity, a 150° F. range of temperature was covered in 50° intervals. The results are presented in Table I.

The high pressure, dynamic, bench scale unit used in this work and the procedure used in its operation have been described (1). Pure cyclohexane, methylcyclopentane, and hexane obtained from the Phillips Petroleum Corp. were used as received.

PRESSURE. Two pressures were investigated, 175 and 500 pounds per square inch gage. These were chosen

because at higher pressures the benzene-cyclohexane equilibrium is unfavorable for the production of benzene except at very high temperatures, and at pressures below 175 pounds per square inch gage deactivation as a result of coke laid down on the catalyst becomes a problem.

Pressure affects both the dehydrogenation of cyclohexane and the dehydroisomerization of methylcyclopentane. Its effect on dehydrogenation is shown in Figure 1, A, B, and C. In these plots, only the reaction between benzene and cyclohexane is considered. The percentage of benzene in the product is computed and compared to the equilibrium values, shown by the lines calculated from thermodynamic data (8), with corrections for nonideality. Because of the complexity of the temperature distribution in the catalyst bed, it is difficult to check the attainment of equilibrium accurately. The experimentally found benzene concentrations, therefore, are plotted against three different temperatures:

That obtained by averaging the readings taken at small intervals through the bed, using a thermocouple located in a well through the center of the bed.

The catalyst bed outlet temperature, also measured in this well. The catalyst furnace temperature.

In the first two cases the observed concentrations of benzene are equal to or higher than the equilibrium values, which is to be expected, as these temperatures are equal to or lower than the furnace temperature. In the plot against furnace temperature, agreement within experimental error is obtained except for two points at the lower temperatures at 175 pounds per square inch pressure and a space velocity of 6.0 volumes of feed per volume of catalyst per hour. Even here, however, the experimental value corresponds to an equilibrium value at a temperature that lies between the observed outlet and furnace temperatures. These data, then, indicate that under the conditions investigated the dehydrogenation reaction goes rapidly to approximately equilibrium, as reported for other platinum catalysts (5). For

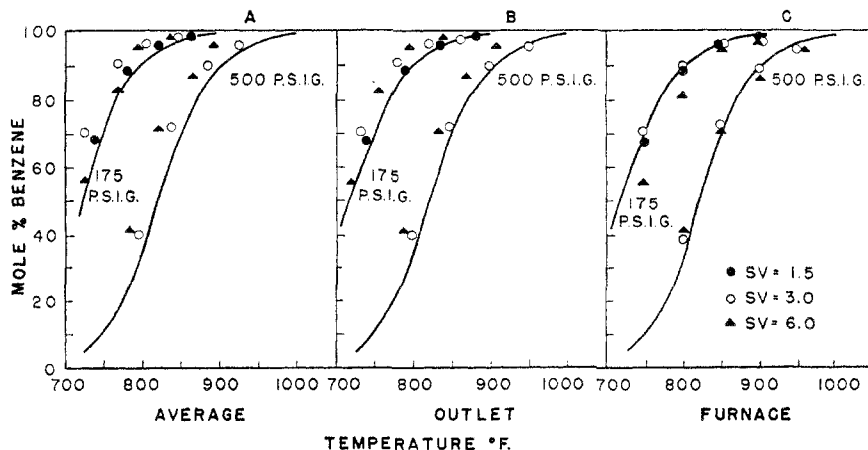


Figure 1. Dehydrogenation Equilibrium of Benzene-Cyclohexane
40% n-C₆-30% MCP-30% CH

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TABLE I. 40% HEXANE-30% METHYLCYCLOPENTANE-30% CYCLOHEXANE
(H₂/HC = 10)

Pressure, lb./sq. inch gage LHSV	175			175			500			500		
	1.5			3.0			6.0			3.0		
Temp., ° F.												
Furnace	751	800	849	750	802	852	901	902	849	902	950	950
Inlet	750	796	840	750	800	850	901	901	800	848	899	949
Minimum	750	796	840	750	800	850	901	901	800	848	899	949
Outlet	742	788	834	732	778	820	862	837	786	839	885	927
Average	738	778	818	726	766	806	847	837	786	839	885	927
Products, moles/100 moles feed												
C ₆ -C ₁₀ ^a	3.5	3.0	1.2	3.0	1.1	1.1	2.3	1.9	1.5	2.3	6.8	16.5
n-C ₆	39.5	25.0	16.9	38.6	35.0	30.7	25.2	26.7	36.9	26.5	21.7	18.5
iso-C ₆	8.7	14.0	25.2	2.6	7.7	13.6	17.9	10.2	0.1	12.4	19.3	23.6
MCP	28.3	39.0	31.9	28.0	35.1	29.9	21.3	22.9	29.0	45.6	40.8	39.7
Bz	30.0	6.5	3.1	30.9	7.9	3.1	1.3	0.5	31.5	8.3	4.9	2.8
	2.2	14.5	27.2	2.5	19.1	30.1	40.8	41.9	2.5	5.5	12.7	26.4
Naphthenes converted, %	22.0	40.0	69.8	27.0	44.0	61.6	77.6	61.3	10.9	24.5	51.6	78.2
Benzene formed, %	21.1	42.9	68.8	28.2	46.9	65.0	81.3	65.1	5.0	16.9	39.5	56.5
Selectivity, naphthene conversion	0.96	1.07	0.99	1.04	1.07	1.06	1.05	1.06	0.46	0.69	0.77	0.72
n-C ₆ converted, %	23.8	36.7	57.2	9.3	20.5	34.7	47.1	27.6	28.2	41.2	49.8	55.8
Iso-C ₆ formed, %	22.0	35.4	63.8	6.7	20.0	35.2	46.4	27.4	33.3	52.0	63.7	72.9
Selectivity, paraffin conversion	0.92	0.96	1.11	0.72	0.98	1.01	0.99	0.99	1.18	1.26	1.28	1.31
Bz	69.0	89.8	96.8	70.7	90.7	96.9	98.8	98.8	39.9	72.2	90.4	96.1
Bz + CH × 100	24.2	43.7	70.6	30.8	47.7	64.4	79.2	64.2	9.3	21.7	47.4	73.5
Bz + CH + MCP × 100												

^a Analyses questionable because of difficulty of accurately determining small amounts of hydrocarbons in hydrogen gas stream.

this reason, further detailed consideration is given here only to the dehydroisomerization reaction.

The effect of pressure on the selectivity of the naphthene conversion can be seen also in Table I by examining the selectivity factor of naphthene conversion. Here a selectivity of 1.0 indicates that all the naphthenes reacting form the desired benzene; a lower value indicates hydrocracking of rings to paraffins. The term "hydrocracking" here is used to describe the reaction in which any carbon-t-carbon bond is replaced by two carbon-to-hydrogen bonds, whether or not there is a resulting reduction in molecular weight. The conversion of naphthenes is considered as a class and not as individual components—i.e., the interconversion of cyclohexane and methylcyclopentane is not included. Selectivity then is only a measure of the reaction of a γ naphthene to form benzene, as compared to hydrocracking.

All the data obtained at the lower pressure over the range of space velocities studied fall within 10% of a value of 1.0. At the higher pressure, in the case of a space velocity of 3.0 volumes/volume/hour, the benzene yield is decreased by hydrocracking, while at a space velocity of 6.0 volumes/volume/hour, the selectivity is again good. Lower pressure is then more favorable for high conversions to benzene with little loss.

Dehydrocyclization of hexane to form benzene does not occur to an appreciable extent under the conditions of this investigation, and is not a factor here. It would be an important consideration in the case of heptane and paraffins of higher molecular weight.

LIQUID SPACE VELOCITY. Liquid hourly space velocities of 3.0 and 6.0 at 500 pounds per square inch gage and 1.5, 3.0, and 6.0 volumes of feed per volume of catalyst per hour at 175 pounds per square inch gage were investigated.

The effect of space velocity on the selectivity of the total naphthene conversion is shown by the data in Table I. At the higher pressure, where the selectivity at a space velocity of 3.0 volumes/volume/hour is poor, the higher space velocity gives better selectivity. In fact, at a furnace temperature of 950° F. only 72% of the naphthene conversion at the lower space velocity is to benzene; the remainder is hydrocracked to paraffins. The total benzene produced at the two rates is the same, 56%. At 175 pounds per square inch the selectivity is good over the whole range studied, 1.5 to 6.0 volumes/volume/hour.

The effect of space velocity on the combined dehydrogenation and dehydroisomerization can be shown by again comparing the experimental results with equilibrium data. To do this, the percentage of the total C₆ cyclics in the product which was in the form of benzene was computed. In Figure 2, A, B, and C, these values for the three space velocities at the lower pressure and at space velocities of 3.0 and 6.0 volumes/volume/hour at 500 pounds per square inch gage are compared to the equilibrium values calculated from thermodynamic data. Again they are plotted against average central catalyst bed temperature, outlet central temperature, and furnace temperature.

It is obvious from Figure 2, A, that the average catalyst bed temperature is the poorest method of defining the reaction temperature, as all the data lie well above the equilibrium line. The data obtained using a pressure of 500 pounds per square inch gage at a space velocity of 3.0 volumes/volume/hour fall close to the equilibrium line in the higher temperature range when the reaction temperatures are defined as either outlet temperature (Figure 2, B) or furnace temperature (Figure 2, C). The outlet and furnace temperatures for these runs, as shown in Table I, are similar. In the lower temperature range of Figure 2, B and C, somewhat higher concentrations of benzene in the product were found than expected at equilibrium. When one considers that the cyclohexane in the feed can either dehydrogenate to benzene or isomerize to methylcyclopentane, the formation of more benzene than expected in the over-all equilibrium must be due to a difference in the rates of the two reactions, the dehydrogenation but not the isomerization equilibrium being attained.

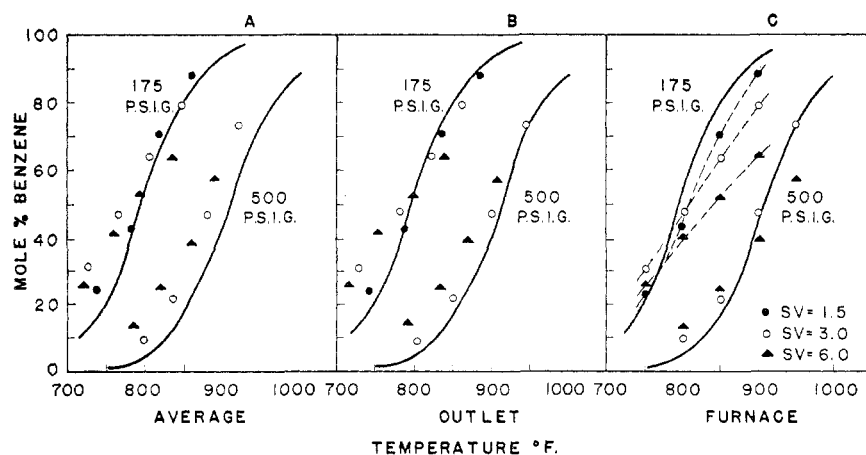


Figure 2. Dehydroisomerization Equilibrium of Methylcyclopentane-Cyclohexane-Benzene

40% n -C₆-30% MCP-30% CH

The same reasoning will explain the still higher benzene concentration obtained at the two lower temperatures of the runs at a space velocity of 6.0 volumes/volume/hour. A comparison of the points for the two higher temperature runs at a space velocity of 6.0 volumes/volume/hour plotted in Figure 2, B and C, indicates that the temperature corresponding to that for which the experimental results are equilibrium values falls between the outlet and furnace temperature.

At the lower pressure, where the contact times for an equivalent space velocity are shorter, and at lower temperatures and higher space velocities, there is appreciable isomerization, but not sufficient to establish equilibrium methylcyclopentane values. At the higher temperatures, except for the runs at a space velocity of 6.0 volumes/volume/hour, if the average or outlet temperatures are considered, the equilibrium appears to be established, but this is not true if the furnace temperatures are used. Because of the large difference between the furnace and central outlet temperature, benzene concentrations equivalent to the higher temperature would not be expected. The progressively greater difference between the experimental and equilibrium values shown in Figure 2, C, as the space velocity increases is, then, a result of both an increasingly large difference between outlet and block temperatures and less isomerization.

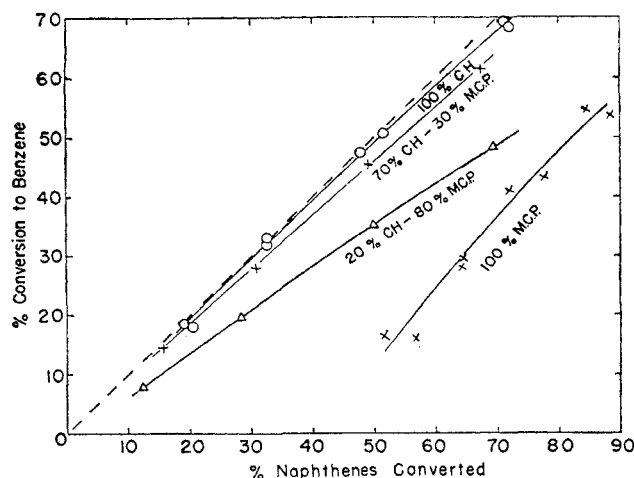


Figure 3. Effect of Methylcyclopentane Concentration on Selectivity

500 pounds per square inch gage
LHSV, 2.0 vol./vol./hour (3.0 for 100% MCP)

It becomes readily apparent in considering Figures 1 and 2 that it is difficult to define the reaction temperature of a highly endothermic catalytic reaction. No single method of indicating the temperature will fit all the conditions used. If only one method must be chosen, the authors feel that outlet temperature is the best representation of the true value.

Although in the runs made at a pressure of 500 pounds per square inch, the space velocity data at 3.0 volume/volume/hour follow the equilibrium line, appreciable losses of cyclics to paraffins because of poor selectivity make these conditions less desirable. At 175 pounds per square inch, very nearly equilibrium concentrations of methylcyclopentane, cyclohexane, and benzene can be established under conditions where there is a very small loss of naphthenes to undesired by-products. The actual conversions and yields of benzene, as shown in Table I, indicate that at a space velocity of 1.5 volumes/volume/hour almost 90% of the naphthenes can be converted to benzene with only a 3% loss to by-products.

EFFECT OF COMPOSITION OF HYDROCARBON MIXTURE

Early work on benzene production at 500 pounds per square inch gage using completely naphthenic materials showed (Figure 3) that the selectivity became much poorer as the concentration of methylcyclopentane in the hydrocarbon mixture increased. In this plot, the 45° line indicates a selectivity of 1.0, or no loss of naphthenes by hydrocracking. With pure methylcyclopentane, these losses to paraffins were very large and resulted in low yields of benzene.

VARIATIONS IN METHYLCYCLOPENTANE CONTENT. As the conditions for maximum selectivity have been determined, it is of interest to investigate the effect of variation of methylcyclopentane under these more suitable conditions. To do this

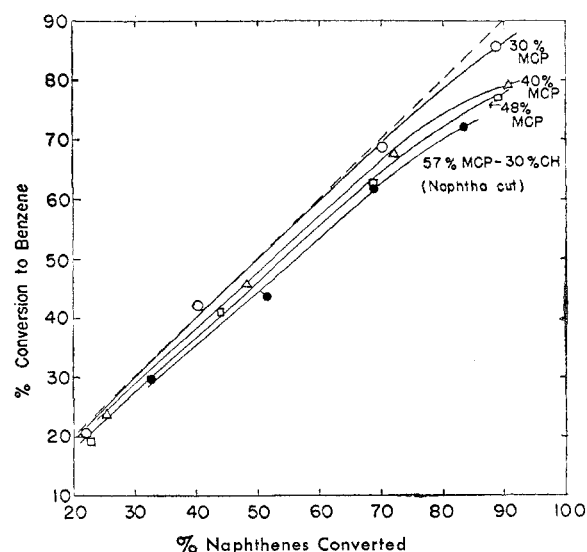


Figure 4. Effect of Methylcyclopentane Concentration on Selectivity

175 pounds per square inch gage
LHSV, 1.5 vol./vol./hour
40% n -C₆-60% MCP plus CH (except naphtha cut)

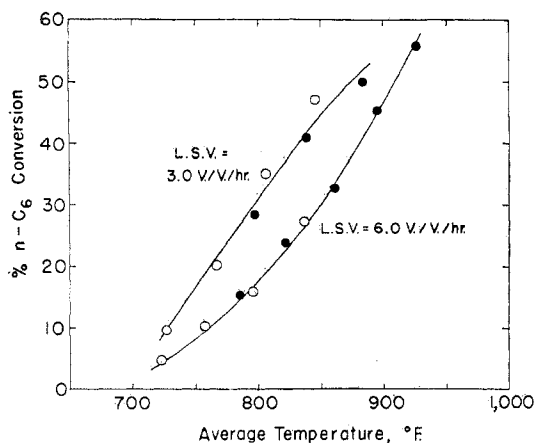


Figure 5. Effect of Pressure on Hexane Conversion

40% n-C₆-30% MCP-30% CH
 ○ 175 pounds per square inch gage
 ● 500 pounds per square inch gage

the 40% hexane-30% methylcyclopentane-30% cyclohexane blend was altered to maintain the 40% hexane, but increase the methylcyclopentane concentration at the expense of the cyclohexane. Runs were then carried out at a pressure of 175 pounds per square inch and a space velocity of 1.5 volumes/volume/hour. The effect of this increasing concentration of methylcyclopentane on the naphthene conversion selectivity is shown in Figure 4. The trend shown previously is observable in these data, but to a considerably smaller extent. The selectivity of the conversion falls off as the concentration of the methylcyclopentane increases. But even at a 4 to 1 ratio of methylcyclopentane to cyclohexane in the 60% naphthenes present, good selectivity is obtained, since at 89% naphthene conversion, 77% benzene is produced. Under these conditions, high conversions can be obtained with charge stocks high in methylcyclopentane with relatively little loss through hydrocracking.

Data obtained on a C₆ naphtha fraction are also included in this graph. Analysis of this particular cut showed it to contain 57% methylcyclopentane, 30% cyclohexane, 3% benzene, and 10% hexanes and heptanes. These points fall in line with the rest of the data, the selectivity being inversely related to the methylcyclopentane content. Here an 83% conversion results in 72% benzene.

As the data indicate that the presence of small amounts of cyclohexane reduces the hydrocracking of methylcyclopentane, it was of interest to investigate whether this was a result of the presence of benzene formed rapidly from the cyclohexane, since benzene has been shown to be a cracking inhibitor in some cases (6, 7), or a heat effect wherein the endothermic dehydrogenation reaction offsets the exothermic hydrocracking reaction. Either would explain the observed improved selectivity as the cyclohexane content is increased, since the cyclohexane would rapidly dehydrogenate to supply benzene as an inhibitor and in so doing would lower the catalyst temperature. To distinguish between the two effects, a hydrocarbon mixture of 40% hexane, 30% methylcyclopentane, 3% cyclohexane, and 27% benzene was used, the latter two being approximately in equilibrium concentrations for the conditions used. In this way, the occurrence of the endothermic dehydrogenation reaction was kept to a minimum and there was still benzene present to reduce the hydrocracking of methylcyclopentane, if it were effective in doing so. Table II shows that good selectivity was obtained at high naphthene conversions, which seems to confirm the role of benzene as an inhibitor.

PARAFFIN REACTIONS. The production of benzene is, of course, the aim of the investigation, and 40% hexane was added to the blend only to make it representative of a C₆ naphtha frac-

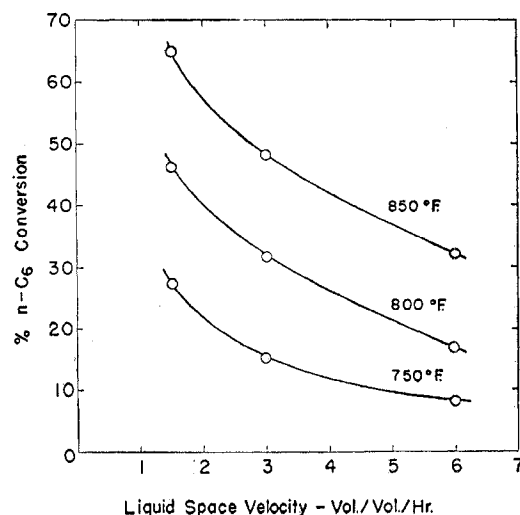


Figure 6. Effect of Space Velocity on Hexane Conversion

175 pounds per square inch gage

tion. Because, however, complete analyses of the products were obtained, the reactions which the paraffins were undergoing at the same time as the naphthene reactions were also evaluated.

Figure 5 shows the effect of pressure on the conversion of hexane to branched isomers. It is evident that, as pointed out for nickel on silica-alumina catalysts (1), at a constant space velocity the conversion is a function only of temperature and not of pressure. Previously it was shown that if the total pressure were increased and the contact time maintained constant, the hexane conversion decreased. Since here the space velocity is maintained constant, the increased contact time balances the effect of total pressure, and the conversion remains constant. Other explanations, such as competition of other molecules for adsorption on

active sites at the higher pressure, are ruled out because pure hexane gives similar results (1). The data obtained at the lower pressure shows very good selectivity, as was the case for the naphthene reactions. At 500 pounds per square inch gage, however, higher yields of isomers were obtained than could be expected from the

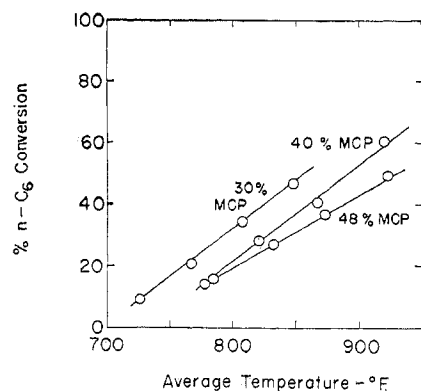


Figure 7. Effect of Methylcyclopentane Concentration on Hexane Conversion

175 pounds per square inch gage
 LHSV. 3.0 vol./vol./hour

hexane converted. As under these conditions the selectivity of the naphthene conversion was only 0.46 to 0.77, the additional hexane isomers must be a result of the hydrocracking of the naphthenes. Because of this it is not possible to calculate accurately the true selectivity of the hexane conversion for these runs.

Figure 6 shows the effect of space velocity on hexane conversion at 175 pounds per square inch gage, where the conversions are not obscured by the naphthene reactions. Compared to the earlier graph showing the effect of space velocity on naphthene conversion, hexane isomerization is more sensitive to space

TABLE II. EFFECT OF BENZENE ON SELECTIVITY

(40% *n*-C₆-30% MCP-3% CH-27% benzene.
LHSV 6.0 vol./vol./hour. H₂/HC = 10.
175 lb./sq. inch gage)

Temp., ° F.	% Naphthenes Converted	Selectivity
850	39.2	0.99
900	52.5	0.85
950	77.7	0.98

velocity than is the dehydroisomerization of methyleyclopentane.

Throughout this study of the effect of methyleyclopentane concentration, the hexane content of the charge was kept constant at 40%. Nevertheless, there is an observed difference in its conversion level in each series of runs made at a different methyleyclopentane concentration, as shown in Figure 7. An increase in the methyleyclopentane appears to lower the hexane conversion. This cannot be explained either by more hydrocracking, since the runs where there was the most hydrocracking showed the lowest hexane conversions, or by difference in temperature profiles, since the 48% methyleyclopentane runs had the highest temperature throughout the bed and still showed the lowest conversions. The only explanation appears to be a competition for the catalytic surface between the methyleyclopentane and the hexane, with the

former having the better of the competition. A more detailed explanation is not possible, but it is clear that the hexane reactions are influenced by the nature of the cyclic components present.

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Thermoplastic Water-Soluble Synthetic Gum

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THE water-soluble natural gums have served man for centuries as thickeners and binders for a wide range of industrial and pharmaceutical products. As our industrial economy expanded, a need for similar water-soluble products of improved properties arose. Thus the synthetic cellulose ethers came into being in an attempt to increase the knowledge of the structure of carbohydrate polymers and to broaden the fields of application for carbohydrate gums.

Suida (22) in 1905 proposed the etherification of cellulose and reacted dimethyl sulfate with an alkali-swollen cellulose, but he did not obtain the cellulose ether as an entity. Lilienfeld (20) in 1912 and later in 1928 (21) outlined the field of cellulose ether technology. He described organo-soluble ethers, ethers soluble in cold but not in hot water, mixed ethers, and ethers of varying degrees of substitution (D.S.). Leuchs (19) and Dreyfus (12) in 1912 also claimed organo-soluble cellulose ethers. Worden (23) described the resulting patent race.

Denham and Woodhouse (5, 6) prepared methylcellulose as an aid to establishing the structure of cellulose. Haworth (15) prepared methylcellulose by simultaneous hydrolysis and methylation of cellulose acetate. Jansen (17) described carboxymethylcellulose in 1921. This derivative was manufactured in Germany prior to 1924 (4). Hydroxyethylcellulose was mentioned by Hubert (16) in 1920. Benzylcellulose, which is manufactured in Europe but not in the United States, was described by Gomberg and Buchler (14). Several mixed ethers, hydroxy-

propylmethylcellulose (11) and carboxymethylhydroxyethylcellulose (18) have also been described.

However, since these water-soluble natural and synthetic gums lack a melting point, and since the difficulty of finding a suitable plasticizer-solvent for these materials has been considerable, the use of either of the above classes of gums in the field of thermoplastic fabrication has been negligible.

A new type of modified methylcellulose has recently been synthesized which overcomes the barriers described and again opens the door to an entirely new field of use for synthetic water-soluble gums. This cellulose derivative combines the water-soluble properties of the hydrophylic gums with solubility in certain hot and cold organic solvents. By use of the proper techniques it is possible to extrude, injection mold, compression mold, and hot cast a water-soluble cellulose derivative using standard plastic fabricating equipment.

EFFECT OF MODIFICATION OF THE SUBSTITUTION ON THE ANHYDROGLUCOSE RING

The steps in the development of this product, which has been given the designation of Methocel 2602, afford an interesting study of the effects which the type and amount of substitution on the anhydroglucose ring of cellulose can have on the properties of cellulose ethers.

The synthetic gum methylcellulose is produced by reacting alkali-cellulose with methyl chloride. By a suitable choice of