ticizer compatibility, and the properties of films formed from solutions in various solvent-diluent-plasticizer mixtures.

Solubility of cellulose acetate propionates in organic liquids improves with increasing propionyl and with increasing hydroxyl content. The dilution tolerance of the solutions for toluene and for butyl alcohol is greater with the higher propionyl materials.

The flexibility of cellulose acetate propionate films cast from single solvents and from solvent-diluent mixtures improves with increasing hydroxyl content and, usually, with increasing propionyl content.

Films cast from solvent-diluent mixtures are characterized by much greater shrinkage than can be obtained from single solvents. This is a consequence of the gel structure set up in such mixtures at a critical stage in the drying process.

There is no systematic correlation between cellulose ester composition and compatibility with the plasticizers examined.

The most satisfactory solvent mixtures for cellulose acetate propionate dopes contain methyl ethyl ketone and ethyl acetate as the low boiling active solvent constituents, Cellosolve acetate or diacetone alcohol as the high boiling solvent, and butyl alcohol as the nonsolvent diluent, together with butyl acetate in some instances.

Promising experimental dopes formulated on the basis of the data obtained have been applied to fabric-covered test panels and are currently undergoing outdoor weathering tests to provide a final evaluation of their suitability as airplane dopes. The results of these tests will be given in a subsequent report.

ACKNOWLEDGMENT

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Dehydrogenation of Methylcyclopentane over Chromia-Alumina Catalysts

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The work was undertaken in an effort to produce cyclohexene from petroleum fractions, in order to open up an increased supply of this important chemical.

The dehydrogenation at atmospheric pressure of methylcyclopentane over chromia-alumina catalysts in the presence of hydrogen and small amounts of benzene gives better yields of mono-olefins and lower coke deposits than either dehydrogenation at reduced pressure in the absence of hydrogen and benzene, or dehydrogenation in the presence of hydrogen or benzene individually. Pretreating of the catalyst with benzene with the feed gives larger yields of desired products. More than enough hydrogen and benzene are produced in the process to make the process self-sufficient for these materials.

The results obtained in this work show that product distribution in the dehydrogenation of methylcyclopentane can be varied by selectively treating or poisoning the dehydrogenation catalyst.

THE preparation from petroleum hydrocarbons of cyclohexene has been described (7). Dehydrogenation of cyclohexane over conventional dehydrogenation catalysts leads primarily to benzene and cannot be easily arrested at cyclohexene. It has been suggested to dehydrogenate methylcyclopentane (MCP), a hydrocarbon relatively abundant in naphthenic crude oils (3–6) and isomerize methylcyclopentene to cyclohexene (7). Dehydrogenation steps described in the literature have been carried out over molybdena-alumina or chromia-alumina catalysts in the absence or presence of external hydrogen. As most dehydrogenation catalysts at dehydrogenation conditions are also active for the isomerization of olefins, mixtures of methylcyclopentene, cyclohexene, and benzene are usually obtained. Depending on operating conditions and catalysts used, other products, such as diolefins and coke, are formed.

It was the purpose of this investigation to find a method of dehydrogenating methylcyclopentane to mono-olefin, either methylcyclopentene or cyclohexene and to reduce the amount of by-products formed—namely, coke, aromatics, and diolefins. Methylcyclopentene produced can then be separated from the reaction mixture by such methods as extractive distillation and can be isomerized over aluminous or siliceous catalysts (1, 2, 7, 8). The process variables of the dehydrogenation step were studied using a chromia-alumina catalyst. The effect of external hydrogen and of added aromatics on the reaction was investigated.

EQUIPMENT, MATERIALS, EXPERIMENTAL PROCEDURE, AND ANALYSIS

The apparatus consisted of an electrically heated lead bath furnace, holding a quartz reactor tube, 2.5 cm. in diameter and 100 cm. long. The catalyst in the reactor was preceded by a quartz chip preheater layer and flow was downward. Feed stock was charged to the reactor from a pressure buret to equalize pressure.

The effluent from the reactor was cooled in a glass condenser, through the jacket of which a brine solution flowed at 0° to 5° C. Following an ice-cooled receiver flask, vapors were passed through a copper coil condenser in an acetone–dry ice bath and a second receiver to a wet test gas meter and a vent or a gas collector.

The temperature in the reactor was controlled by means of a pencil thermocouple extending into the upper third of the catalyst section and a sliding thermocouple between the reactor and furnace wall.

In the case of runs made under reduced pressure, two Presso-Vac pumps in parallel were connected through a Cartesian monostat to the second receiving vessel and the pump discharge was passed through a wet test gas meter and vented or collected over water. The desired pressure was maintained fairly constant with the mercury-operated Cartesian monostat.

The catalyst used in this study was a commercial chromia-alumina catalyst (Houdry Type R) containing 80% alumina–20% chromia and prepared by dipping alumina pellets in chromic acid solution, drying, decomposing, and heat treating at 1400° F. with 10 to 20% steam.

Methylcyclopentane was obtained from Phillips Petroleum Co. in two grades, pure (99.5%) and technical (95+%). The pure material was used in nearly all cases in which additives such as benzene were used. In a few cases, the technical grade was used after percolation over silica gel. The percolated product was benzene-free.

Separation of products by distillation is unsatisfactory because of the close boiling points of the compounds.

The raw product was weathered (to remove lower boiling hydrocarbons) and then was analyzed. The proportions of mono-olefins, diolefins, and benzene were obtained by means of bromine number determinations before and after maleic anhydride treatment and acid absorption. This method gave excellent results on a number of synthetic blends (±0.2% for olefins, ±1% benzene).

Coke was determined either by combustion of a representative catalyst sample or by purging the catalyst with nitrogen at the end of a run and regenerating it at 1000° to 1100° F. in a slow stream of air which was passed over a carbon monoxide burner, a gas drying vessel, and an ascarite absorption tower.

Gas was measured in a wet test gas meter. Hydrogen charge was metered in a flow meter and/or wet test gas meter. If no gas was added during the run, the gas produced was collected over water and analyzed in the mass spectrograph. Gas density was calculated from the composition or was determined directly. If gas was added to the charge, gas production volume was calculated by difference between the charge and effluent. The amount of gas was calculated on the assumption that gas composition was similar to that obtained in the absence of external hydrogen. Errors thus introduced are relatively small.

Weight balances were made on all runs and losses did not exceed 9%. The loss was apportioned over all products in a ratio corresponding to the product distribution, so that all yields are reported on a loss-free basis.

Catalysts were reduced for 1 hour at 900° F. in a slow hydrogen stream prior to use.

DEHYDROGENATION OF METHYLCYCLOPENTANE

Influence of Operating Conditions on Product Composition. Passage of methylcyclopentane over chromia-alumina catalyst within the 950° to 1150° F. temperature range is characterized by high coke deposits and low mono-olefin yields (Table I). Pressures of less than atmospheric are required to reduce the coke deposition somewhat. Production of benzene is relatively high in all cases, frequently higher than that of mono-olefin. Variation of space rate changes the conversion level, conversion dropping with increasing space velocity. (Conversion is expressed as the sum of all products other than unreacted feed.) A liquid space velocity of 0.5 volume per volume per hour was found too low and 3 volumes per volume per hour too high for a desirable product distribution. Best results were obtained at 1050° F. and a space velocity of 2 volumes per volume per hour at 10 to 100 mm. of mercury. While the mono-olefin yield of 10.5% obtained under these conditions is fairly high and while little benzene was produced (0.8%), the coke was still very high (9.7%).

Effect of Addition of Hydrogen and/or Benzene. From the results obtained in the dehydrogenation of methylcyclopentane (Table I), it is apparent that a reduction of coke and an improvement in the mono-olefin to benzene ratio are necessary to achieve a process of commercial interest. Therefore, experiments were carried out in the presence of hydrogen in the hope of reducing coke formation. Results in Table II show that the addition of hydrogen reduced coke deposition to about the same extent as a reduction in total pressure and that the effect of hydrogen appears to be primarily one of lowering the partial pressure of methylcyclopentane and its products. Benzene was blended with the charge stock in order to suppress benzene formation by dehydrogenation of cyclohexene. The addition of benzene did not repress benzene formation, but surprisingly lowered coke deposition (10% benzene was used arbitrarily). When both benzene and hydrogen are charged along with methylcyclopen-

Table I. Variation of Operating Conditions in Dehydrogenation of Methylcyclopentane over Chromia-Alumina

Catalyst. Chromia-alumina
Catalyst to oil ratio. 2:1 vol./vol.

Reaction Conditions			Product Distribution, Weight % of Charge					
Temp., ° F.	Liquid space velocity, vol./vol./hr.	Pressure	Mono-olefin	Diolefin	Benzene	Gas	Coke	Conversion
950	2.0	Atm.	4.7	1.1	4.8	3.5	6.1	20.2
950	1.0	Atm.	5.4	1.0	6.9	4.7	7.2	25.2
950	2.0	Reduced[a]	3.2	1.6	7.2	1.0	3.5	16.5
1050	0.5	Reduced	3.6	1.5	8.3	11.7	15.0	40.1
1050	1.0	Reduced	6.4	1.7	4.3	4.9	12.5	29.9
1050	2.0	Reduced	10.5	1.9	0.8	3.3	9.7	26.2
1050	3.0	Reduced	2.1	0.8	4.5	1.0	3.3	11.7
1150	3.0	Reduced	3.7	1.3	9.5	2.6	5.4	22.5
1150	2.0	Reduced	6.5	2.0	3.8	3.5	10.6	26.4

[a] 10 to 100 mm. Hg.

Table II. Effect of Addition of Hydrogen and/or Benzene to Methylcyclopentane

Catalyst. Cr_2O_3–Al_2O_3
Catalyst to oil ratio. 2 vol./vol.

Operating Condition			Charge			Product Distribution, Wt. % of MCP Charge					
Temp., ° F.	Liquid space velocity, vol./vol./hr.	Pressure	H_2:oil mole	Benzene, wt. %	MCP, Wt. %	Mono-olefin	Diolefin	Benzene	Gas	Coke	Conversion
1050	1	Reduced[a]	0	0	100	6.4	1.7	4.3	5.0	12.5	29.9
		Atm	3.0	0	100	9.6	1.4	5.2	1.8	11.3	29.3
		Reduced[a]	0	10	90	3.8	2.4	7.8	5.7	8.3	28.0
		Atm.	1.5	10	90	12.9	2.6	7.9	3.6	6.5	33.5
		Atm.	3.0	10	90	14.1	3.1	6.6	4.9	3.6	32.3
		Atm.	3.0	100	0	0.6	0		0.4	0.2	1.2
1150	3	Reduced[a]	0	0	100	3.7	1.3	9.5	2.6	5.4	22.7
	1	Atm.	3.0	0	100	16.9	0.1	12.1	2.2	17.4	48.7
	1	Atm.	3.0	10	90	14.1	3.1	10.4	4.6	7.1	39.3

[a] 10 to 50 mm. Hg.

tane to the catalyst, coke deposition is lowered appreciably. The effect of the combination is greater than the effect of either component alone. The conversion to desirable products was also found to be improved. This effect is even more remarkable, considering that benzene is a product of reaction and must be present in the reaction in all but the first few moments. It seems that benzene is selectively adsorbed and selectively poisons the catalyst for coke-forming reactions. In order to determine the contribution of benzene to the products formed, benzene and hydrogen only were charged to the catalyst (Table II). Coke and mono-olefin formation were found to be very small.

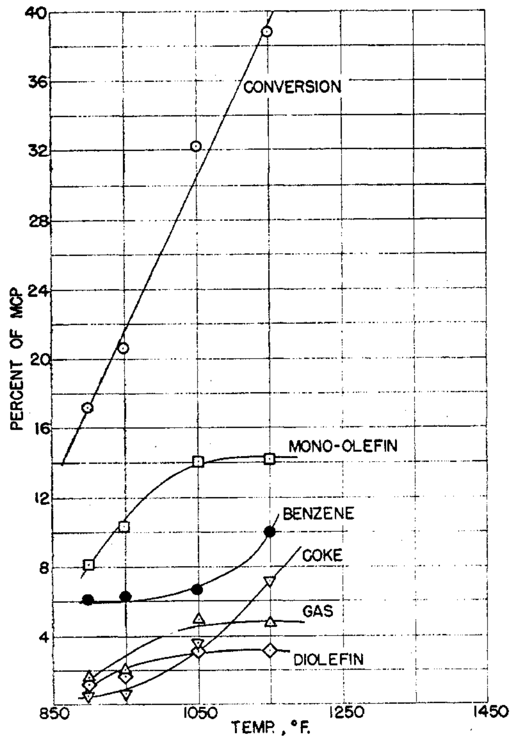


Figure 1. Effect of Temperature on Dehydrogenation of Methylcyclopentane

Cr_2O_3–Al_2O_3 catalyst
L.S.V. 1 vol./vol./hour
Feed. 90% MCP + 10% benzene
H_2:oil ⊙ 3:1 mole

The effect of benzene and hydrogen on coke formation was obtained at all temperatures studied and at different space velocities and hydrogen to oil ratios.

Effect of Temperature. The effect of reaction temperature on conversion and product distribution was determined at the following conditions: liquid space velocity of 1 volume per volume per hour, catalyst to oil ratio of 2 to 1, hydrogen to oil ratio of 3 to 1 mole, and feed stock of 10% benzene and 90% methylcyclopentane.

The data of Figure 1 indicate that conversion increases with temperature as an almost linear function. Mono-olefin production increases sharply to about 1050° F., then levels out rapidly (14%). Benzene formation increases more rapidly at higher temperatures. Diolefin production levels out at a perhaps somewhat lower temperature than mono-olefin production (3%). Coke increases sharply with temperature.

Optimum conditions will depend on economic considerations. For experimental purposes a temperature of 1050° F. was selected for the study of other variables.

Effect of Changes in Space Velocity and Hydrogen to Oil Ratio. The effect of space velocity and of changes in the hydrogen to oil mole ratio were studied at 1050° F. with a catalyst to oil ratio of 2 to 1 and a feed of 90% methylcyclopentane and 10% benzene.

Table III. Effect of Variation of Space Velocity and Hydrogen-Oil Ratio

Catalyst. Cr_2O_3–Al_2O_3
Temperature. 1050° F.
Catalyst to oil ratio. 2:1
Feed. 90% MCP + 10% benzene
Pressure. Atmospheric

	Liquid Space Velocity, 1 Vol./Vol./Hour			Liquid Space Velocity, 2 Vol./Vol./Hour	
Hydrogen-oil mole ratio	7.0:1	3.0:1	1.5:1	1.5:1	0.75:1
Mono-olefins, wt. % of MCP	8.7	14.1	13.7	9.4	8.7
Diolefins, wt. % of MCP	3.8	3.1	2.4	3.1	2.8
Benzene, wt. % of MCP	8.9	6.6	5.1	8.1	9.8
Gas, wt. % of MCP	4.4	4.9	3.6	2.6	2.7
Coke, wt. % of MCP	1.4	3.6	6.8	4.1	4.6
Conversion, wt. % of MCP	27.2	32.3	31.6	27.3	28.6

The results are summarized in Table III. It appears that an increase in space velocity at constant hydrogen to oil ratio lowers production of mono-olefin, gas, and coke in about the same ratio. On the other hand, the benzene and diolefin formation was increased.

The reduction of the hydrogen to oil mole ratio at constant space velocity increases the coke formation noticeably. The effect on the distribution of other products is relatively small, except for a considerable lowering of mono-olefin yield at very high hydrogen to oil ratios.

In view of these results, a liquid space velocity of 1 volume per volume per hour, and a hydrogen to oil mole ratio of between 3 and 3.5 were selected as conditions for future experiments.

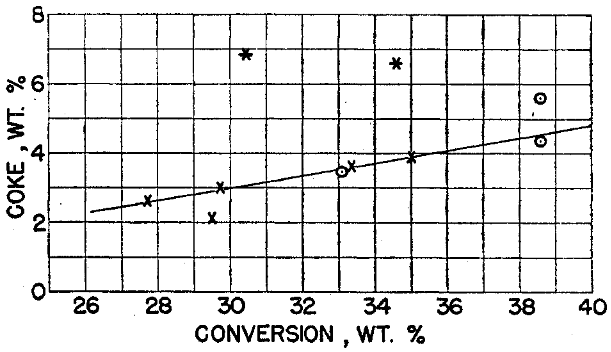


Figure 2. Conversion of Methylcyclopentane *vs.* Coke

× Benzene added in feed
⊙ Catalyst pretreated with benzene
* No benzene added

Effect of Change of Benzene to Methylcyclopentane Ratio in Feed. The effect of benzene, and of benzene and hydrogen combined, on the dehydrogenation of methylcyclopentane had been observed using a feed of composition 90 to 10 methylcyclopentane–benzene weight-ratio. In a series of experiments, this ratio was now varied under otherwise constant conditions (1050° F., liquid space velocity = 1 volume per volume per hour; hydrogen to oil ratio = 3.5 mole, catalyst to oil ratio = 2 to 1). The results are presented in Table IV.

The most striking differences occur in the coke deposition. It is apparent that very small amounts of benzene are as effective as or more effective than larger concentrations in inhibiting coke formation. An optimum is obtained between 0.5 and 2.0%. The benzene concentration in the feed does not seem to affect other products markedly. Variations in the amount of gas formed must be attributed to the large error in obtaining this figure (by difference), while increases in mono-olefins at high

Table IV. Effect of Changes of Benzene Concentration in Feed Stock

Catalyst. Cr_2O_3–Al_2O_3
Liquid space velocity. 1 vol./vol./hour
Hydrogen to oil ratio. 3.5 mole
Catalyst to oil ratio. 2:1
Pressure. Atmospheric

MCP in charge, %	100	99.8	99.5	99.2	99.0	98.0	95.0	90.0	80.0
Benzene in charge, %	0	0.2	0.5	0.8	1.0	2.0	5.0	10.0	20.0
Mono-olefins, wt. % of MCP	12.1	11.8	11.5	11.2	12.2	12.1	13.3	13.5	15.0
Diolefins, wt. % of MCP	3.7	3.0	3.5	3.8	2.3	3.6	3.8	3.9	3.1
Benzene, wt. % of MCP	9.5	9.2	8.7	8.9	10.4	8.8	9.3	10.0	9.9
Gas, wt. % of MCP	2.8	3.1	1.4	3.5	1.8	2.7	3.4	2.2	3.1
Coke, wt. % of MCP	6.5	5.8	2.6	2.1	3.0	2.8	3.6	3.5	3.9
Conversion, wt. % of MCP	34.6	32.9	27.7	29.5	29.7	30.0	33.4	33.1	35.0

benzene concentrations are probably due to the lower space rate. As far as coke is concerned, lower space rate should, at least, be partially compensated for by reduction of the methylcyclopentane partial pressure.

Impurities in the methylcyclopentane may consist partly of benzene and may, therefore, increase the benzene concentration slightly. However, this effect would be the same at all concentrations and the impurities do not exceed 0.5 mole %.

Effect of Pretreating Catalyst. The effect which benzene in the feed has in changing the dehydrogenation characteristics of methylcyclopentane must occur in the first moments of contact with the catalyst. After this, enough benzene is produced by dehydrogenation to make the presence of added benzene unnecessary. It was, therefore, decided to investigate the effect of passing benzene over the catalyst to treat it prior to charging methylcyclopentane and hydrogen.

Several check experiments in which the catalyst was treated with 5 ml. of benzene per 100 ml. were carried out. Results are given in Table V. The coke deposits when plotted against conversion are the same as when adding benzene with the feed (Figure 2). Over-all conversion was about 20% higher and the mono-olefin yield was increased by 22%. Further work on this effect is in progress in the Houdry Laboratories, but no additional information is available at this time.

Dehydrogenation By-Products. The dehydrogenation of methylcyclopentane discussed above always yields mono-olefin, diolefin, benzene, gas, and coke.

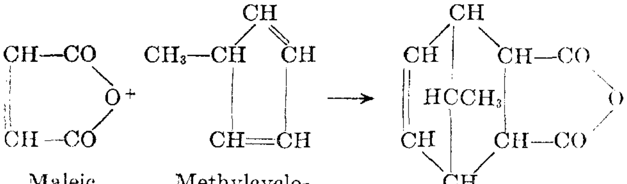
Of these, mono-olefin (either methylcyclopentene or cyclohexene) is the desired product. Benzene can be partially recycled and has a definite product value. Coke has to be disposed of during catalyst regeneration.

Table V. Effect of Pretreating of Catalyst

Catalyst. Cr_2O_3–Al_2O_3
Temperature. 1050° F.
Liquid space velocity. 1 vol./vol./hour
Hydrogen to oil ratio. 3 mole
Catalyst to oil ratio. 2
Pressure. Atmospheric

	Charge				
Benzene, %	0	0	0	0	0
MCP, %	100	100	100	100	90
Pretreating, ml. benzene/100 ml. catalyst	0	5	5	5	0
Mono-olefin, wt. % of MCP	12.1	16.9	16.4	16.4	13.5
Diolefin, wt. % of MCP	3.7	3.9	2.2	4.4	3.9
Benzene, wt. % of MCP	9.5	13.7	12.6	9.4	10.0
Gas, wt. % of MCP	2.8	3.6	3.0	3.3	2.2
Coke, wt. % of MCP	6.5	5.1	4.4	5.1	3.5
Conversion, wt. % of MCP	34.6	43.2	38.6	38.6	33.1

Diolefin is formed in appreciable quantities (2 to 4% of methylcyclopentane) and on recycling might increase coke formation. It could conceivably be hydrogenated to the desirable mono-olefin. The diolefin will react even at room temperature with maleic anhydride, with formation of a camphorlike product which may be of commercial interest. The reaction is a straight Diels-Alder reaction:



Maleic anhydride

Methylcyclopentadiene

Finally, methylcyclopentadiene can readily be polymerized. The polymer has been mentioned as a desirable paint base.

Table VI. Composition of Gas in Dehydrogenation of Methylcyclopentane

Reaction Temp., ° F.	Gas Composition, Mole %					
	H_2	CH_4	C_2	C_3	C_4	C_5+[a]
950	91.7	5.1	0.6	0.3	0.4	1.9
1050	86.0	5.5	0.3	0.8	0.7	6.7
950	91.5	4.3	1.1	1.3	0.2	1.6
950	96.0	2.3	0.2	0.2	0.1	1.2

[a] Noncondensed condensable product.

The gas formed consists predominantly of hydrogen from the dehydrogenation. A few typical gas analyses for runs carried out at reduced pressure in the absence of external benzene or hydrogen are given in Table VI. In the runs in which external hydrogen is added, the ratio of hydrogen to hydrocarbons in the effluent gas becomes, of course, much larger. There seems to be no doubt that the effluent gas could be recycled instead of fresh make-up hydrogen.

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