Catalytic Hydrogenation of delta-3-carene
by Henry Ernest McFarlin

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in CHEMICAL ENGINEERING
Montana State University

Abstract:
Carane, C10H18, a new and unique saturated bicyclic hydrocarbon, can be produced by.the continuous, three-phase, catalytic hydrogenation of delta-3-carene in a trickle bed reactor. Delta-3-carene can be recovered from the crude turpentine produced by Kraft pulp mills in the Rocky Mountain region. Among the various catalysts investigated, Harshaw 1404-T nickel catalyst was found to give the best results in a fixed bed flow tube reactor. The reaction conditions for maximum carane production in this study were found to be about 85°C, 1200 psig, and .025 hr^-1 liquid hourly space velocity.

Hydrogenation reactor product was distilled in a column with 40 theoretical stages at 28:1 reflux ratio to yield .9 gallons of 92% to 93% carane per gallon of delta-3-carene charged to the process.

Several methods of feed pretreatment to remove impurities which act as catalyst poisons were evaluated. Suspected poisons are sulfur, water, and auto-oxygenation products. The best pretreatment method appeared to be contacting the delta-3-carene with dilute caustic followed by steam evaporation under nitrogen and drying with CaSO4 desicant. The delta-3-carene feed was then passed over spent Harshaw l404-T catalyst from the previous hydrogenation run at reaction conditions — 1200 psig, 70-80°C, and 0.10 hr^-1 space velocity.

By using this feed pretreatment procedure, catalyst ages of approximately 65 cc’s of feed per gram of catalyst could be obtained. before the delta-3-carene conversion dropped below 50%. • Hydrogen purging and solvent leaching with a variety of solvents were used unsuccessfully to regenerate spent hydrogenation catalyst.

CATALYTIC HYDROGENATION OF DELTA-3-CARENE

by

HENRY ERNEST McFARLIN

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

CHEMICAL ENGINEERING

Approved:

Lloyd Berg
Head, Major Department

Lloyd Berg
Chairman, Examining Committee

R. J. Greene
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1967

ACKNOWLEDGEMENT

The author wishes to thank Dr. Lloyd Berg, Head of the Department of Chemical Engineering at Montana State University, for his guidance and assistance during this project. Thanks are also extended to Messrs. James R. Tillery and Silas Huso for their aid in construction and maintenance of the research equipment.

The United States Public Health Service is also thanked for their financial support which made this research project possible.

ABSTRACT

Carane, $C_{10}H_{18}$, a new and unique saturated bicyclic hydrocarbon, can be produced by the continuous, three-phase, catalytic hydrogenation of delta-3-carene in a trickle bed reactor. Delta-3-carene can be recovered from the crude turpentine produced by Kraft pulp mills in the Rocky Mountain region. Among the various catalysts investigated, Harshaw 1404-T nickel catalyst was found to give the best results in a fixed bed flow tube reactor. The reaction conditions for maximum carane production in this study were found to be about 85°C, 1200 psig, and .025 hr^{-1} liquid hourly space velocity.

Hydrogenation reactor product was distilled in a column with 40 theoretical stages at 28:1 reflux ratio to yield .9 gallons of 92% to 93% carane per gallon of delta-3-carene charged to the process.

Several methods of feed pretreatment to remove impurities which act as catalyst poisons were evaluated. Suspected poisons are sulfur, water, and auto-oxygenation products. The best pretreatment method appeared to be contacting the delta-3-carene with dilute caustic followed by steam evaporation under nitrogen and drying with $CaSO_4$ desicant. The delta-3-carene feed was then passed over spent Harshaw 1404-T catalyst from the previous hydrogenation run at reaction conditions -- 1200 psig, 70-80°C, and 0.10 hr^{-1} space velocity.

By using this feed pretreatment procedure, catalyst ages of approximately 65 cc's of feed per gram of catalyst could be obtained before the delta-3-carene conversion dropped below 50%.

Hydrogen purging and solvent leaching with a variety of solvents were used unsuccessfully to regenerate spent hydrogenation catalyst.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (continued)

I INTRODUCTION

A. Turpentine History

Turpentine is the term applied to the liquid hydrocarbon fraction that can be obtained from various soft woods. Turpentine has been classified with the group of products obtained from the long-leaf pine known as "Naval Stores". Naval Stores were initially produced by steam distillation of the gum produced by slashing the pine tree or by destructive distillation of the wood itself. The introduction of the Kraft or sulphate wood pulping process into the United States in 1908 allowed various coniferous woods to be successfully pulped with "Kraft" turpentine produced as a by-product. The Kraft process has grown to be the major pulp producing process and large volumes of crude Kraft turpentine are produced annually (7).

Crude turpentine is a mixture of many different hydrocarbon terpenes (compounds that are found in essential oils of plants and are constructed from head-to-tail linkages of isoprene). Turpentine fractions are characteristic of the various plant and tree species and the geographic location (6).

This is true of Hoerner-Waldorf mill in Missoula, Montana. A unique terpene, delta-3-carene (Table I), occurs in recoverable quantities (approximately 40%) in the crude turpentine from the Hoerner-Waldorf mill. Delta-3-carene is also reported as being in recoverable quantities in crude turpentine produced at other Kraft mills in the Rocky Mountain region but in only a few other locations throughout the world.

B. Turpentine Uses

Early turpentine production associated with the Naval Stores was consumed by the construction and maintenance of the wooden ships of the period. The paint and varnish industry has also been a major user of turpentine but much of this market has been taken by relatively inexpensive hydrocarbon solvents from other sources. The major use of turpentine today is in the chemical and pharmaceutical industries where the individual terpenes serve as starting materials for various chemical processes (7).

Unfortunately, at the present time there is little demand for turpentine fractions containing major quantities of delta-3-carene. Crude turpentines containing more common terpenes such as alpha- and beta-pinene (Table I) are more desirable and command proportionately high prices. Thus, in most Rocky Mountain area Kraft pulp mills, crude turpentine recovery is not profitable and the material is disposed of in some other fashion. The most common method is burning to recover the fuel value or, in some cases, the crude turpentine is not condensed at all but is allowed to vaporize into the atmosphere.

Crude turpentine contains sulfur as hydrogen sulfide, mercaptans, and organic sulfides, besides the hydrocarbon terpenes themselves. All of these materials are or can be contributors to air and water pollution whether the crude turpentine is burned or disposed of in some other manner.

The possibility of utilizing this unique chemical, delta-3-carene, for the syntheses of new or presently existing organic compounds may provide the potential for increasing the value of Rocky Mountain Kraft process turpentine and make turpentine recovery a profitable operation at all Rocky Mountain Kraft mill locations. This would also eliminate some present and future pollution sources.

Possible uses for delta-3-carene are in the fragrance, flavor, and cosmetic industries. Several compounds including Menthol (Table I) have structures similar to delta-3-carene and bring lucrative prices. Since the majority of these compounds contain functional groups that could be substituted by the fission of the cyclopropane ring of delta-3-carene, the logical starting compound for the many possible organic syntheses from delta-3-carene would be the saturated derivative of delta-3-carene -- carane (Table I). Carane is not reported as being naturally occurring but carane can be produced by the catalytic hydrogenation of delta-3-carene.

C. Delta-3-Carene Research

The chemistry of delta-3-carene has been investigated by early researchers and more recently by individuals at Trinity College, Dublin, Ireland, and Montana State University, Bozeman. The reaction mechanism, intermediate products, and effects of temperature and pressure for the catalytic hydrogenation of delta-3-

carene were investigated on a micro-batch scale at Trinity College. The reaction mechanism proposed by these researchers can be seen on Figure 2. One of the products that can be obtained from the reaction in high yields is cis-carane (hereafter referred to as carane). The structures of the cis- and trans-isomers and delta-3-carene can be seen in Figure 1. Dr. Mark Hannah, Montana State University, also studied the reaction producing carane, both as a batch operation and in a small continuous pilot plant. Several catalysts were evaluated, operating conditions further investigated, analytical procedures established, and enough carane (85% to 90% pure) was produced to use as a raw material for a terpene alcohol synthesis. Carane and several of the terpene alcohols produced are unknown in nature and their commercial possibilities have never been investigated.

D. Continuous Delta-3-Carene Hydrogenation

The basic problems associated with developing a continuous hydrogenation process for producing carane were established by Dr. Hannah during his research. Generally, the problem can be stated as three separate problems: (1) finding the best catalyst; (2) improving feed quality; and (3) determining optimum reaction conditions.

A good catalyst for this process must be very selective. Besides the possible reaction products shown in Figure 5, meta and para menthane isomers (Table I) are also very likely reaction

products. As the reaction temperature increases, the reaction approaches isomerization with complete rearrangement of the molecule and a host of saturate and unsaturate products possible. Since all the saturate products from even a mild reaction are of similar molecular weight and structure, separation by distillation becomes very difficult if not impossible. Thus, a catalyst should be reasonably active (give high conversion of the delta-3-carene feed) at relatively low temperatures and still be selective enough to maintain high yields of the desired product. The catalyst must also be rugged enough to withstand poisoning. Reaction conditions below 100°C (because of isomerization) and at high pressures offers the possibility for adsorption of liquid water on the catalyst, which would act as a catalyst poison. Water could be produced in the system by side reactions or carried in with delta-3-carene and hydrogen feed. A variety of other catalyst poisons are also present.

Delta-3-carene has been shown to be very reactive with oxygen (see Discussion and Results). Impure delta-3-carene can introduce oxygenated products which may be poisons themselves or produce water as a product from reacting with hydrogen. Thus, very pure delta-3-carene is important in maintaining high catalyst life. Initial economic work indicated that as much as 90% of the cost of producing carane could be catalyst expense because of rapid catalyst deactivation.

Optimum reaction conditions are desired for a number of obvious reasons. Besides wanting to maintain high conversion and yield, the effects of operating conditions on catalyst life are very important in developing a commercial process.

At all reaction conditions considered, the delta-3-carene is liquid. Thus, the reaction is two-phase (excluding catalyst considerations) or heterogeneous and hydrogen flow rate does not affect hydrogen concentration. As long as hydrogen flow is kept high enough to supply reaction requirements and low enough so that the liquid is not swept through the catalyst bed, hydrogen flow is not a variable. Variables affecting the reaction are, then, temperature, pressure, and liquid hourly space velocity (LHSV).

II RESEARCH OBJECTIVES

Research objectives can be summarized as an engineering study of the catalytic hydrogenation of delta-3-carene with a goal of gathering enough engineering data to outline a commercial process, and produce enough product to offer samples.

Research done by Dr. Mark Hannah with a continuous pilot plant indicated that the major problem centered on the catalyst. Both low product purity and short catalyst life were experienced by Dr. Hannah. Thus, obtaining carane in high purity with the best catalyst life possible became the major research objective.

III MATERIALS AND EQUIPMENT

A. Hydrogen Gas

Hydrogen gas used in this research was purchased from H & R Oxygen and Supply Company, Billings, Montana, in 2000 psig cylinders. The hydrogen circuit of the reaction system contains a catalytic (platinum) "Deoxo" unit to remove residual traces of oxygen and a drying cartridge containing "Drierite" $CaSO_4$ desicant for final moisture removal from the hydrogen.

B. Delta-3-Carene

Delta-3-carene feed stock used in this research was steam distilled (to prevent decomposition), in a batch system, from a crude turpentine fraction produced at the Hoerner-Waldorf, Mill Division, Missoula, Montana. An 8-inch diameter, 52-foot packed column containing 45-50 theoretical trays, operated at a 30:1 reflux ratio, was used to produce delta-3-carene at 95 to 99% (weight percent) purity. Physical properties of delta-3-carene are shown on Table I. The major detectable impurity was myrcene (Table I and Figure 6). Delta-3-carene reacts with oxygen and a variety of oxidation products were also contained in the feed, but no method of analysis for these compounds was found. Traces of sulfur were also identified in the delta-3-carene.

C. Catalysts

Table IV shows the catalysts used and their properties. Harshaw Chemical Company was the major supplier. Harshaw cat-

alysts were received from Elyria, Ohio in one-pound sample cans and in gallon cans containing ten-pound quantities. Raney Nickel was supplied by W. R. Grace & Company, Raney Catalyst Division, So. Pittsburg, Tennessee. Houdry "C" series Co-Mo catalyst was obtained from a previous research project.

The alundum SA-103, 1/8" pellet (87% Al_2O_3, 12% SiO_2, 1% impurities) used as a catalyst bed support was obtained from material on hand at the Montana State University Chemical Engineering Laboratories. One-quarter inch glass balls were also used as a feed dispersing medium on top of the catalyst bed. These glass balls were obtained from Fisher Scientific Company, Chicago, Illinois.

D. Continuous Hydrogenation Equipment

Figure 3 shows the schematic diagram of the continuous hydrogenation equipment. This was the equipment used by Dr. Hannah but with several improvements. The system is, or can be, nitrogen-blanketed, piping and valves were added to allow in-place activation of aluminum-nickel catalysts, and the heat medium loop was modified so that tap water could be circulated through the reactor jacket for cooling.

Delta-3-carene feed rate to the reactor was set with a Hills-McCanna proportioning positive displacement pump. Feed rates were from 0.2 cc/min to 2.5 cc/min and were determined with a 10 cc graduated sight glass and by checking product rate over extended

periods of time. A "Drierite" desicant cartridge was placed in the feed line. A conventional screen and bowl filter to protect the delta-3-carene feed pump from desicant particles and pipe scale was used after the drying cartridge.

Hydrogen gas was metered to the reactor through a pressure regulator (Matheson). Flow rate was adjusted with a Nuclear Products Company micrometer needle valve. Hydrogen flow at the beginning of each run was set with a precision wet test meter and then checked periodically through the run. Hydrogen flow rates varied from 0.005 ft^3/min to 0.01 ft^3/min at 630 mm Hg and 70°C. Reactor pressure was maintained with a Mitey-Mite back pressure regulator set from the hydrogen supply pressure regulator.

Reaction temperature was maintained by circulating a heat medium through the jacketed reactor. A circulation of about 40 gallons per hour was maintained with a small centrifugal pump. Initially, water was used as the heat medium but this was replaced with ethylene glycol (commercial anti-freeze) to allow higher operating temperatures and minimize corrosion.

A four-gallon tank with a 1000 watt immersion heater controlled by a conventional on-off immersion temperature controller was used to maintain the heat medium or reaction temperature. Four thermocouple readings from the catalyst bed were continuously recorded to indicate reaction temperature. A stick

thermometer was maintained in the heat medium tank to check the temperature recorder. Temperature range used was from 12°C to 125°C.

Nitrogen was supplied continuously from 2000 psig cylinders, through a Matheson pressure regulator, to the delta-3-carene feed tank at 2 to 5 psig. Additional lines allowed the reactor to be purged during catalyst loading or in place, and nitrogen was available for delta--3-carene feed loading. To avoid contamination by oxygen during feed tank loading, delta-3-carene was placed in nitrogen-purged one-gallon cans and then forced into the stainless steel feed tank with nitrogen pressure.

E. Continuous Reactor

Reactor detail can be seen on Figure 4. Two reactors were used, both 31 inches long. One had a volume of 280 cc's and was used for Runs 1 to 23. A second larger reactor with a volume of 2800 cc's was used for Runs 24 through 29. Both reactors were stainless and could be used interchangeably in the reaction system. Both reactors were designed to be removed for catalyst loading and unloading. Standard pipe unions were used for the inlet and outlet heat medium connections and for the connection to the pressure relief vent (2050 psig monel rupture disc). Thermocouple leads were connected with a standard multi-lead electrical connector. Hydrogen, nitrogen, and delta-3-carene connections were 1/8-inch "Swagelok" connections. A bolted flanged union sealed

the reactor to the product cooler. This seal did not leak at pressures as high as 1500 psig. Both reactors could be removed, spent catalyst dropped, re-loaded with fresh catalyst and re-connected in 30 to 45 minutes.

F. Batch Reactor

A Parr #4001 rocking bomb (Figure 5) was used for several delta-3-carene residue tests. The bomb is equipped with a 750-watt heater, adjusted with a Variac or Powerstat variable transformer for temperature control. Continuous gas addition was available but was not needed for tests performed with this apparatus.

G. Distillation Equipment

Small distillations (one liter or less hydrocarbon and water total) were made with two four-foot, one-inch diameter, externally heated, glass column sections. Each section is packed with Fenske rings (¼-inch stainless steel helices). The sections had been previously calibrated and found to contain approximately 25 theoretical stages per section or 50 stages for the entire column. A "Corad" variable reflux condensing head set at 30:1 reflux ratio was used for a condenser. Heat input to column section and still-pot was adjusted with Powerstat variable transformers. Overhead rate was about 12 cc's of hydrocarbon per hour.

Larger distillations (up to five gallons of hydrocarbon) were performed with a four-inch diameter column packed with ¼-inch

Fenske rings. This column was calibrated by previous researchers and found to contain 40 theoretical stages. A "Berg" adjustable reflux condenser was used, set at 28:1 reflux ratio. Still pot capacity was 50 liters. Heat input to the still pot heating mantle was adjusted with three Powerstat variable transformers. Hydrocarbon product rate was approximately 50 cc's per hour. Heat input was the limiting factor for this distillation system.

The 50-liter still pot and heating mantle were also used with a small one-inch glass column containing about five theoretical stages, to evaporate delta-3-carene for removal of oxidation product. A cold finger condenser was used and no reflux was returned to the column during this operation.

H. Analytical Equipment

All quantitative terpene analysis done during this project was done on an Aerograph Model A-90-C chromatograph equipped with a thermal conductivity detector. A Sargent model SR recorder was used. The column used was a ¼-inch by 20 feet, 10 percent β,β'-dipropionitrile on 60-80 mesh Chromosorb support. These columns were constructed by the experimenter and were replaced at approximately three-month intervals, depending upon usage. Column conditions were 60-70°C, hydrogen carrier gas, and one-tenth microliter sample size. Sample chromatograms of delta-3-carene feed and reactor product can be seen on Figures 6 and 7.

No qualitative analytical work was done during the course of this research. All compounds mentioned were identified or isolated by Dr. Hannah or by other individuals in previous work.

IV DISCUSSION AND RESULTS

A. Feed Quality Improvement

Catalyst deactivation was blamed on one or more contaminants in the delta-3-carene feed. Possible catalyst poisons considered were water, sulfur, and oxygen or oxidation products resulting from auto-oxidation of the delta-3-carene. An analysis was performed on a typical untreated delta-3-carene feed sample by Huffman Laboratories, Inc., of Wheatridge, Colorado. Results were as follows: nitrogen -- less than 0.01%; sulfur -- 0.09%; and water -- 0.012%. Specific analysis for oxygen was not performed but there is no doubt that oxygenated product is contained in the untreated delta-3-carene.

Delta-3-carene used as feed in this project had an ample chance to become contaminated by oxygen. The initial separation of delta-3-carene from the crude turpentine was done by steam distillation with the column, condenser, and accumulator open to the atmosphere. Delta-3-carene produced with this column over a two-year period (from research on crude turpentine fractionation) was collected and stored in metal five-gallon containers and 55-gallon drums. Some of the oxidation product is acidic in nature and in combination with the residual water from the steam distillation resulted in severe corrosion in some of the containers. No indication of relative age of the delta-3-carene was known for the majority of delta-3-carene used in the experiment. Obviously a constant quality feed supply was not used for the major portion

of this research. Very pure delta-3-carene is water-white, while delta-3-carene, after storage as described above, appeared to vary in color from pale yellow to dark yellow.

1. Elimination of Oxygen and Oxidation Products

An anti-oxidant, 2,6-di-tert-butyl-p-cresol, 0.05% by weight, was added to the delta-3-carene feed to eliminate auto-oxidation. To verify elimination of auto-oxidation, two one-hundred-milliliter samples of delta-3-carene were taken, one treated with 0.05 wt % auto-oxidant and the other untreated. Each sample was allowed to rock for 24 hours in the Parr batch reactor. The samples were sealed in the bomb at atmospheric pressure and the rate of reaction with oxygen measured by recording the bomb pressure. Figure 8 shows the rate of reaction for the untreated sample. Essentially all the oxygen was consumed in a 24-hour period. The treated sample showed no reaction after 48 hours.

Run 1, Figure 9, was made to test the effect of anti-oxidant addition on catalyst life. Run 1 also established the standard conditions used for comparing catalysts and catalyst deactivation rates. Harshaw 104-T catalyst was used. Catalyst charge was 140 cc's or 187.4 grams. Approximately 150 grams of ¼-inch alundum support was used on top and on the bottom of the catalyst charge. Reaction conditions were 70°C, 1000 psig, 3.5:1 hydrogen to delta-3-carene mole ratio, and .10 hr^{-1} liquid hourly space velocity (LHSV). These conditions will be referred to as

standard conditions. Results of this run can be seen on Figure 9. Deactivation rate was 4.25 percentage units of conversion per catalyst-age (Table II). This deactivation rate is quite rapid but obviously anti-oxidant alone will do nothing for the oxygenated product already present in the delta-3-carene feed.

After Run 1, the reaction system was modified to allow nitrogen blanketing of the feed tank and to supply nitrogen for purging other parts of the reaction system.

Reaction of the anti-oxidant could also be a source of water in the reaction zone. For this reason, anti-oxidant addition was discontinued after Run 21.

Run 2 was made with Houdry Series C Co-Mo hydrotreating catalyst in an attempt to remove oxygenated product and possible sulfur and nitrogen compounds, also. Reaction conditions were 70°C, 500 psig, 4:1 hydrogen to terpene mole ratio, and 0.8 hr^{-1} to 1.6 hr^{-1} LHSV. These conditions were typical for desulfurization of turpentine (5). The treated product was collected in gallon cans under the excess hydrogen. Nitrogen pressure was used to force the treated delta-3-carene through a P_2O_5 dryer. Nitrogen pressure was used again to force the delta-3-carene into the feed tank. This was the standard procedure for loading the feed tank in all other runs.

Run 3 was made using feed prepared in Run 2. Catalyst for Run 3 was Harshaw 104-T and conditions were standard. Deactivation rate was again rapid -- 3.13 units per catalyst-age. This indicated that hydrotreating alone did not improve feed quality. The product from Run 2 (after treating) was a very noticeable yellow color. This prompted work to improve this color.

Several filtering agents were considered but activated alumina was finally chosen in an attempt to improve the delta-3-carene color by filtering. A three-inch diameter filter containing one-half gallon of activated alumina was constructed. Delta-3-carene treated in Run 2 and dried with P_2O_5 was pressured through the alumina filter with nitrogen pressure. There was a definite improvement in the delta-3-carene color after filtering. In an attempt to quantitatively measure the effect of filtering, two 100-cc samples of delta-3-carene, before and after filtering, were evaporated and the residue weighed. Residue before evaporation was 0.83%, while residue after filtering was 0.087%. This is a reduction by a factor of 10. The measurement is subject to certain limitations, though. Evaporation conditions are difficult to control with respect to temperature and exposure to oxygen, so the measurements should be used to indicate trends only. Run 5 was made, testing the effect of this filtered feed on deactivation rate.

Run 5, Figure 10, was made with Harshaw 104-T catalyst. Conditions were standard. Deactivation rate was zero to a catalyst age of 6.8 (cc's of feed per gram of catalyst). At catalyst age 6.8, a mechanical failure caused the run to be interrupted for several days. Hydrogen was purged through the bed during this period but when delta-3-carene was fed again, conversion had dropped considerably. This effect was noted several other times. Even though deactivation was improved during Run 5, yield was poor and no 90% to 95% product was obtained.

Hydrotreating delta-3-carene on Houdry Series C catalyst did not appear to enhance carane production and was discontinued. The improved catalyst deactivation rate during Run 5 was attributed to the activated alumina filtration, which also produced a noticeable improvement in delta-3-carene color.

After several gallons of delta-3-carene had been treated with the alumina filter, there appeared to be little change in the delta-3-carene color before and after filtering. This was verified with a residue test. Acetone was flushed through the filter to remove the filtered residue. The acetone was very discolored after flowing through the bed. The alumina was then purged with air to remove residual acetone. When delta-3-carene was filtered after the alumina was acetone-leached, there was still no change in color. Apparently the alumina became permanently deactivated. This suggested investigation of other methods to improve the delta-3-

carene color. Evaporation was tried. Steam evaporation was used to prevent delta-3-carene decomposition. Water was added to the delta-3-carene to produce the steam required.

After evaporation, a 100-cc sample had a residue content of 0.15% which compares, within the accuracy of the test, to the 0.087% residue content after alumina filtering. Analysis by Huffman Laboratories indicated that sulfur was reduced from 0.09% to 0.03% by evaporation, also. Evaporation was used to improve feed quality for the remainder of the experimental work. Run 9 was the first run testing evaporated feed.

Run 9, Figure 12, was inaugurated using Harshaw 104-T. Other conditions were standard. Deactivation rate (Table II) was 1.33 units per catalyst age. This compared favorably with Run 5 as well as Run 6, both of which used alumina-treated feed. Feed for these runs was also treated with 0.05 wt% anti-oxidant.

Difficulty in reproducing results from Runs 5 and 6 with regard to deactivation rate was encountered during Runs 18 and 19 and prompted treating of the delta-3-carene for myrcene removal (Table I) on the assumption that myrcene was a poison and that the myrcene content of the feed between Runs 5 and 6, and 18 and 19, was significantly different. Analysis for myrcene is relatively inaccurate since the myrcene content can vary from 4% to a trace. Analysis for compounds less than 5% of the total can easily be up to 50% in error from errors made in calculating chromato-

gram peak areas. All calculations made were based on delta-3-carene feed purity of 100% although the average was probably 98-99%.

Myrcene can be removed with a Diels-Alder reaction (2). Myrcene reacts with maleic anhydride, forming a product which is water soluble when treated with caustic. Myrcene removal by this method appeared 100% complete by chromatographic analysis.

Run 20 was made with Harshaw 1404-T, as were Runs 18 and 19. Other conditions were equal to Runs 18 and 19. Deactivation rate (Table II) was slightly improved. After more consideration, the possibility of myrcene acting as a poison in an atmosphere of hydrogen seems very remote; however, during the myrcene removal process, the delta-3-carene was caustic washed, which will aid in the removal of oxygenated products.

Various caustic contacting procedures were tried. Dilute caustic (5% to 10%) was used. Caustic contacting before and after evaporation, caustic addition to water in the still pot during evaporation, and delta-3-carene storage on a caustic layer were all tried separately or in combination. All methods removed oxygenated product. Caustic in the still pot appeared to darken the delta-3-carene and this procedure was not used although the caustic became very discolored, also. Delta-3-carene stored on a caustic layer, even after evaporation, would discolor the caustic. This indicates that not all the oxygenated product is removed by evap-

oration. The final caustic treating method is discussed in the Conclusion section of this thesis. It is unfortunate that caustic treating was used since spent caustic disposal can be a major pollution problem in itself. Hopefully, delta-3-carene produced from a commercial process would not contain all the contamination experienced during this research and caustic contacting would not be required.

Dilute sulfuric acid (5%) wash was tried as a method of delta-3-carene purification. No significant change in the color of the dilute acid was noted and no improvement in catalyst deactivation rate resulted from using acid washed delta-3-carene, either.

Contacting delta-3-carene with a solution containing 5% sodium hydrosulfite and 5% sodium bisulfite was also tried to remove additional oxidation product. This method is reported in the literature and was used by Hannah (3). Delta-3-carene contacted had already been evaporated. No color change in the hydrosulfite-bisulfite solution was noted, while the same delta-3-carene contacted with caustic resulted in a caustic color change. Thus caustic seemed to be more efficient than the sulfite solution for removing oxygenated product.

Reactor product appears water-white even when delta-3-carene conversion was less than 50%. This obviously indicates that impurities are being removed by the catalyst even when

delta-3-carene conversion is very low. Spent Harshaw 1404-T catalyst from Run 28, Figure 16, was used to treat feed for Run 29. Conditions were 1200 psig, 80°C, and 0.10 hr^{-1} liquid hourly space velocity. Space velocity was reduced to .03 hr^{-1} at the end of the run so the catalyst deactivation rate could be compared with Run 29, also performed at .03 hr^{-1} space velocity.

Run 28 was terminated at a catalyst age of 30 where the delta-3-carene conversion was only 20% but the product still appeared water-white. Huffman Laboratories' analysis indicated that sulfur was reduced from 0.03% after evaporation to less than 0.01%. Several cc's of water appeared in the collection flask during Run 28 and the flask was very discolored with what appeared to be rust stains. No water or rust stains were observed during Run 29, indicating that Run 28 removed considerable oxygenated product from the delta-3-carene.

Run 28 was stopped at a catalyst age of 30 cc's of feed per gram of catalyst. Conversion was still 20% at a catalyst age of 30. There is good reason to believe that the catalyst could have been used considerably longer as a treating catalyst. Seven gallons of feed with a delta-3-carene content of 64% was produced by Run 28.

Run 29, Figure 17, used feed prepared by Run 28. Conditions for Run 29 were 1200 psig, 70°C, and .03 hr^{-1} space velocity. Catalyst was, of course, Harshaw 1404-T. Comparison be-

tween Figures 16 and 17 shows the effect of treating the delta-3-carene with spent catalyst. Feed for Run 29 was exhausted before delta-3-carene conversion dropped to below 50%. By extrapolation, it appears that conversion would have reached 50% during Run 29 at a catalyst age of about 65. This compares to a catalyst age of 15 for 50% conversion during Run 28.

The lack of poisoning during Run 29 was also evident by a lack of water or rust stains in the collection flask. Product was collected to a catalyst age of 18 cc's of feed per gram of catalyst. No water or discoloration of the flask occurred during this period. Run 29 is the only run in which discoloration or water did not appear, indicating the majority of water and/or oxidation product were removed during the pretreating stage.

Pretreating delta-3-carene feed with spent catalyst appears to greatly improve catalyst life and was used to treat all delta-3-carene used for future carane production.

2. Water Removal

The effect of water as a poison was definitely established by Run 9, Figure 12. The catalyst bed was completely saturated with water. When delta-3-carene was returned to the bed, the effect on conversion and yield was obvious. Neither hydrogen purge nor continuation of the run restored the condition of the catalyst to what it had been previously.

The presence of water in the reaction zone during normal operation was definitely established, also. Small amounts of water (less than .05%) appeared frequently in the collection flask and small drops of water were practically always present when the reactor was removed after a run.

Hydrogen as a source of water was eliminated with the installation of a "Deoxo" unit followed by a $CaSO_4$ (Drierite) dryer. This left entrained or dissolved water in the delta-3-carene feed or water formed as a result of the reaction of oxygenated product still contained in the delta-3-carene as sources of water. The solubility of water in delta-3-carene could not be found in the literature but the solubility for compounds of similar structure, i.e., alpha pinene, etc., was reported as being very slightly soluble (6). This amount of water was considered negligible and contacting delta-3-carene with various drying agents could introduce the potential for further contamination. Using these assumptions, a search was made for a material that would

act as co-solvent for water formed as a reaction product. This would allow the water to go into solution with hydrocarbon reaction product and be continuously removed from the reaction zone. Absolute ethanol and acetic anhydride were selected as possible co-solvents. An added benefit was also hoped for from these co-solvents. The residue remaining after evaporation of delta-3-carene was almost insoluble in hydrocarbon solvents but very soluble in acetone and soluble in varying degrees in ethanol and acetic anhydride. Thus, a co-solvent might also remove residual unreacted oxidation products from the catalyst.

A mixture of 50% absolute ethanol, 50% delta-3-carene (by volume) was used as feed for Run 6, Figure 11, beginning at a catalyst age of 10. As Figure 11 shows, there was no regeneration of the catalyst per se, but deactivation rate was decreased and another interesting effect was noted. The ethanol shifted the yield in favor of carane to practically a 100% carane yield. Unfortunately, this effect could never be duplicated. Runs 7, 10, 16, 22, and 24 all were made with feed containing ethanol but in these runs the ethanol appeared to react. A second phase appeared in the collection flask (probably water) and catalyst deactivation was very rapid. The effect of ethanol was tested with both Harshaw 104-T and 1404-T catalysts. Apparently the catalyst activity was unique in Run 6; in all other attemps the catalyst was either too active or perhaps had not been selectively poisoned in the

correct manner. Although this effect of yield shift could not be duplicated and was not considered further in this research, it is in itself interesting and still may offer some potential for future research. No explanation or mechanism was attempted to explain this effect. An error in analysis is not likely since the ethanol peak is not near any of the usual peaks and Runs 7, 10, 16, 22, and 24 gave different results.

Results with acetic anhydride were equally disappointing. Acetic anhydride is only slightly soluble in delta-3-carene, approximately 1% by volume at room temperature.

Acetic anhydride in concentrations of 0.05% to 0.5% was added to the feed from Run 16 to Run 21. Different catalysts and conditions were used during these runs so that the effect of the anhydride was difficult to assess. After Run 21, considerable water was found in the reactor. Conversion and deactivation rate had generally been poor during Runs 16 to 21, also. Acetic anhydride use was discontinued after Run 21. Thermodynamic calculations seemed to substantiate this decision. Table III shows a summary of these calculations.

The reaction of acetic anhydride going to ethanol and water is favorable, also the reaction of acetic acid (assuming some water would react with the anhydride forming acetic acid) going to water is at least possible. If equilibrium conditions were

established for the acetic acid reaction, the reaction would probably be shifted toward completion since the catalyst would remove the water from the system by becoming poisoned.

No thermodynamic data were available for the anti-oxidant (2,6-di-tert-butyl-p-cresol) but a similar hydrogenation reaction with water as a product seems very possible. As mentioned earlier, anti-oxidant addition was discontinued after Run 21.

Delta-3-carene, after evaporation, had a cloud point anywhere from room temperature (70°F) to about 20°F. "Drierite" ($CaSO_4$) was used to dry feed after Run 21. Approximately a ¼-inch layer of desicant was kept in the bottom of the glass container used for delta-3-carene feed storage after evaporation. Delta-3-carene in contact with Drierite for at least 24 hours had a cloud point of less than -20°C. This improvement was considered significant and Drierite contacting was used for drying all delta-3-carene feed.

B. Catalyst Evaluation

Table IV shows catalysts used and their compositions. The table also shows catalysts investigated by Hannah (3). Harshaw 104-T was the only catalyst used by Hannah in the continuous hydrogenation process. All other catalysts were evaluated by him in the Parr batch apparatus. All catalyst evaluation in this research was done with the continuous hydrogenation apparatus.

1. Harshaw 0104-T

Runs 1 through 6, 9, 14, and 24 were made with Harshaw 0104-T catalyst (Table IV). This catalyst was found by Hannah to be the best catalyst of the series which he evaluated. No carane 90% pure or above could be produced with this catalyst during this project.

2. Harshaw 4401-E

Harshaw 4401-E (nickel-tungsten) catalyst was evaluated during Run 8. Feed was alumina filtered and treated with anti-oxidant. Reaction conditions were standard. There was a noticeable exothermic effect evident by a temperature rise across the catalyst bed. A multitude of products, all in small yields, appeared from chromatographic analysis, none of which could be identified. Infrared spectrum indicated a predominance of double bonds. Apparently the reaction was of an isomerization or cracking type. No further product identification was attempted.

3. Al-Ni Catalysts

Two Al-Ni catalysts were investigated -- Harshaw 3001-T and "Raney Nickel". These catalysts are activated in place by caustic leaching of the aluminum content of the catalyst. This active surface, after leaching, is very fragile and this is the main reason that the catalyst is difficult to use, activated outside the reactor. The active form is also pyrophoric, which further complicates trying to use the preactivated form of the catalyst.

Runs 10 to 12 were made attempting to use Harshaw 3001-T catalyst. The manufacturer's recommended activation procedure was followed as closely as possible for Run 10. This consisted of soaking the catalyst in tap water for one hour (7°C). One gallon of caustic, containing a stoichiometric amount of NaOH required to react with 10% of the Al present in the catalyst charge, was circulated at a 15 cc/min rate. Temperature was 70°C. Circulation was maintained for 36 hours. Gas evolution appeared almost zero at the end of the 36-hour period. The catalyst bed was then flushed with tap water for four hours. No caustic could be detected in the effluent water after this period. Nitrogen was then purged through the bed at 72°C for 24 hours to dry the catalyst.

Reactions conditions for Run 10 were standard. Initial conversion was only 10%. This dropped to zero by a catalyst age of 4.0. Obviously very poor results. Feed containing ethanol was tried but conversion was still zero.

Run 11 was an attempt to reactivate catalyst from Run 10. Acetone was circulated for two hours to remove residual traces of delta-3-carene from the catalyst. Caustic circulation was resumed at 70°C. No gas evolution could be detected during a 10-hour circulation period; the catalyst was assumed to be completely deactivated and was removed.

Several changes in activation procedure were tried for Run 12. Caustic normality was increased from .11 to .31 and an

excess of caustic was used. The possibility of water remaining on the bed after purging was considered. Absolute ethanol was circulated after washing and purging in an attempt to remove any residual water. This was followed by circulation of delta-3-carene to dilute any residual ethanol. Caustic was circulated for only 24 hours rather than 36 hours, as in Run 10.

Drying procedure was as follows: nitrogen purge for 12 hours at 72°C, circulation of two ¼-gallon absolute ethanol portions for two hours each, nitrogen purge at 72°C for 12 more hours, and finally, circulation of ¼-gallon of delta-3-carene for two hours at room temperature.

Reaction conditions for Run 12 were standard. Initial conversion was zero and did not increase after 12 hours operation. At this point, samples and activation procedure were requested from Grace Chemical Company (Raney Nickel manufacturers).

Several shortcomings of the 3001-T activation procedure were recognized. Caustic and wash water circulation may have been too rapid and resulted in damage to the activated surface of the catalyst. The equipment was also modified so that the catalyst bed could be maintained at temperatures above 100°C. An attempt was made, too, to follow the reaction by measuring the rate of gas evolution with a wet test meter but this was found impractical because the gas evolution rate was so slow that the meter would not record the flow. Grace Chemical Company also recommended more concentrated caustic.

Five percent caustic was used for Run 17. Activation procedure for Run 17 was as follows: caustic circulation for 10 hours (gas evolution appeared almost nil at this time) at 70°C, wash water rate very low for one hour, and hydrogen purge at 120°C for 24 hours. Conditions were standard for Run 17 except for temperature, which was 80°C. Figure 15 shows Run 17. Yield was poor and deactivation rate appeared quite rapid (Table II).

4. Harshaw 1404-T

Run 7 was made testing Harshaw 1404-T. Conditions were standard with the exception of temperature, which was 80°C rather than 70°C. Initial conversion and yield were better than any experienced until that time with any other catalyst. A pump failure caused the run to be stopped for six days. When feed was returned to the catalyst, conversion and yield had dropped substantially. Runs 7, 13, 15, 16, and 18 through 29 (excluding Run 24) were made with 1404-T. Harshaw 1404-T was the best catalyst found based on conversion of delta-3-carene and yield of carane. Rate of deactivation did not appear significantly different for 1404-T than for other catalysts but 1404-T was the only catalyst found in this research which produced carane at a purity above 90%.

Run 13, Figure 13, showed that very good results could be obtained with 1404-T. Unfortunately, these results could not be duplicated or even approached until Run 27. This is indicative of the extreme and uncontrolled variable nature of the ex-

periment. The variation of feed quality has already been discussed. Similar problems also exist with the catalyst. Run 13 was a case of catalyst condition and feed quality matching perfectly but since no method of characterizing feed or catalyst condition could be found, results were difficult to duplicate precisely.

5. Oxygen as a Catalyst Poison

Harshaw 104-T and 1404-T were found to be the best catalysts evaluated, with 1404-T being rated first. The active form of these catalysts is elemental nickel and is thus subject to poisoning by oxygen through the mechanism of oxide formation. The manufacturer warns against exposure but gives no indication of how rapid deactivation proceeds. It is virtually impossible to handle the catalyst during weighing and reactor charging without some exposure to oxygen. All containers used for handling and storing catalyst were nitrogen purged. The reactor was also purged with nitrogen during loading and, of course, purged with hydrogen when in place. Unfortunately, there is no difference in appearance between fresh and deactivated catalyst so catalyst activity with regard to delta-3-carene conversion was the only means available to detect catalyst deactivation. The main problems with oxygen contamination appeared to have occurred during shipment and storage.

Catalyst is normally received in metal containers with the catalyst sealed inside a plastic bag and the containers sealed. Twenty pounds of 1404-T were ordered and received in fiber board containers. The catalyst was not needed for a two-month period and was stored without opening the fiber containers. When the containers were finally opened, it was found that the inner plastic bags had become punctured by sharp catalyst pellets and catalyst was loose inside the fiber containers. Since the fiber board containers had not been opened before use, the assumption that the catalyst had not deactivated was made and this catalyst was used for Runs 23 through 26. Conversion and yield were poor for these runs although the catalyst deactivation rate was not noticeably different. Apparently the fiber board container offered little resistance to oxygen. This catalyst was replaced by the manufacturer and was received in metal containers. Run 27 was made with fresh catalyst and both conversion and yield improved. This indicates that catalyst deactivation from oxygen contamination can be a very important factor but unfortunately is essentially uncontrollable or directly measureable with facilities available.

C. Catalyst Regeneration

Several procedures for regenerating 104-T and 1404-T catalyst were investigated. Purging with hydrogen and catalyst leaching with a variety of solvents were tried but were unsuccessful. The

problem of catalyst and delta-3-carene reaction with oxygen eliminates the possibility of burning or firing the catalyst and removing the catalyst from the reactor. When 104-T and 1404-T catalyst containing residual traces of delta-3-carene was removed from the reactor it would immediately become very warm, indicating a rapid reaction with oxygen. Even catalyst that was almost entirely deactivated showed this effect. Thus, all regeneration procedures were evaluated with the catalyst in the reactor.

1. Hydrogen Purging

Hydrogen purging was reported by Hannah to partially restore catalyst activity but this effect was not noted during this work. Hydrogen purging was tried during Runs 4, 15, 16, and 21. Hydrogen temperatures varied from 25°C to 80°C; length of purging from 12 to 68 hours. No noticeable improvement in yield or conversion was noted. This might be explained by considering water as a temporary poison and oxygenated products as permanent poisons. If the poisoning was predominately water, then hydrogen purging might temporarily restore a fraction of the original catalyst activity while hydrogen would have little or no effect on resinous oxidation products.

2. Solvent Leaching

Assuming the catalyst was being poisoned by a tacky resinous oxidation product similar to that left after the evaporation of delta-3-carene, solvent leaching to restore catalyst activity was suggested. Using the residue after delta-3-carene evaporation

as test material, various solvents were evaluated. Solvents containing oxygen were found best, while hydrocarbon solvents appeared poorest. A partial list of solvents tested included acetone, ethanol, isopropylalcohol, dioxan, morpholine, normal butylacetate, benzene, toluene, normal hexane, and acetic anhydride. Acetone was found to be the most effective solvent with the resinous material going into solution almost instantly at room temperature. Other oxygen-containing solvents would slowly dissolve the material. The resin appeared almost insoluble in hydrocarbon solvents.

Acetone circulation at 25°C was tried during Run 13 at a catalyst age of 17.6. Conversion had dropped to 80% (Figures 13 and 14). Two 1500 cc portions of acetone were circulated for 4 and 12 hours, respectively. Nitrogen was purged through the bed at 72°C for 12 hours to remove the residual acetone. No acetone odor could be detected in the nitrogen at the end of this 12-hour period. Conversion increased slightly to 84% but then dropped rapidly. Yield remained unchanged at approximately 97%. The acetone also attacked the rubber diaphragm in the back pressure regulator requiring replacement. Acetone leaching was not considered successful.

A variety of solvents were tried on catalyst from Run 15. Fifteen hundred cc's of toluene, normal butyl acetate and acetic anhydride were circulated through the bed for 12

hours at 25°C in the order listed above. Both the toluene and normal butyl acetate appeared to show little color change while the acetic anhydride appeared very dark and smelled of acetic acid. The change of color in the acetic anhydride could have been from acetic acid corrosion products. No improvement in yield or conversion was noted after this treatment.

The possibility of the alumina packing on top of the catalyst promoting isomerization or residue formation was considered. Two 100-cc samples were treated in the Parr rocking bomb at 1000 psig hydrogen pressure and 70°C. One sample was placed in the bomb with 1/8-inch alundum catalyst bed support pellets. Each sample was rocked in the bomb for five hours. No hydrogenation took place. After evaporation the sample that had been with the alumina pellets contained 0.15% residue while the sample treated without alumina present had only 0.05% residue. On the basis of these data, ¼-inch glass balls were used in place of alumina as a feed dispersent after Run 10. No drastic difference in catalyst deactivation was noted. The use of these ¼-inch glass balls is probably a very minor contributor toward reducing catalyst deactivation.

D. 1,1,4-Trimethylheptane Production

As Figure 2 shows, 1,1,4-trimethylheptane (hereafter referred to as 1,1,4) can also be obtained as major reaction product. This was verified by researchers at Trinity College, Dublin, and Hannah

at Montana State University. Preliminary work done by these individuals indicated that the reaction producing high yields of 1,1,4 occurred at high temperatures (100 to 120°C) and low pressures (atmospheric or lower). Runs 13 through 16 were made evaluating catalysts and operating conditions for 1,1,4 production. Run 16 was made with 1404-T; conversion was 100% to a catalyst age of 23 when the run was discontinued. Preliminary analysis indicates yields of about 70% to 80% 1,1,4. The β,β' chromatograph column being used was replaced as a routine procedure during Run 16. The last few samples from Run 16 were analyzed with the new chromatograph column and a shoulder peak appeared on what had been assumed to be a pure 1,1,4 peak. A sample of meta-menthane was obtained and added to the reaction product. One isomer of meta-menthane amplified the shoulder peak but the other isomer appeared to have an identical retention time with what was assumed to be pure 1,1,4. Due to this difficulty in analysis, no further work was done on 1,1,4 production.

The 100% conversion obtained in Run 16 to a catalyst age of 23 or greater appears very good but it is probably a result of the high temperature used (120°C compared to 70°C to 80°C for carane runs). After more careful analysis of the reaction product, the highest purity of any single compound was only 20% or 30%, so obviously the reaction temperature was too high and isomerization conditions were being approached. Deactivation was still un-

doubtedly taking place during this run but because of the high temperature either lengthening the run or higher space velocities would be needed before conversion would drop below 100% and deactivation could be followed.

E. Effects of Reaction Variables

Figures 18 through 21 show the effect of operating variables on delta-3-carene conversion and carane selectivity.[1] The variation associated with feed and catalyst quality makes any qualitative statement about reaction variables very questionable. Ideally a statistical analysis such as a factorial design studying the effect of temperature, pressure, and space velocity as well as catalyst age, on delta-3-carene conversion and carane yield would have been made. With replications of such a design interactions between variables could have been detected and an optimum policy established. Unfortunately, the nature of this work severely limits a design of this type. Besides the variation in feed and catalyst quality already mentioned, the major portion of this research was directed toward experimenting with different catalyst and feed improvement methods. Before a statistical analysis could be undertaken, a catalyst and feed treatment policy would have to be decided on and then held constant while the optimization experiments were being performed. A statistical test, evaluating the

(1) Conversion is the percent of delta-3-carene converted to all products. Selectivity is the yield of carane obtained based on the percentage of delta-3-carene converted. The product of conversion and selectivity gives the actual carane purity at the point considered.

four factors discussed earlier, at two levels (a 2^4 factorial) with two replicates, to check for interaction effects, would require 32 data points. At least eight months to a year of experimental work would be required to obtain these data.

Although definite statements about the effects of reaction variables were difficult to establish, trends were obvious and, by making several assumptions, an operating policy was established. Run 26 was used to generate the data discussed below and, of course, qualitative results of other runs were used in making various assumptions and formulating an operating policy. The data presented from Run 26 are not intended to represent exact quantitative predictions for future runs but rather to support assumptions and statements concerning an operating policy.

Interpreting results from Run 26 is complicated by interaction effects of the variables. Since the catalyst is continually deactivating during the run, changes in yield or conversion may be a result of changes in temperature and pressure or actually an effect of catalyst age which is essentially uncontrollable. Thus qualitative experience from previous runs was relied upon in drawing conclusions about variable effects. A statistical analysis would have eliminated this problem but as mentioned earlier, this was impractical. A period of one catalyst-age was allowed for a line-out period between variable changes. This resulted in time periods of from 4 to 16 hours, depending on LHSV.

1. Pressure

The effect of pressure can be seen on Figure 18. This result was similar to that experienced by Hannah. Increasing pressure improves the selectivity of carane while having little or no effect on delta-3-carene conversion. Assuming no interaction between pressure and catalyst age, increasing pressure increases carane selectivity. Twelve hundred psig was the practical limit for this experiment because of the hydrogen supply and equipment limitations. Higher pressures would probably be used in the design of a commercial process. Pressures in the order of 2000 psig would probably be very practical and result in further reduction of the 1,1,4 yield.

2. Temperature

The effect of temperature on conversion and selectivity is shown in Figure 19. This is the effect expected, based on Hannah's work and previous runs made during this project. Conversion is strongly affected by temperature while selectivity is slightly affected until fission of the cyclopropane ring is approached. This indicates that the desired temperature would be the minimum required to obtain 100% conversion. Often the catalyst would be deactivated and increasing temperature would result in very poor selectivity before 100% delta-3-carene conversion was obtained. Experience seemed to indicate that the maximum possible temperature was about 80-90°C at 1200 psig. After

this temperature was obtained, increased delta-3-carene conversion could be achieved only by decreasing the space velocity. This 85-90°C range would no doubt be higher if higher pressures could be used. Above 85-90°C, at 1200 psig, the carane selectivity would drop below 90%.

Another important temperature effect was noted, also. If the catalyst became overheated to 100°C or higher, permanent damage to the catalyst resulted. The carane selectivity, of course, decreased when the temperature was increased but when conditions returned to what they had been previous to the temperature increase, the carane selectivity would not return to its previous value. A period of three to five catalyst ages would be required before the selectivity would even approach what it had been previously. This effect was noted during two runs. The temperature would have to be maintained at this higher value only for a matter of minutes to cause this effect. Thus, great care must be taken to insure that temperatures in excess of that required to produce 100% conversion are not used. Any overheating from equipment failure could obviously be disastrous to the catalyst.

3. Space Velocity (LHSV)

Figure 20 shows the effect of space velocity on selectivity and conversion. Decreased conversion with increased space velocity is an obvious result. The effect on selectivity is not so obvious, however. Previous experience seemed to indicate that

selectivity was a function of temperature and pressure only. The slight decrease in selectivity with increasing space velocity shown in Figure 20 may be a result of different catalyst ages or could result from poor heat transfer at higher space velocities. Higher space velocities may result in a slightly higher localized bed temperature than indicated. This would, of course, result in lower yields. Redesign of the reactor so that the heat of reaction could be dispersed at higher space velocities could eliminate the apparent effect of space velocity on selectivity shown on Figure 20. Lower space velocities are indicated by Figure 17 but it should be re-emphasized that Figure 20 is from data taken during Run 26 only. Often on different runs, similar conversion and selectivity could be obtained at space velocities different by as much as a factor of five.

4. Catalyst Age

Figure 21 shows the effect of catalyst age on yield and conversion. Again this is the expected result. Catalyst age is defined as cc's of feed per gram of catalyst. The slope of the conversion line becomes the rate of deactivation; i.e., the loss of percentage units of conversion per catalyst age. The horizontal line for selectivity verifies the assumption that selectivity is a function of temperature and pressure only.

5. Hydrogen Flow

Hydrogen flow or hydrogen-to-terpene mole ratio was not considered as a variable during this work. Since the reaction

system is three-phase, pressure has the effect of increasing the hydrogen concentration. Increased hydrogen flow at a fixed pressure has no effect until a hydrogen velocity is reached that sweeps the delta-3-carene through the bed, effectively reducing the delta-3-carene liquid hourly space velocity. This conclusion was verified by Hannah during his research.

A hydrogen to delta-3-carene mole ratio of 3.5:1 was used for this work and held constant. Hannah experienced no change in selectivity for hydrogen to delta-3-carene mole ratios from 2 to 12. A commercial process might utilize a ratio even lower than 3.5:1, eliminating the necessity of recycling hydrogen or of additional costs from the excess hydrogen.

6. Reactor Operating Policy

Optimum reactor conditions can now be established and used as a reactor operating policy for the reactor and equipment used during this project. Low space velocities should be used, .02 to .05 hr^{-1} LHSV, maximum pressure (at least 1200 psig) should be used, and temperature should start at about 30-40°C and be increased gradually to obtain 100% conversion, keeping the selectivity above 90%. As soon as the selectivity drops to 90%, increasing the temperature should be stopped. After the maximum temperature has been reached and the space velocity has been lowered to the limit of the equipment, the catalyst can be used until the delta-3-carene conversion has dropped to about 50-60%.

This policy will be further explained and coordinated with feed treatment and distillation operations in Section G of the Discussion and Results.

F. Distillation Results

Figures 22 through 25 and Table V show distillation results. All distillations were batch steam operations. Steam was generated by adding water to the still pot and was necessary to prevent the decomposition of the delta-3-carene and reactor product. Approximately equal volumes of hydrocarbon and water were required for a still pot charge.

The Figures indicate a surprisingly good separation between delta-3-carene and carane, in view of the small boiling point difference, while the separation between carane and 1,1,4-trimethylcycloheptane is quite poor, as would be expected. Saturated myrcene, 2,6-dimethyloctane, appears as the most volatile component.

The key to high purity carane production is, then, supression of 1,1,4-trimethylcycloheptane production from the hydrogenation process. This is done at the expense of delta-3-carene conversion, as explained in the section on establishment of an operating policy. The temperature used for hydrogenation process is the maximum temperature that will still give a 92-93% carane selectivity at the lowest possible space velocity, as limited by the delta-3-carene pumping equipment. This may result in as low as 50% delta-3-carene conversion when nearing the end of a run but the carane can be recovered by distillation.

Figures 22 and 25 indicate an apparent delta-3-carene volatility enhancement by the presence of 2,6-dimethyloctane. This results in contamination of the first 10% to 15% of the distillation charge with 2,6-dimethyloctane and delta-3-carene. If the delta-3-carene was not present in the first 15% of the overhead, this product would be at least 90% carane. A minimum boiling hydrocarbon azeotrope could be occurring between delta-3-carene and 2,6-dimethyloctane although this was not verified. Myrcene can be removed via the mechanism of Diels-Alder reaction with maleic anhydride as mentioned earlier. However, a detailed economic analysis would be needed to see if the additional carane that could be recovered could justify removing myrcene from the delta-3-carene feed. Approximately .8 to .9 gallons of 92-93% carane can be produced per gallon of delta-3-carene.

G. Hydrogenation Process

A complete catalytic hydrogenation process for delta-3-carene can now be described. Delta-3-carene, 95-99% pure, prepared by steam distillation of crude turpentine, is first contacted with an equal volume of dilute caustic and allowed to stand for at least 24 hours. Mild agitation would produce better contacting but severe agitation appears to produce relatively stable emulsions. The caustic contacted delta-3-carene is then steam evaporated under nitrogen. From this point the delta-3-carene is handled and stored under nitrogen to reduce oxygen contamination. After

evaporation the delta-3-carene is dried over a layer of $CaSO_4$ desicant for 24 hours.

Spent Harshaw 1404-T from a previous hydrogenation run is then used to further treat the delta-3-carene. Reaction conditions used were 1200 psig, 70-80°C, and 0.10 hr^{-1} liquid hourly space velocity. Milder conditions could probably be used but were not investigated during this work. The delta-3-carene, after being treated with spent catalyst, is again dried over $CaSO_4$ desicant. This material is then used as feed on fresh Harshaw 1404-T catalyst charge.

This elaborate feed pretreatment procedure is necessary in order to remove sulfur, oxygenated products, and water from the delta-3-carene to prevent catalyst poisoning so that high carane selectivity can be obtained to relatively long catalyst ages. Without this pretreating, delta-3-carene conversion drops to below 50% (Figure 16) by a catalyst age of 10-15 cc's of delta-3-carene feed per gram of catalyst, while with pretreating (Figure 17), 50% conversion was extrapolated to a catalyst age of approximately 65.

After the delta-3-carene conversion drops below about 50%, separating the carane by distillation becomes difficult with the distillation equipment available for this project and the catalyst was used to treat delta-3-carene feed for the next hydrogenation run.

Hydrogenation conditions used for carane production were 1200 psig, 70°C, and 0.03 hr^{-1} space velocity. These conditions resulted in carane selectivity of about 92-95%. Unreacted delta-3-carene was separated by steam batch distillation. Forty theoretical stages were used at 28:1 reflux ratio. Almost no separation was obtained between carane and 1,1,4-trimethylcycloheptane. This was why high carane selectivity during the hydrogenation process was essential for producing high purity carane.

Using the process described above, approximately .8 to .9 gallons of 92-93% carane was obtained per gallon of delta-3-carene charged to the process. Unreacted delta-3-carene distillation bottoms was recycled back to the hydrogenation reactor. The yield of less than one gallon of carane product per gallon of delta-3-carene results from the first 10-15% of the product distillation charge being contaminated with 2,6-dimethyloctane (saturated myrcene).

V CONCLUSIONS

Carane, in purities above 90%, can successfully be produced by the catalytic hydrogenation of delta-3-carene in a continuous fixed bed reactor. Carane is favored by high pressure, 1200 psig or more. Temperatures below 70-80°C are required to reduce fission of the cyclopropane ring and result in high carane selectivity. Fairly good separation between delta-3-carene and carane was obtained with 40 theoretical stages and 28:1 reflux ratio. Almost no separation was obtained between carane and other saturated hydrogenation reaction products.

Catalyst deactivation still presents itself as a problem. More rugged and active catalysts or better feed purification may be possible solutions to this problem. Oxygenated products produced from the auto-oxidation of delta-3-carene, water, and sulfur have been shown to be present in the delta-3-carene. Feed for Run 29 had sulfur reduced from .09% to less than .01%. No water or rust appeared in the collection flask during Run 29, indicating almost complete removal of oxygenated product from the Run 29 feed, also. However, the catalyst charge for Run 29 still deactivated at a rate of .75 units of conversion per catalyst age, indicating that some poisoning mechanism is still taking place. This mechanism is still not verified.

Residual traces of sulfur, nitrogen, or oxygen may still be causing the poisoning, or something still not even recognized may be the source. Polymer or resinous material may be causing the deactivation but this seems unlikely in an atmosphere of

hydrogen. The delta-3-carene feed is a very narrow boiling range material (2-4°C) so this further eliminates the possibility of heavy resinous material being contained in the delta-3-carene feed. There is a very strong possibility that the poisoning is actually the result of more than one poisoning mechanism since no feed pretreatment method produced a great improvement in catalyst deactivation ratio.

If catalyst deactivation could be eliminated or greatly minimized, the need for distilling the reactor product could be eliminated and, of course, longer catalyst life would be very desirable from an economic standpoint.

VI SUGGESTIONS FOR FUTURE STUDY

Several areas for continued research are evident after completion of this project. The key to reasonable carane production, catalyst life, and a possible successful commercial process appears to be pretreating the feed to remove impurities which act as catalyst poisons. This operation should be investigated in greater detail. Analytical procedures should be established so that a quantitative measure of the impurities removed can be obtained. The effects of operating variables on the pretreatment operation should be investigated and some indication of the life of the nickel catalyst, when used for pretreating the delta-3-carene feed, should be obtained. A more efficient method for removing impurities may also be found.

Successful development of analytic procedures for impurities in the delta-3-carene feed would also allow a quantitative measure of delta-3-carene feed quality to be obtained. Sulfur, oxygen, and water are the impurities indicated during the course of this research project.

The apparent delta-3-carene volatility enhancement in the presence of 2,6-dimethyloctane and the shift in carane yield when ethanol is added to the delta-3-carene feed are both interesting effects which may suggest future work. Certainly optimum batch distillation reflux ratios and feed compositions could be determined by a distillation study of the hydrogenation reactor product.

If larger volumes of varane are required in the future, a statistical analysis based on a designed experiment testing the effects of operating variables could be made. Better optimum operating conditions or policies could be obtained, these possibly resulting in a longer catalyst life. Preliminary results at higher reflux ratios indicated a slight separation between carane and 1,1,4-trimethylcycloheptane, 1,1,4-trimethylcycloheptane being more volatile. Several distillation samples were taken at carane purities above 95%. A more detailed study of the distillation of the hydrogenation product would establish the distillation conditions for recovering higher purity carane fractions (95% or above).

APPENDIX

Table I. Compounds and Properties

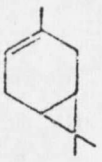
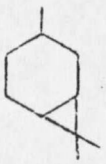
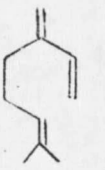
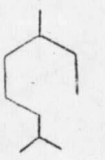
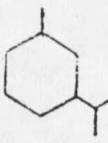
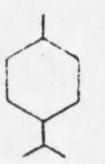
Compound	Structure	Specific Gravity	Boiling Point	Refractive Index	Reference
Delta-3-Carene		d_{30}^{30}	705 mm Hg	n_D^{30}	3
		0.8586	168-169°C	1.469	
Carane		d_D^{20}	684 mm Hg	n_D^{20}	3
		0.8411	162°C	1.455 - 1.4582	
1,1,4-Trimethyl-cycloheptane		d_{25}^{25}	623 mm Hg	n_D^{20}	Exp. Det. (95% pure)
		0.796	160-161°C	1.4414	3
Myrcene		d_4^{20}	760 mm Hg	n_D^{20}	2
		0.799	171-172°C	1.470	
2,6-Dimethyl-octane		d_4^{20}	760 mm Hg	n_D^{20}	2
		0.7291	158.5°C	1.4107	
Meta Menthane		d_4^{20}	760 mm Hg	n_D^{20}	2
		0.7965	168.2°C	1.446	
Para Menthane		d_4^{20}	760 mm Hg	n_D^{20}	2
		0.8008	170.7°C	1.4395	

Table I (continued)

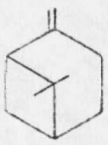
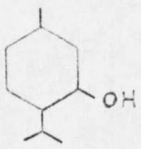
Compound	Structure	Specific Gravity	Boiling Point	Refractive Index	Reference
Alpha Pinene		d_4^{20} 0.8595	760 mm Hg 155-156°C	n_D^{20} 1.4663	2
Beta Pinene		d_4^{20} 0.8654	760 mm Hg 162°C	n_D 1.487	4
Menthol		d_{15}^{15} .890	760 mm Hg 216.3°C	----	5

Table II. Selected Hydrogenation Run Data

Run Number	Catalyst	Deactivation Rate - Units of Conv/C.A.	Maximum Purity	Conditions at Maximum Purity		
				Temp. °C	Pressure psig	L.H.S.V. hr-1
1	104-T	4.25	89	70	1000	.10
3	104-T	3.13	80	70	1000	.10
5	104-T	0.0	83	70	1000	.10
6	104-T	0.75	93	70	1000	.10
9	104-T	1.33	75	75	1000	.10
10	3001-T	----	10	72	1000	.10
13	1404-T	2.80	97	72	1000	.10
17	Raney Nickel	15.0	70	80	1000	.10
18	1404-T	3.8	74	80	1000	.10
19	1404-T	4.0	70	80	1000	.10
20	1404-T	3.0	70	80	1000	.10
26	1404-T	3.6	95	45	1200	.02
28	1404-T	2.5	82	80	1200	.03
29	1404-T	0.75	95	70	1200	.03

Table III. Thermodynamic Calculations

Compound	$H^{\circ}_{f_{298}}$	S°_{298}	$F^{\circ}_{f_{298}}$	Reference
Hydrogen (g)	0	31.21	---	5
Water (1)	-68.32	16.72	---	5
Ethanol (1)	-66.36	38.4	---	5
Acetic Acid (1)	-116.4	38.2	---	5
Acetic Anhydride (1)	-155.16	----	-121.75	5

Reaction 1

Acetic Anhydride (1) + 2 Hydrogen (g) $\longrightarrow$ 2 Ethanol (1) + Water (1)

$\triangle$ F of reaction at 298°K equals -37.1 K cal/mole

$\triangle$ F of reaction equals zero at 1258°C

Reaction 2

Acetic Acid (1) + 2 Hydrogen (g) $\longrightarrow$ Ethanol (1) + Water (1)

$\triangle$ F of reaction at 298°K equals 4.76 K cal/mole

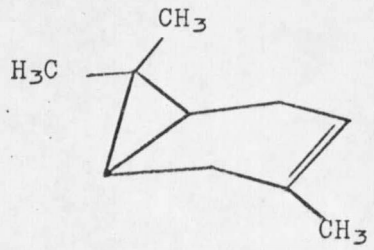
$\triangle$ F of reaction equals zero at 130°C

Table IV. Catalysts and Composition

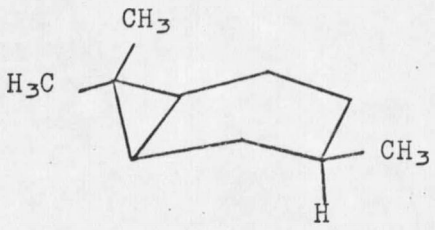
Catalyst	Catalyst Composition
Harshaw 1404-T	70% Ni
Harshaw 104-T	58% Ni on Kieselguhr
Harshaw 4401-E	6% Ni, 19% Tungsten on Si:Al Support; Sulfided
Harshaw 3001-T	49% Ni, 49% Al; Requires caustic activation
Englehard .5% Rhodium	
Girdler G-G9RS	50% Ni on Kieselguhr
Raney #28	Activated Al-Ni catalyst
Raney Nickel	42% Ni, 58% Al; Requires caustic activation

Table V. Batch Distillation Data

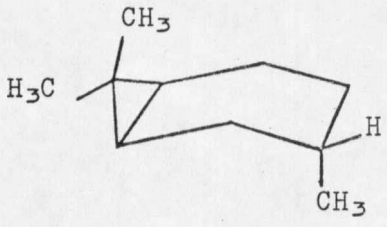
Distillation	Composition, %				Terpene Charge	Col. Diam.	Theor. Plates	Reflux Ratio	% Charge Overhead Above 90% Car.
	Car.	△-3	1,1,4	2,6 Di.					
1	65.5	31.0	3.5 Comb.		275 ml	1"	50	30:1	25+
2	90.6	1.8	6.1	1.5	300 ml	1"	50	30:1	55+
3	87.4	10.3	1.7	0.6	250 ml	1"	50	30:1	45+
4	66.8	28.7	3.4	1.1	29 lbs	4"	40.	28:1	55



Δ -3-Carene



Cis-Carane



Trans-Carane

Figure 1. Structural Comparison of Δ -3-Carene, Cis-Carane and Trans-Carane

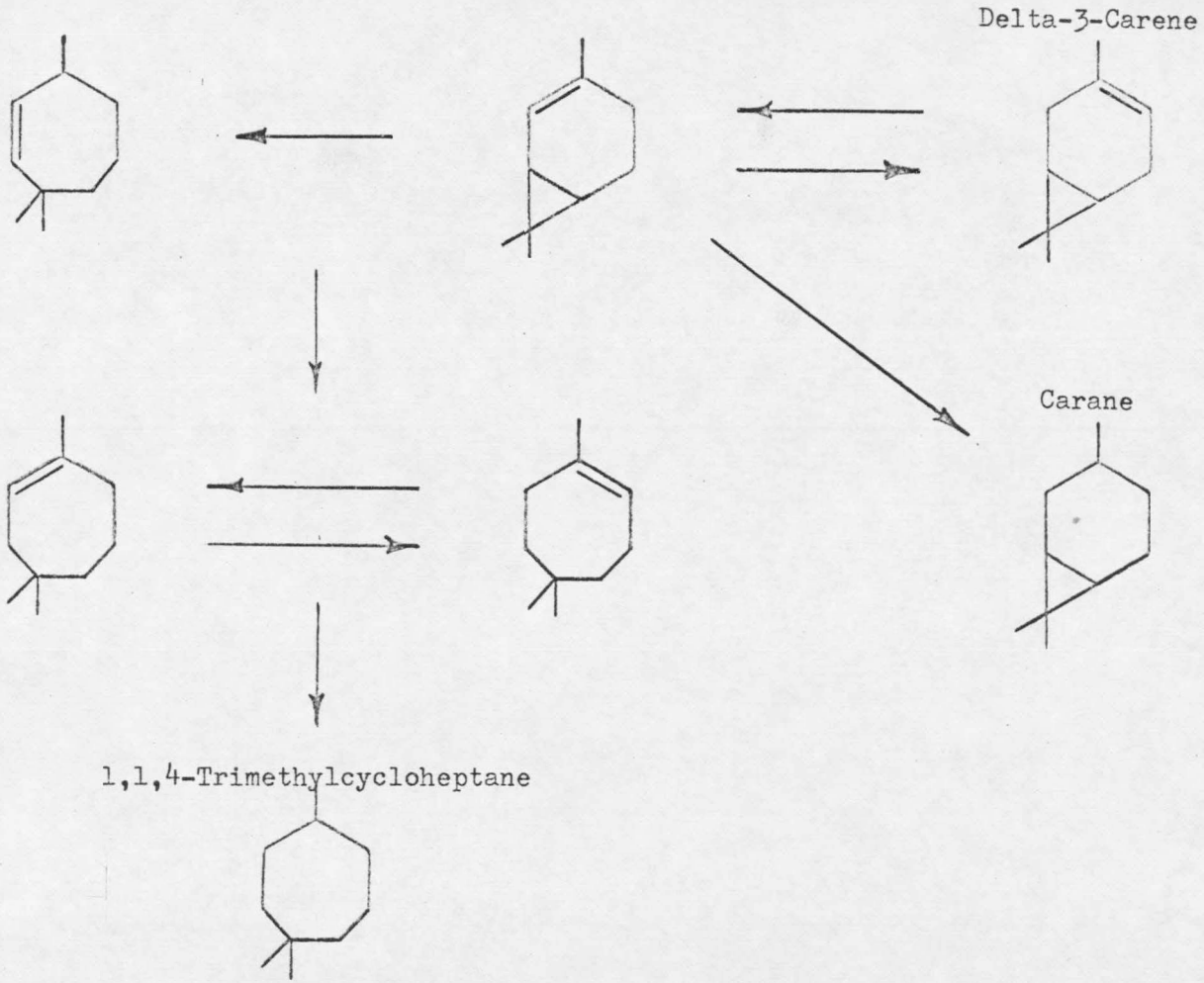


Figure 2. Hydrogenation Mechanism.

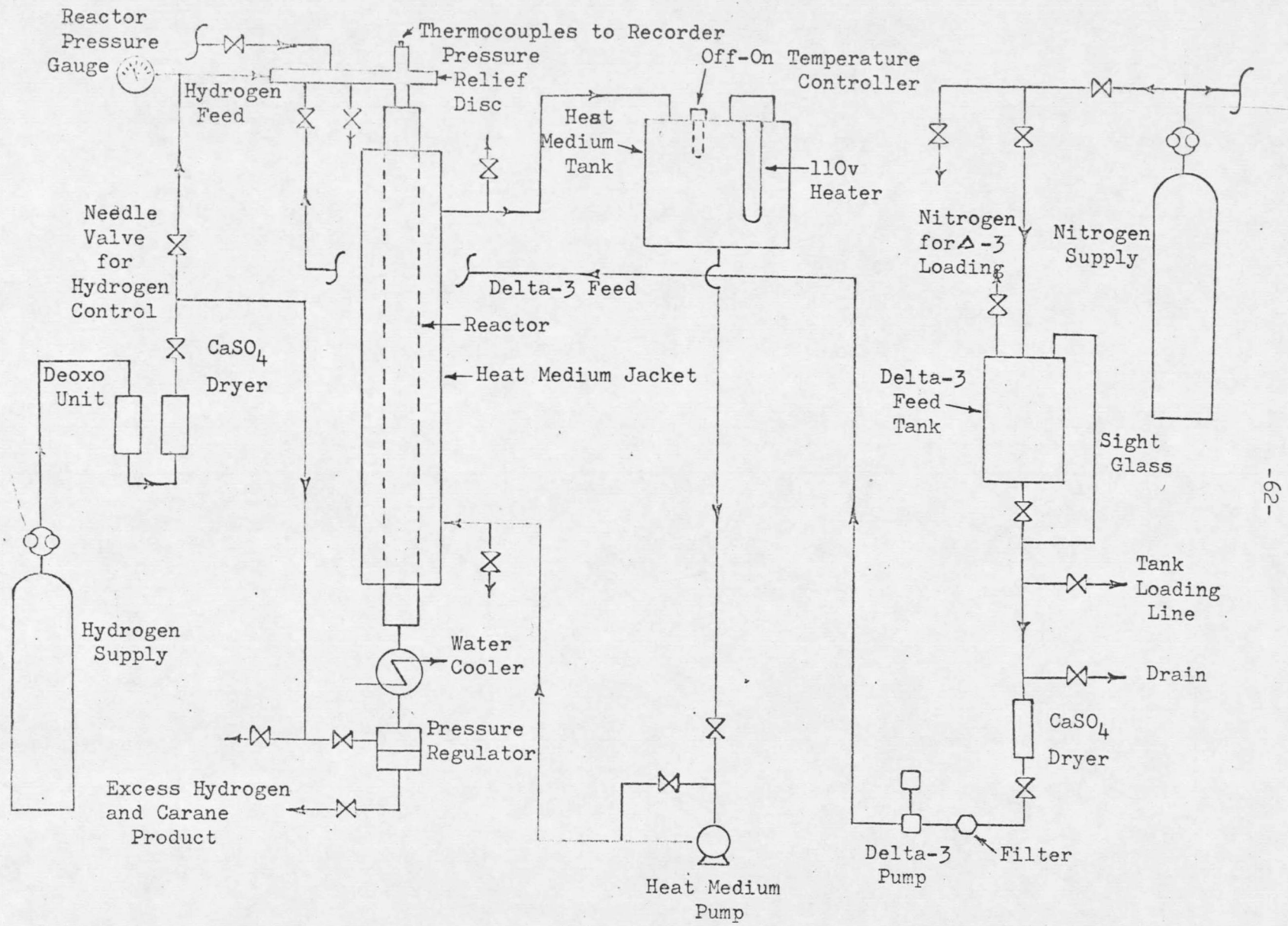


Figure 3. Schematic Diagram of Hydrogenation Unit.

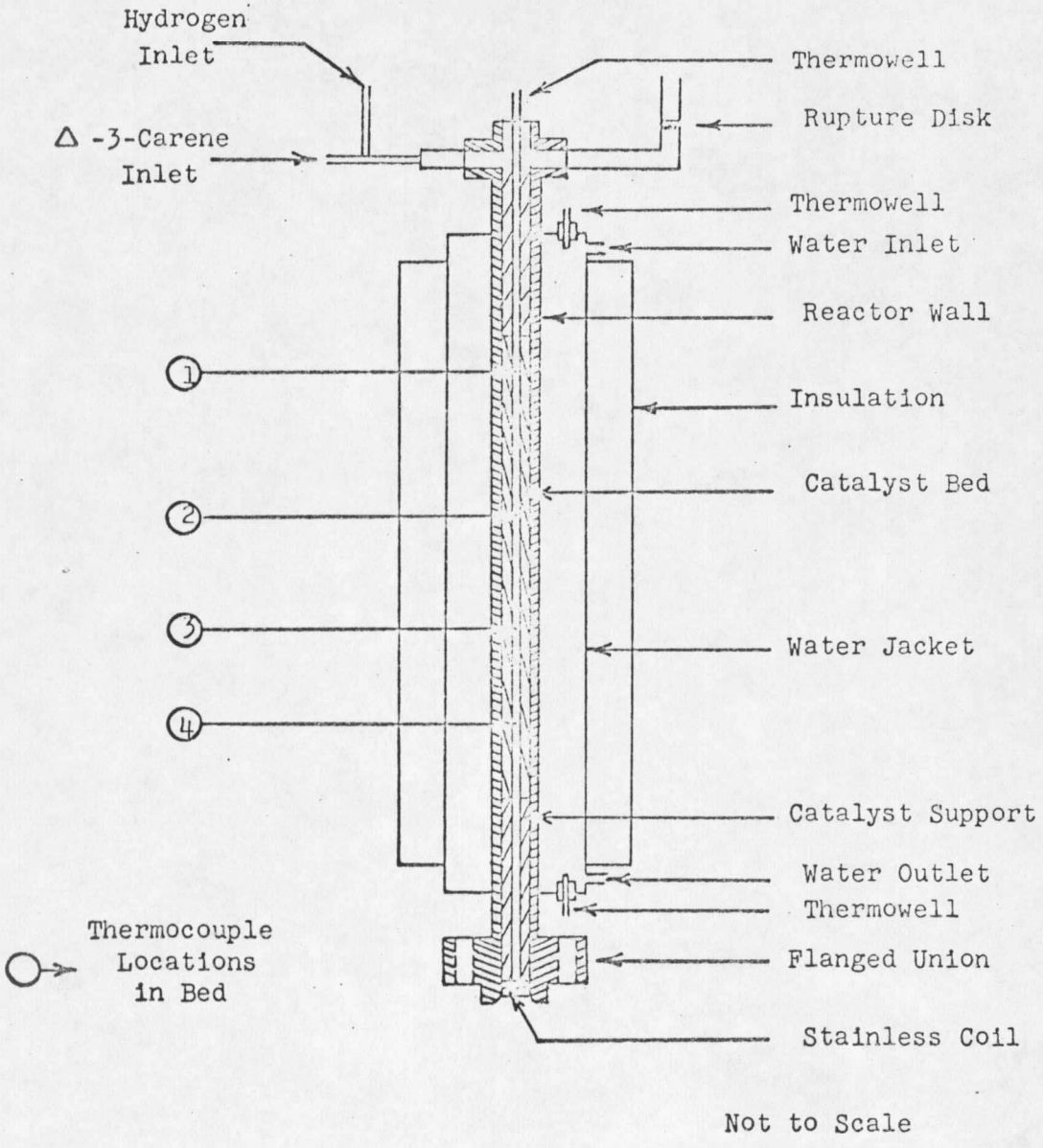


Figure 4. Detailed Diagram of the Fixed-Bed Reactor.

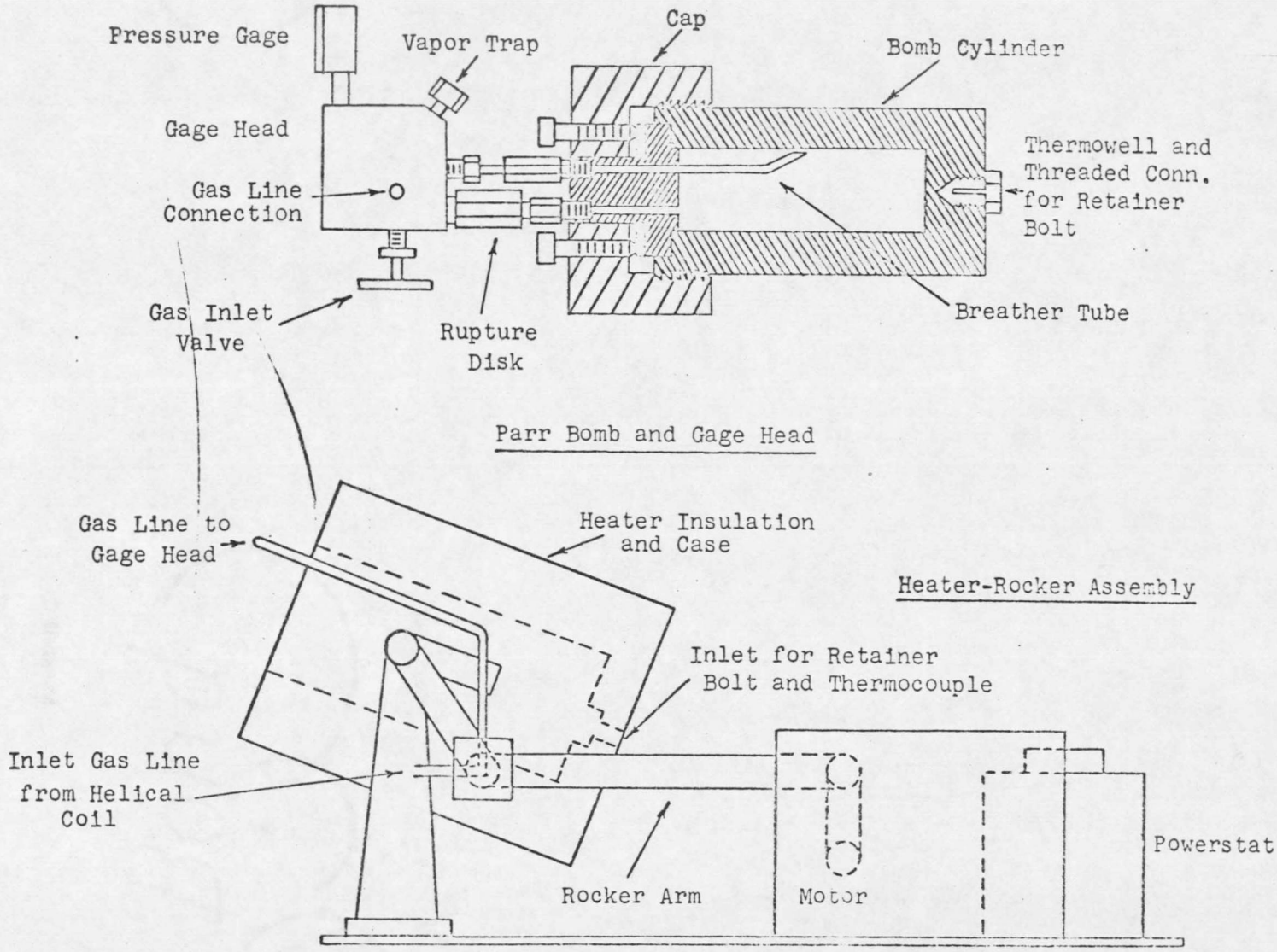


Figure 5. Parr Bomb Reaction Apparatus

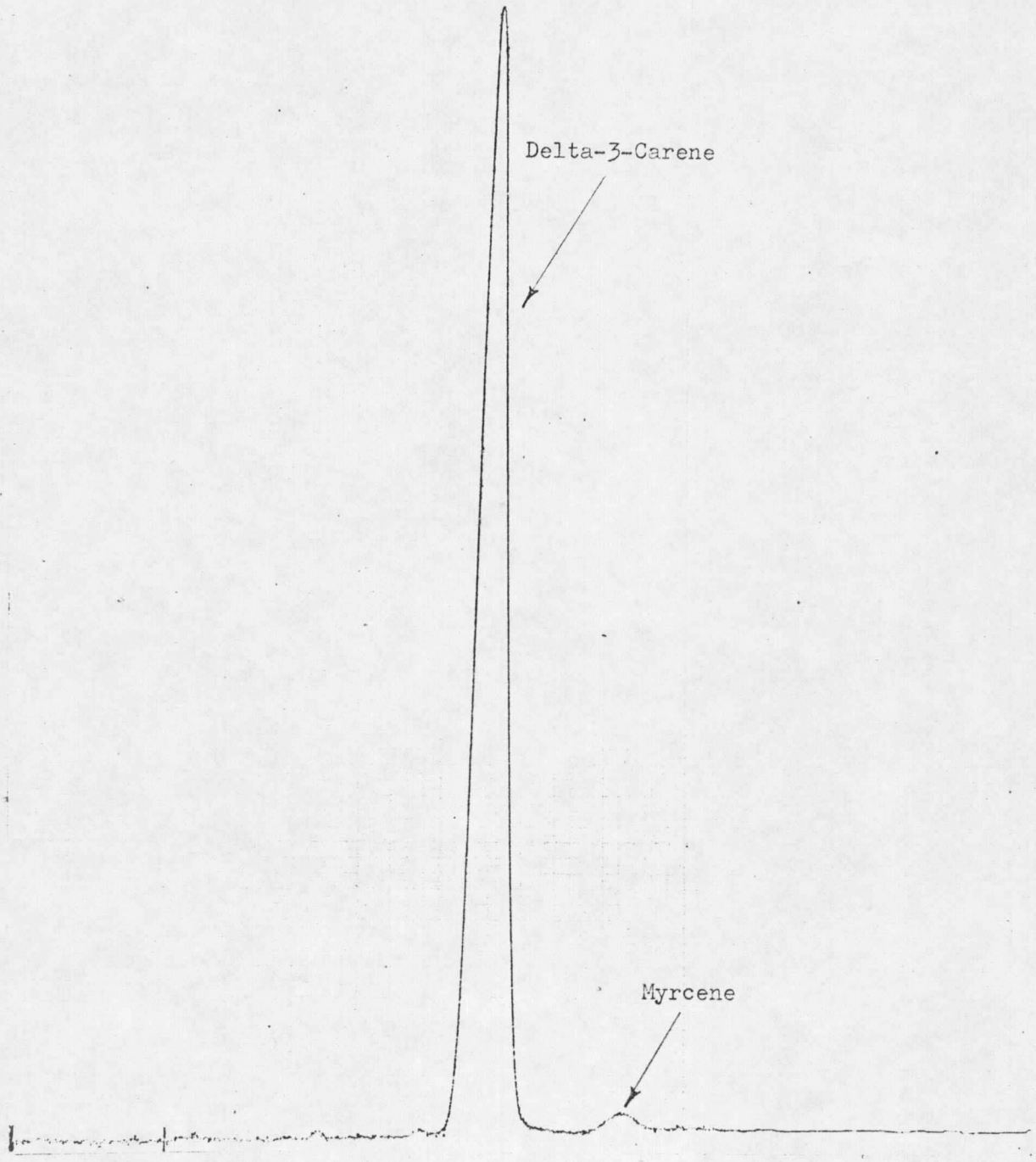


Figure 6. Typical Delta-3-Carene Chromatogram.

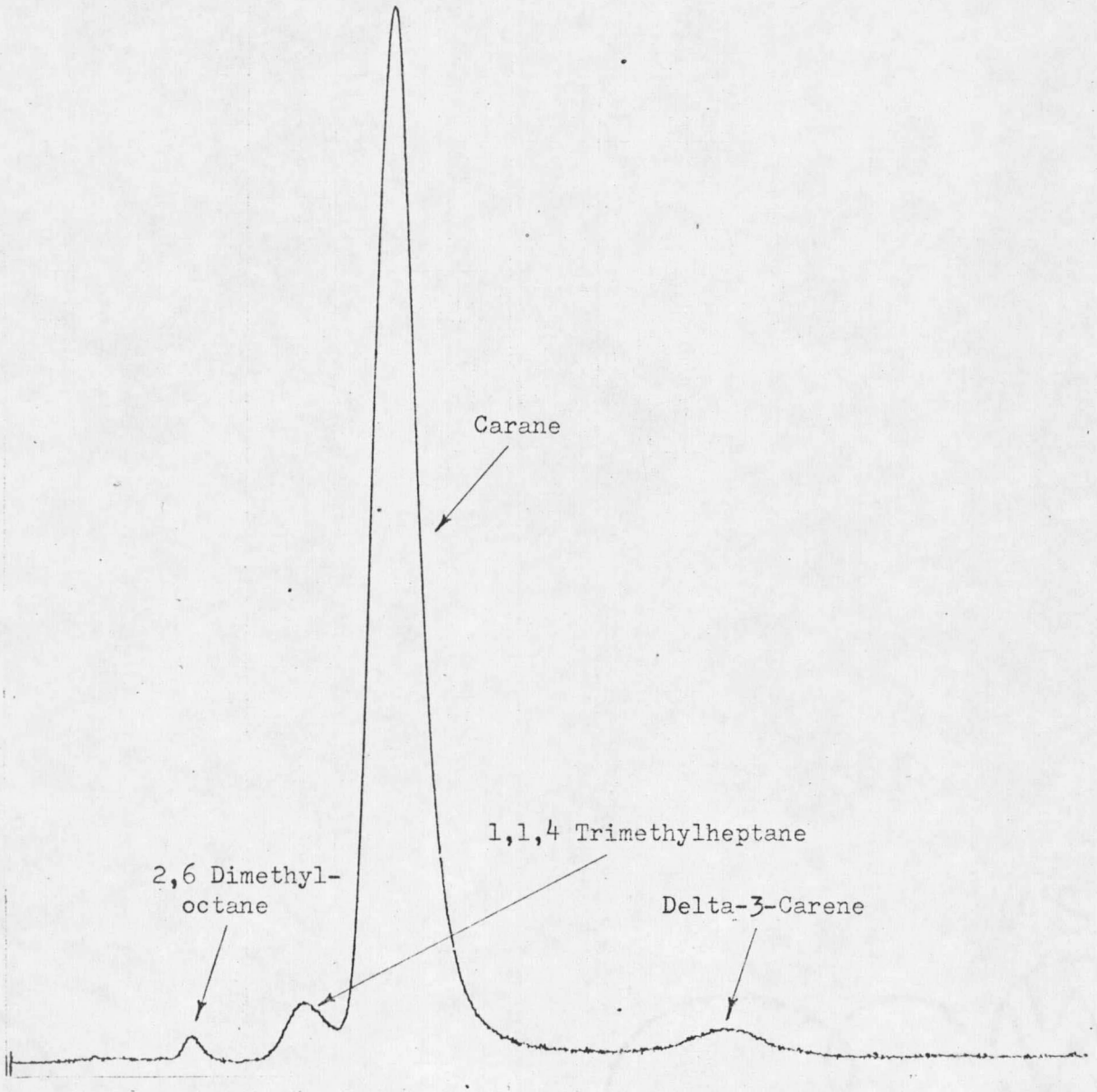


Figure 7. Typical Reactor Product Chromatogram.

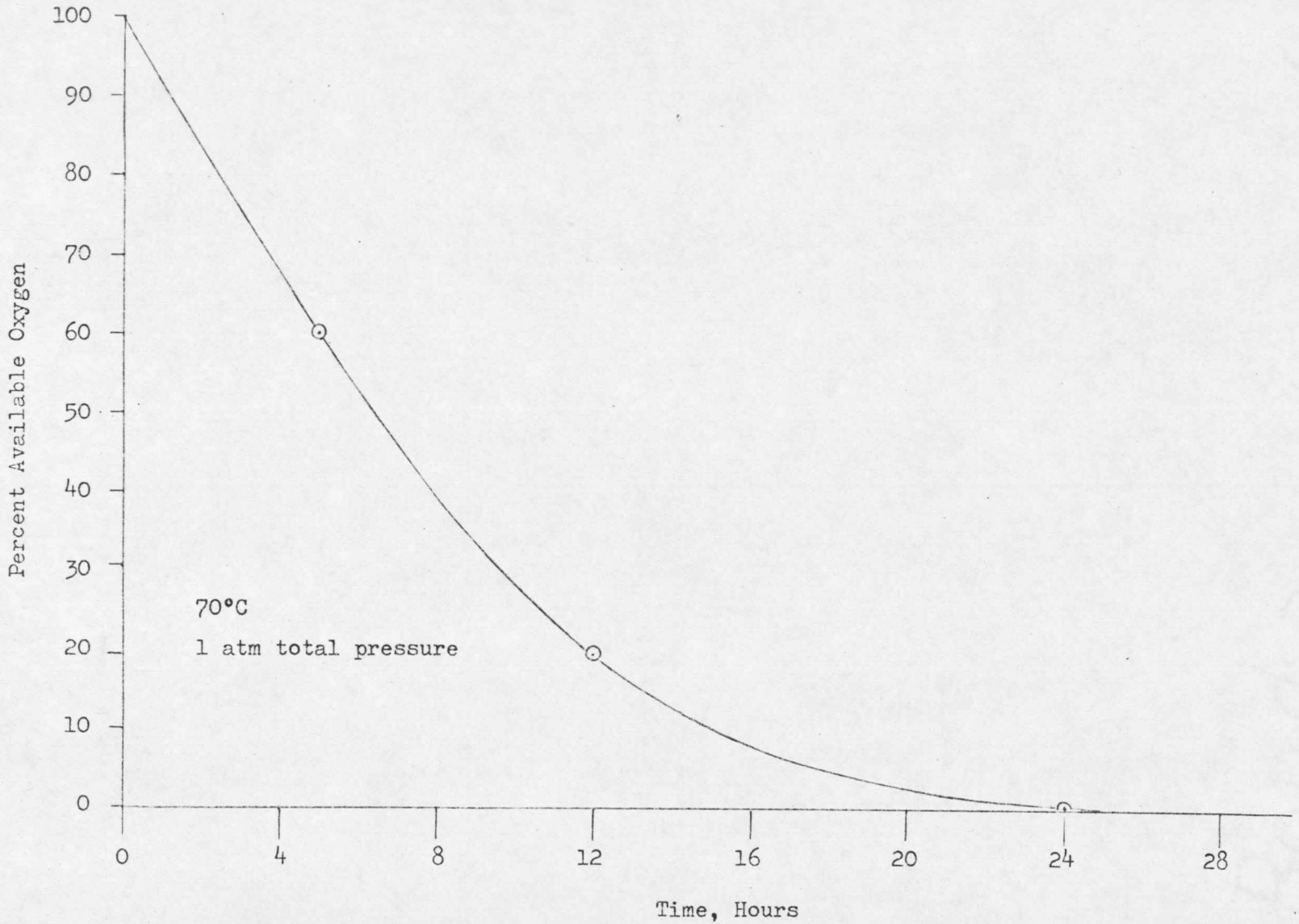


Figure 8. Delta-3-Carene Auto-Oxidation Rate.

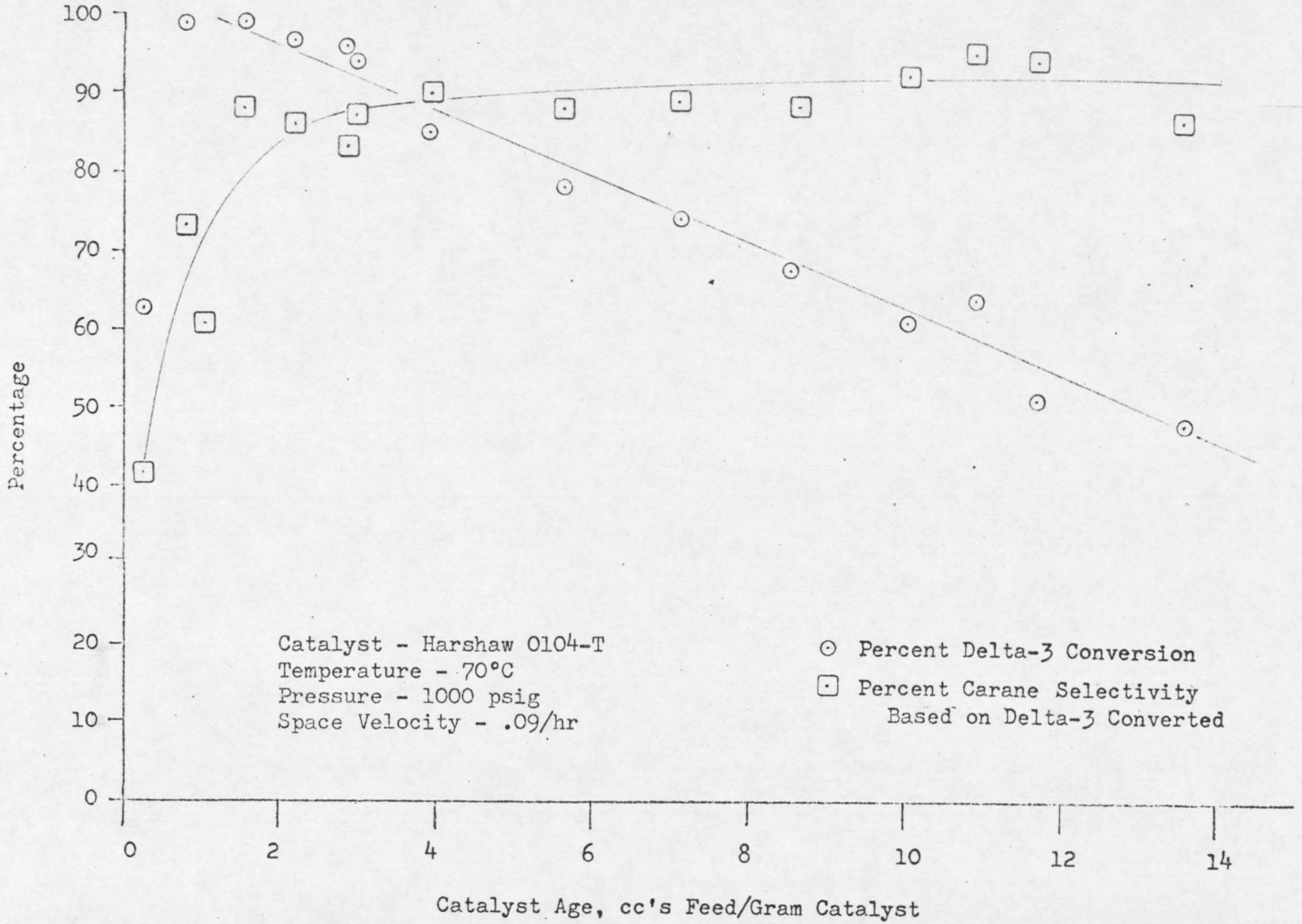


Figure 9 . Run 1.

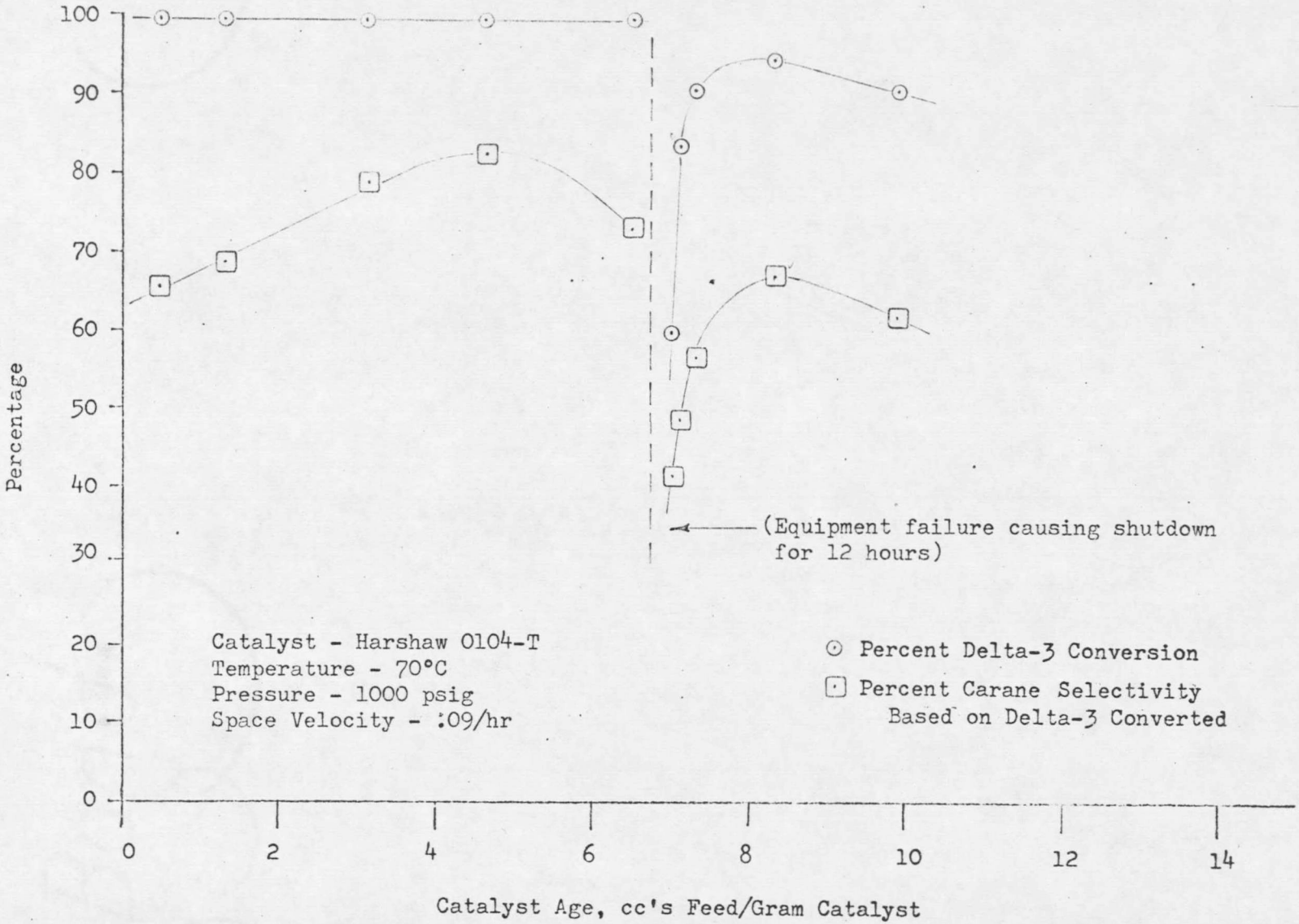


Figure 10. Run 5.

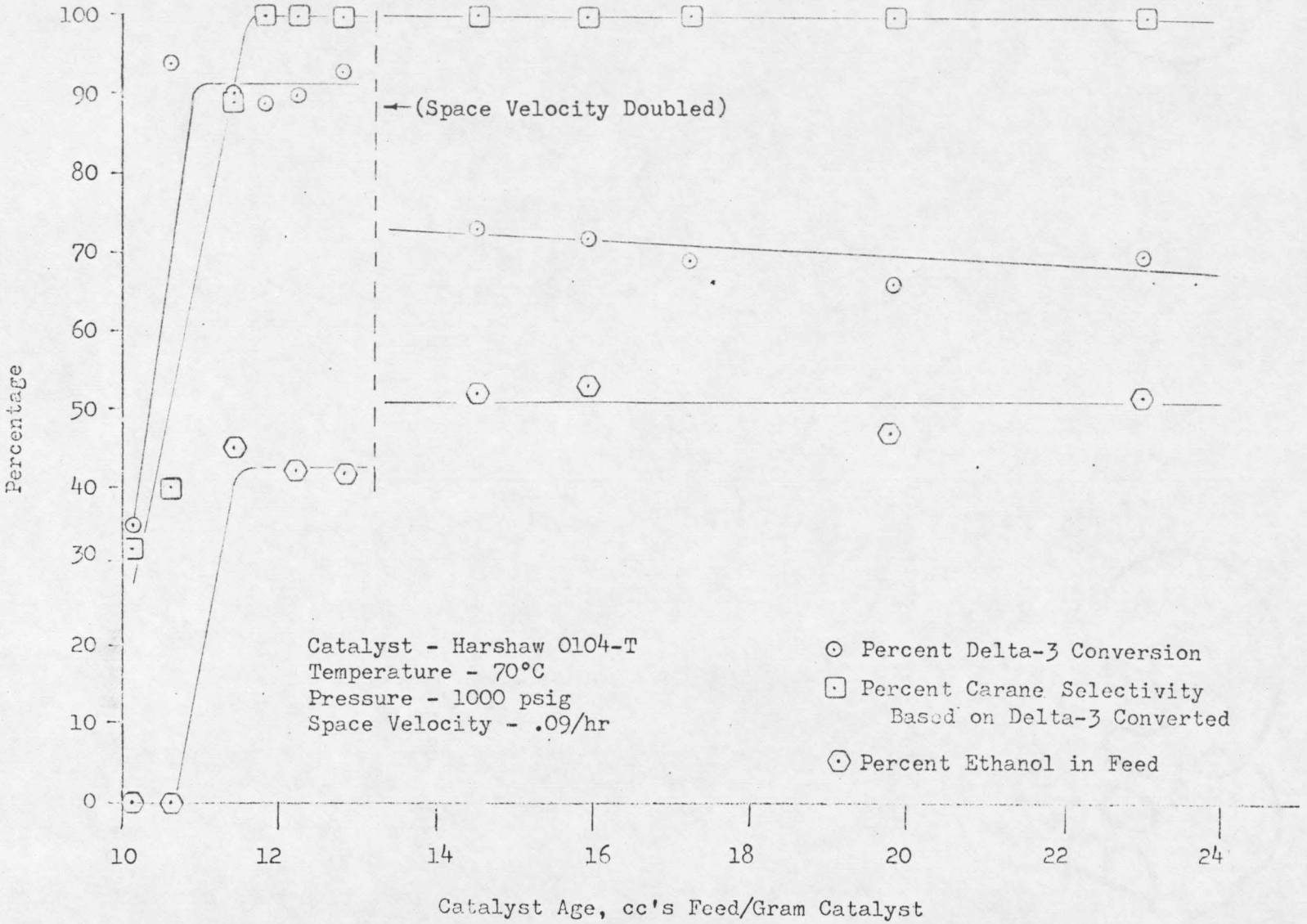


Figure 11. Run 6.

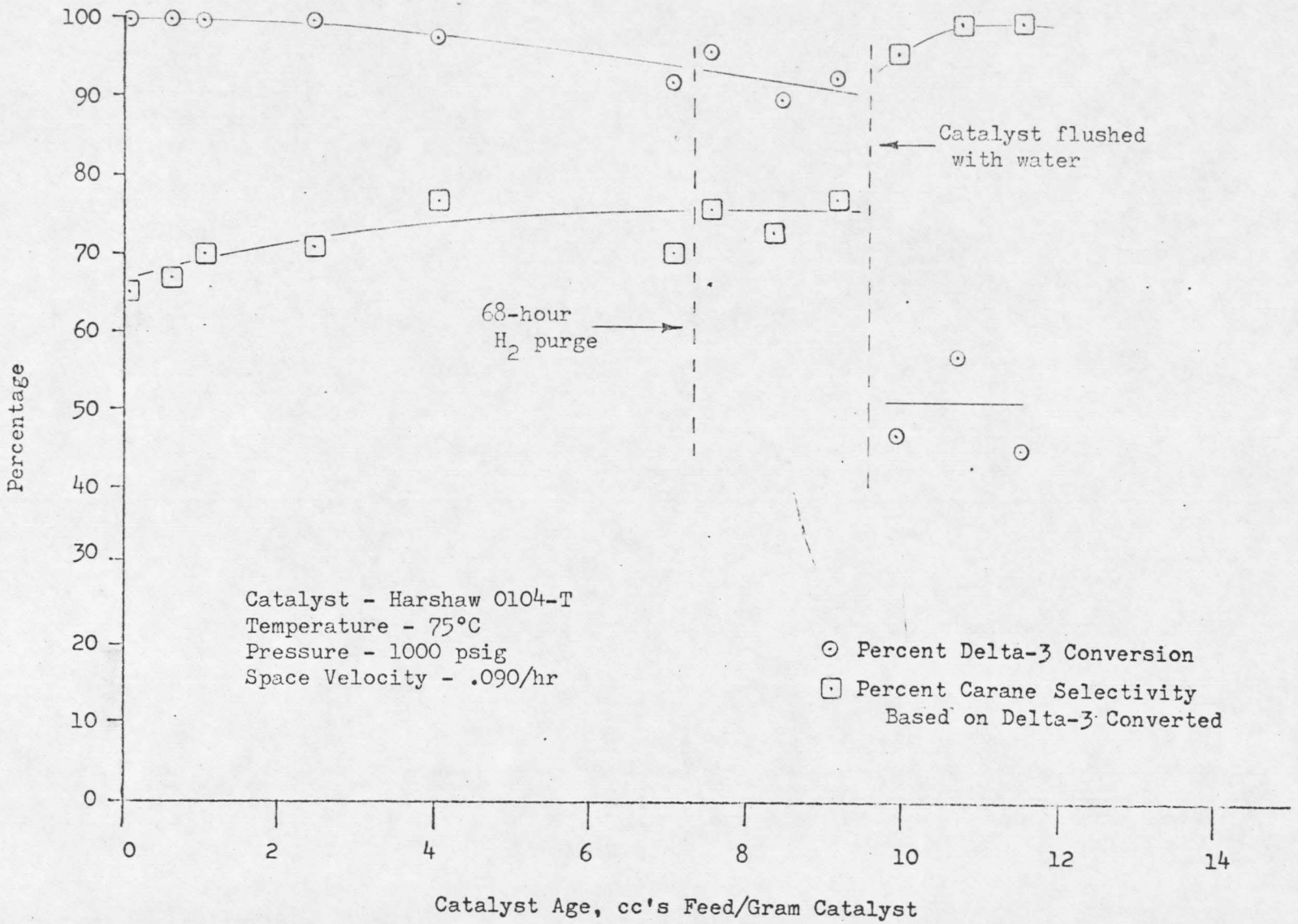


Figure 12. Run 9.

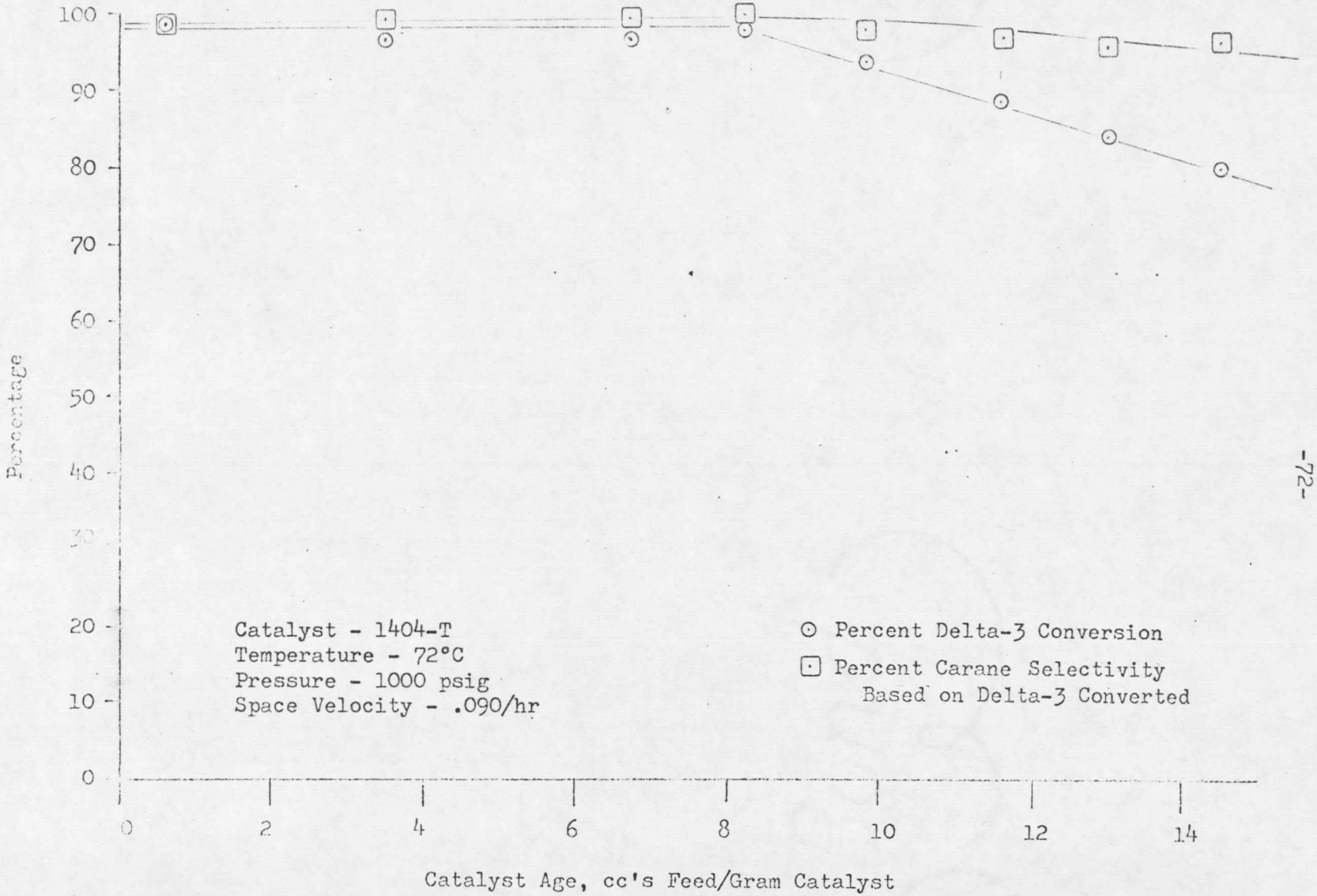


Figure 13. Run 13.

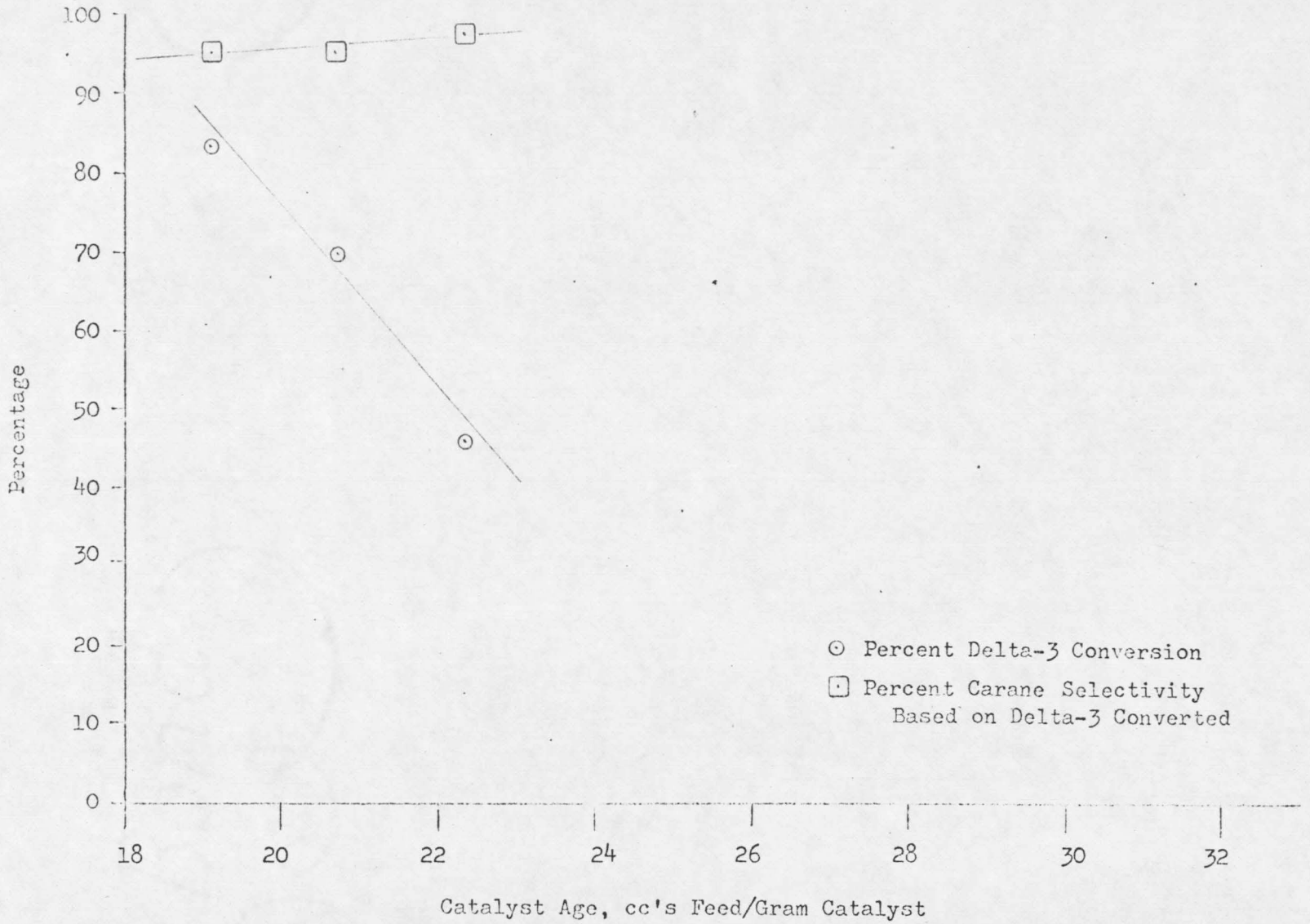


Figure 14 , Run 13 continued.

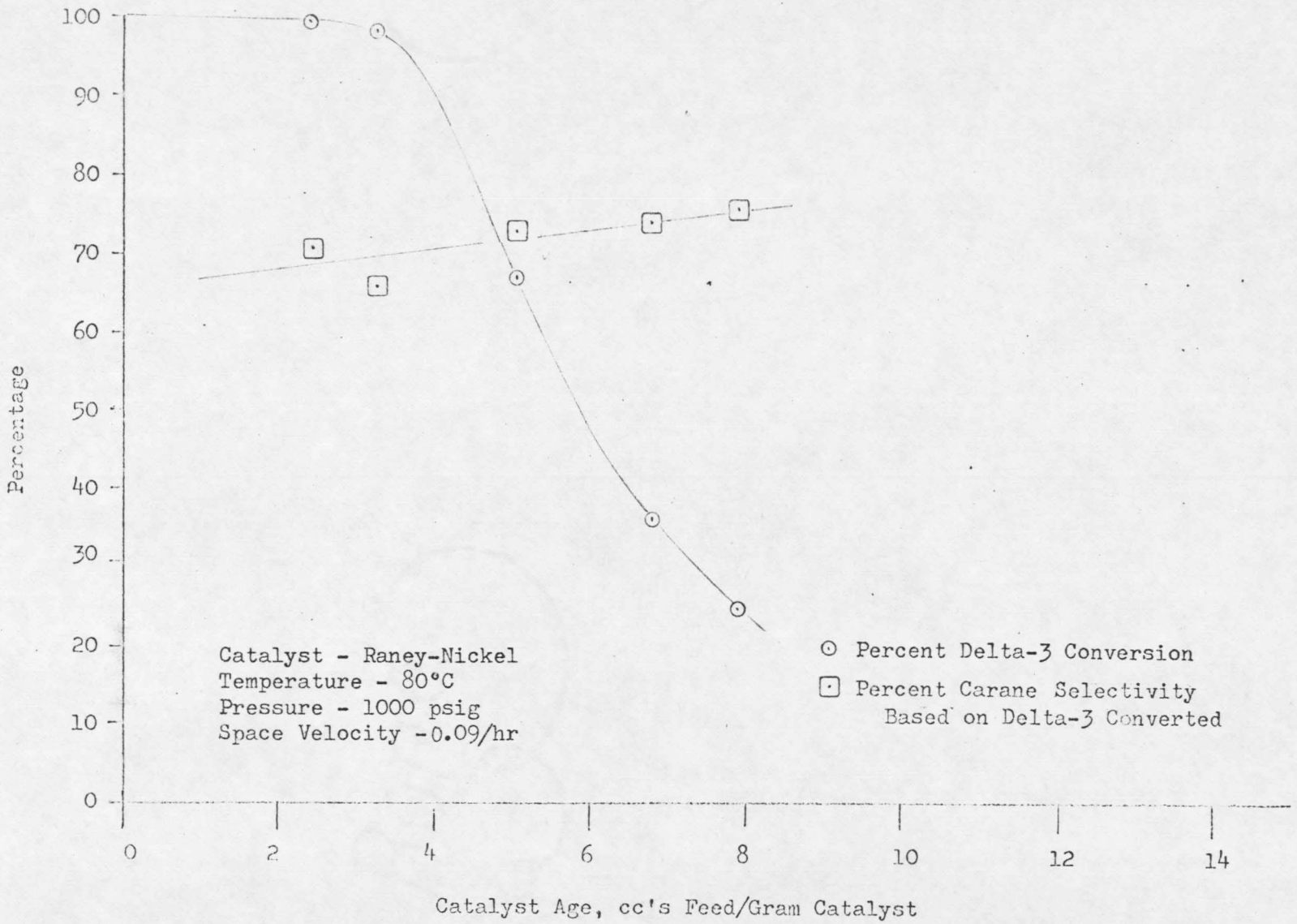


Figure 15. Run 17.

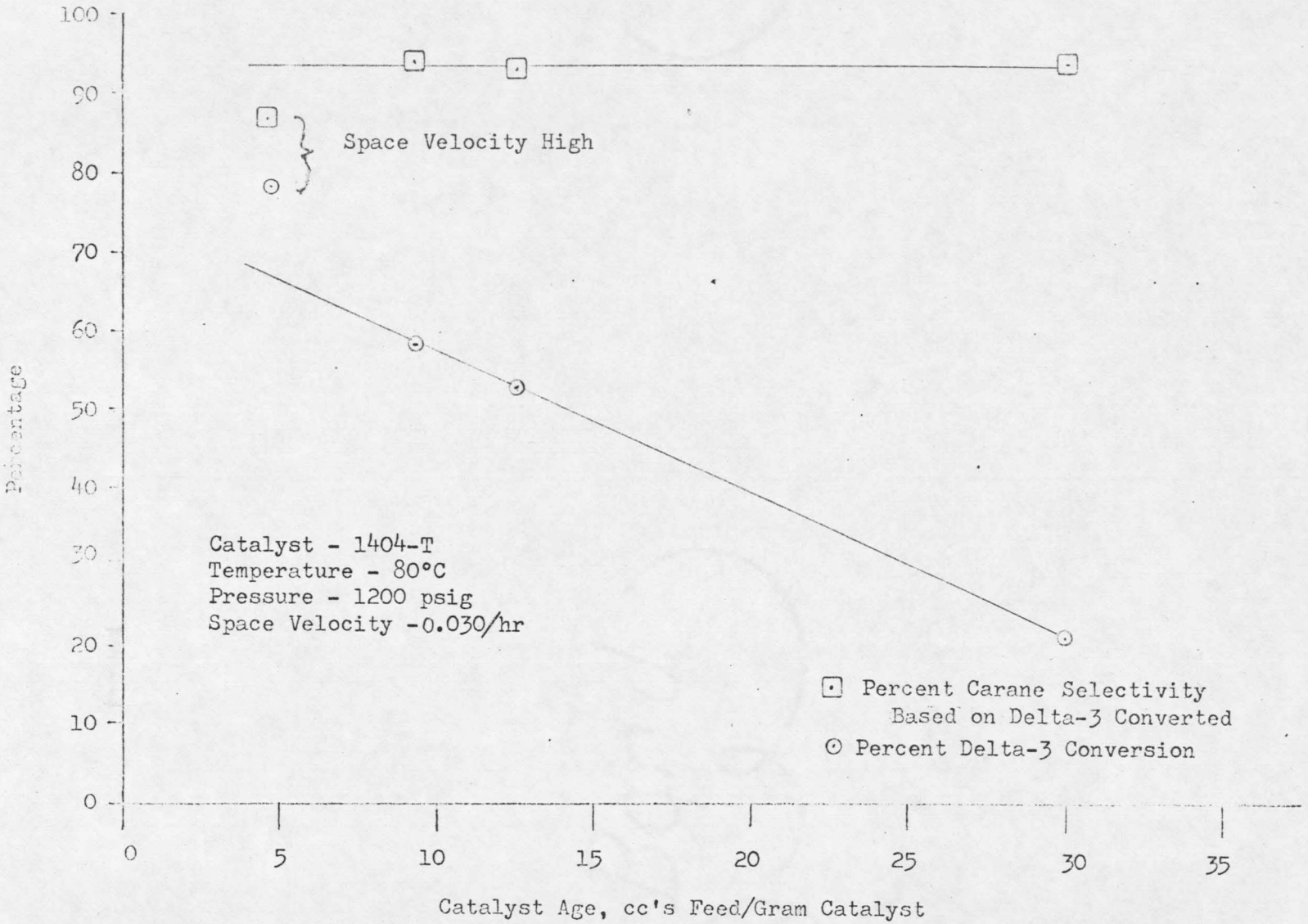


Figure 16. Run 28.

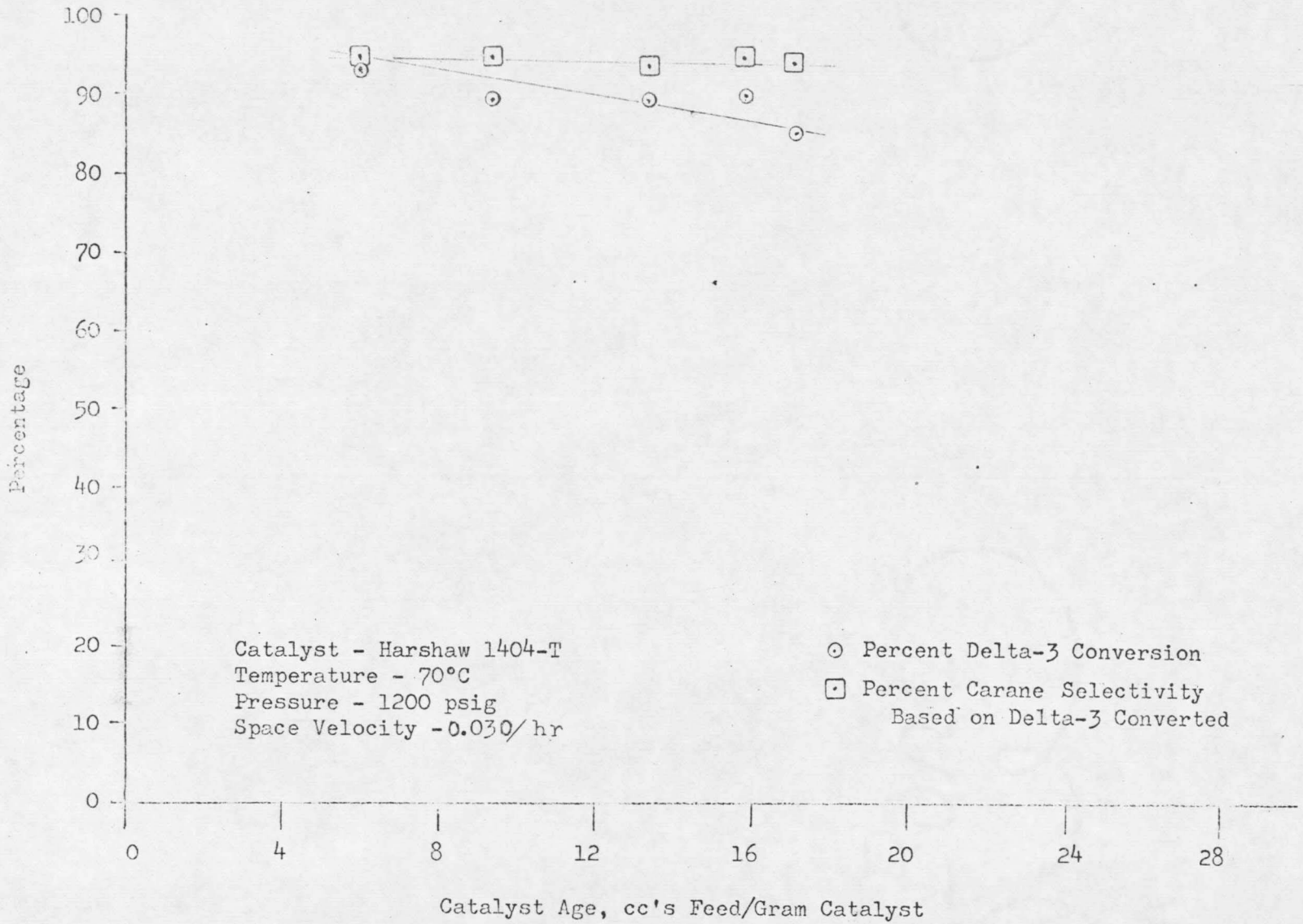


Figure 17 . Run 29.

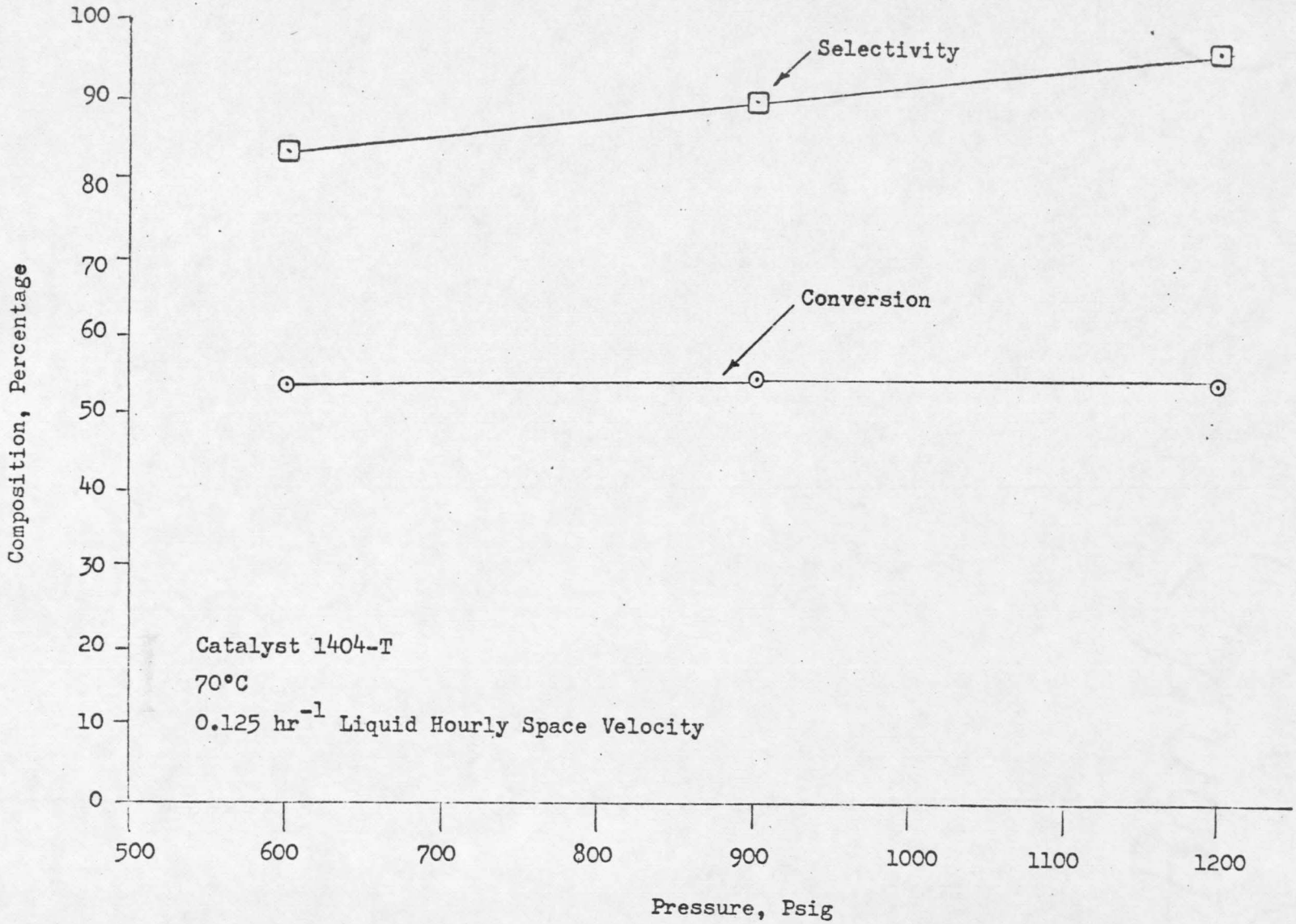


Figure 18. Pressure Effect.

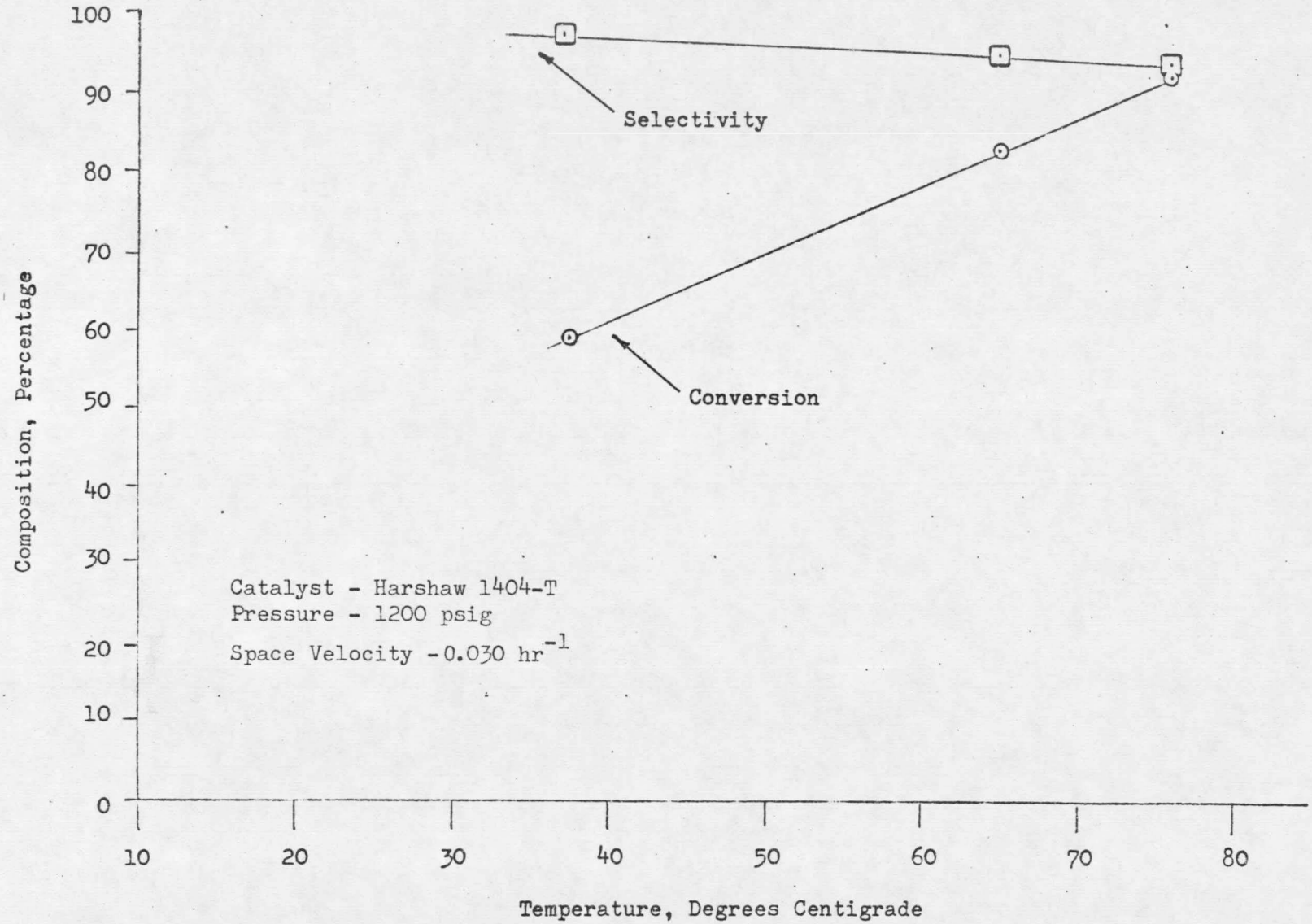


Figure 19. Temperature Effect. Yield and Conversion vs. Temperature.

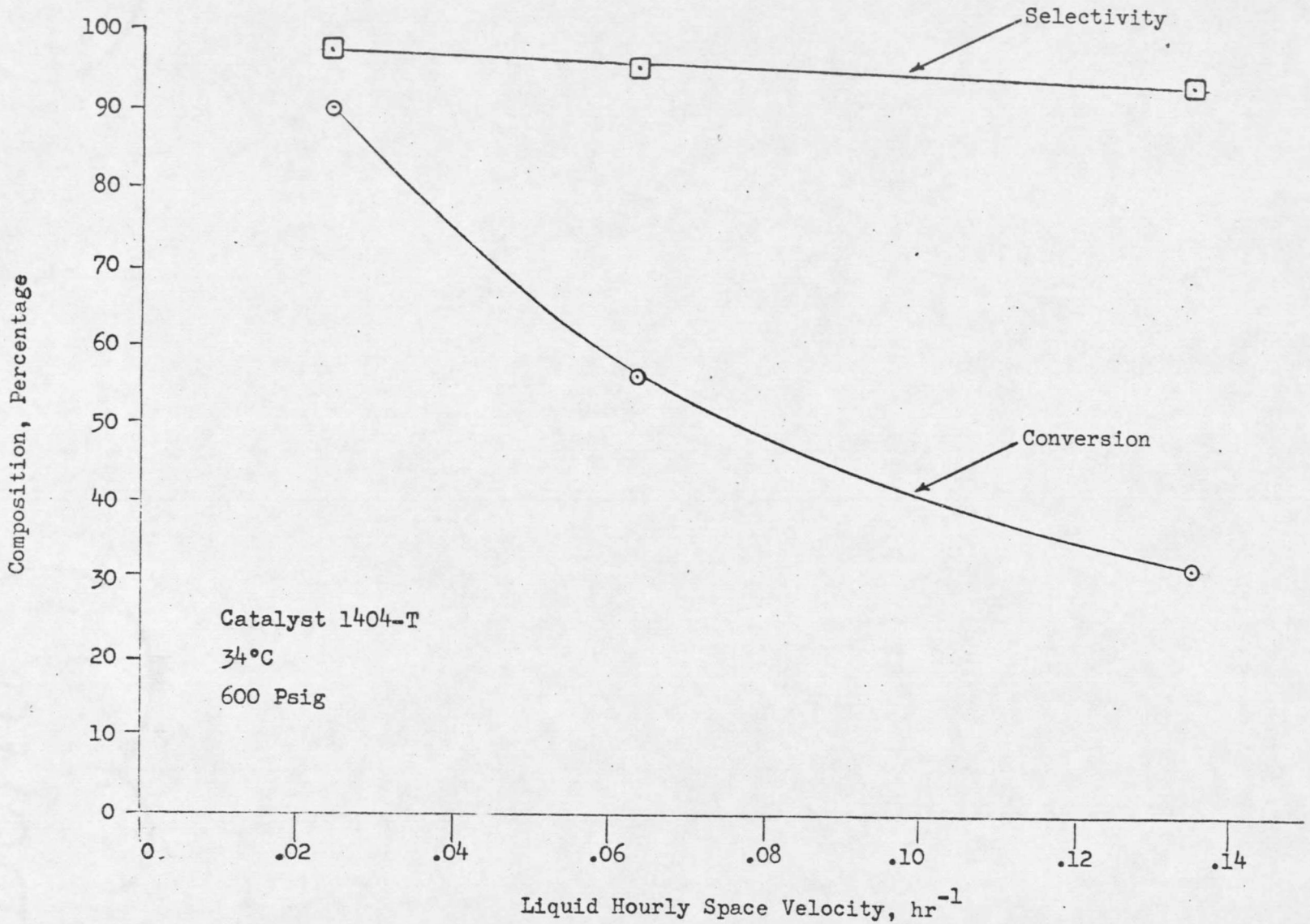


Figure 20. Space Velocity Effect.

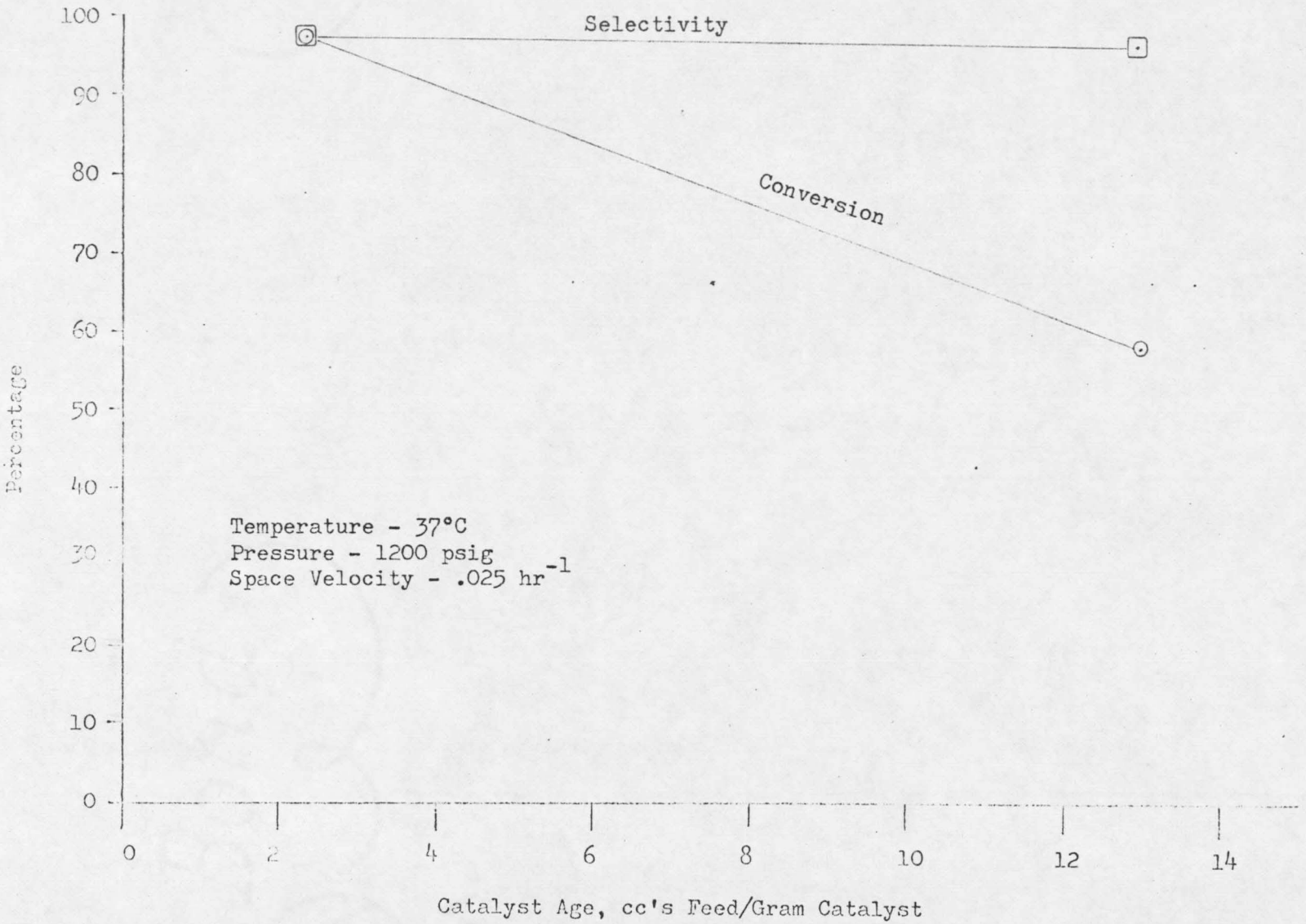


Figure 21. Catalyst Age Effect.

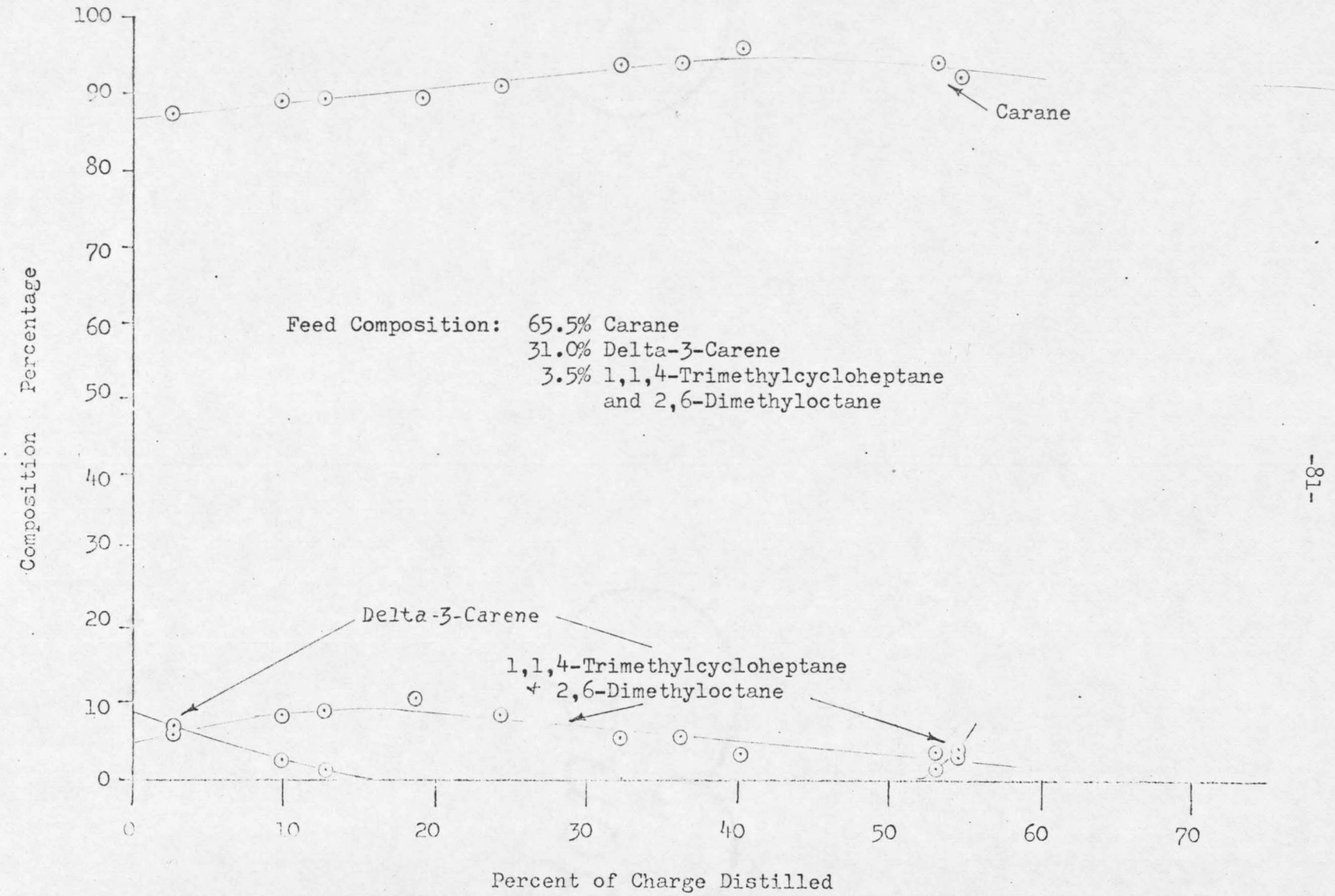


Figure 22. Distillation 1.

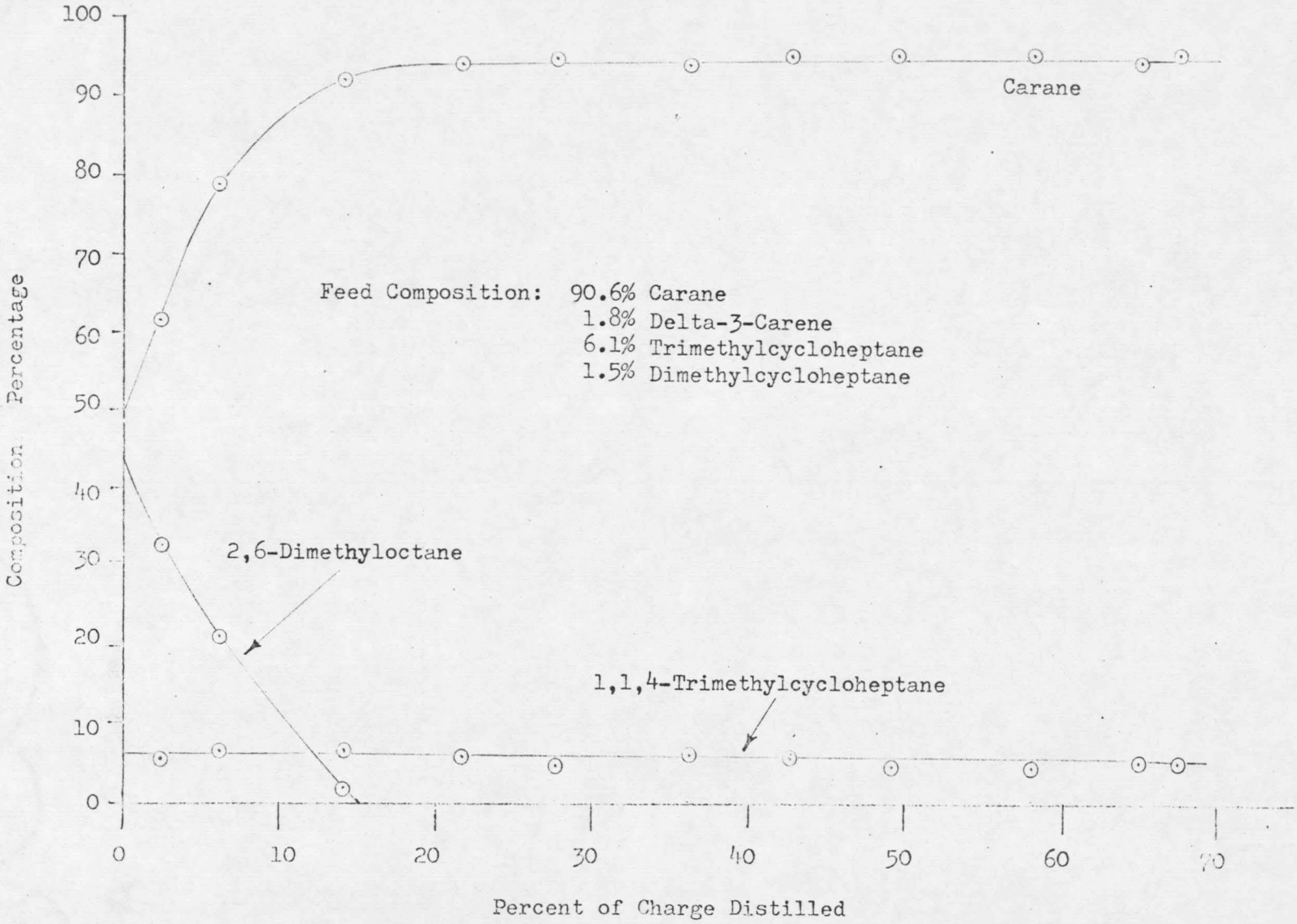


Figure 23. Distillation 2.

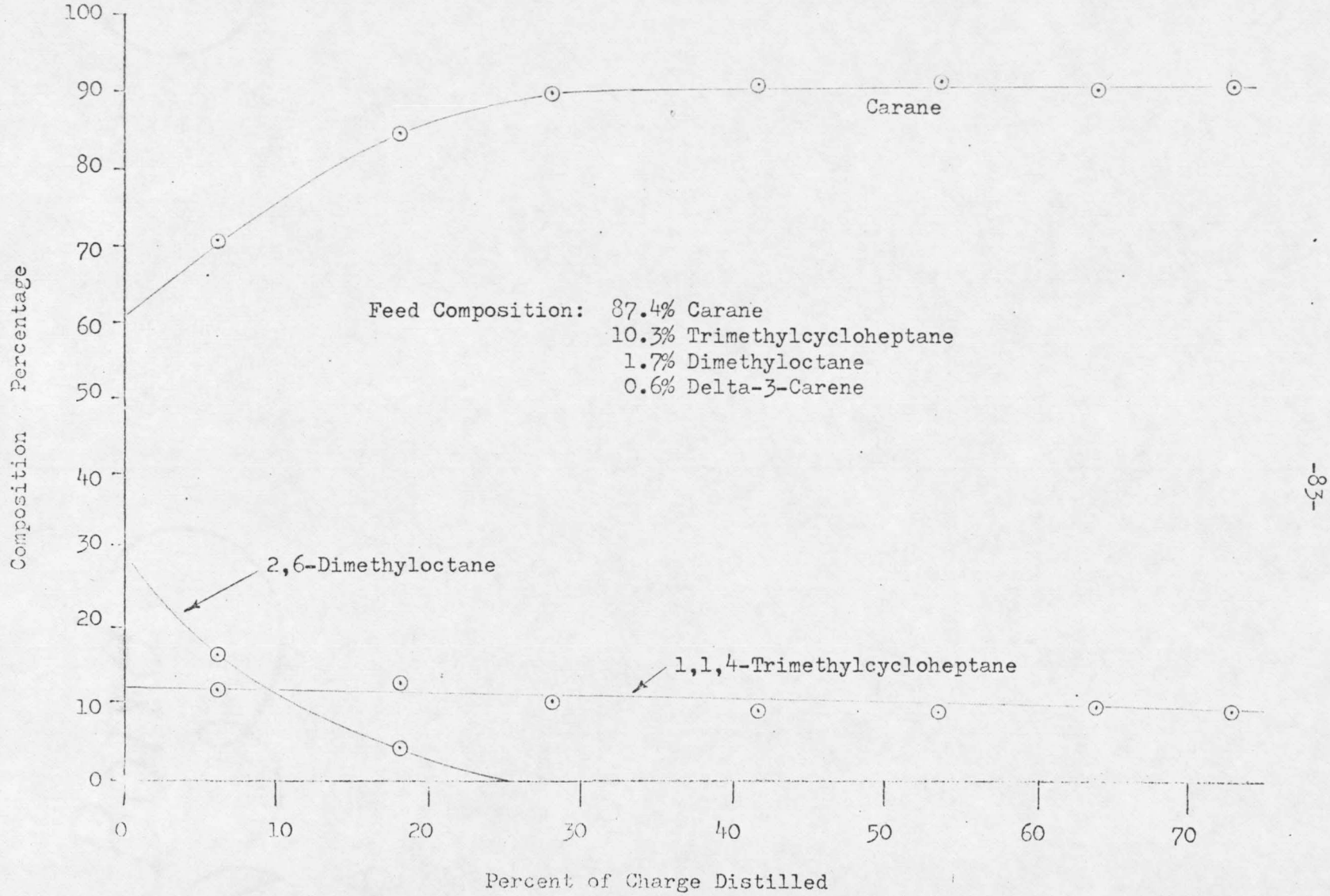


Figure 24. Distillation 3.

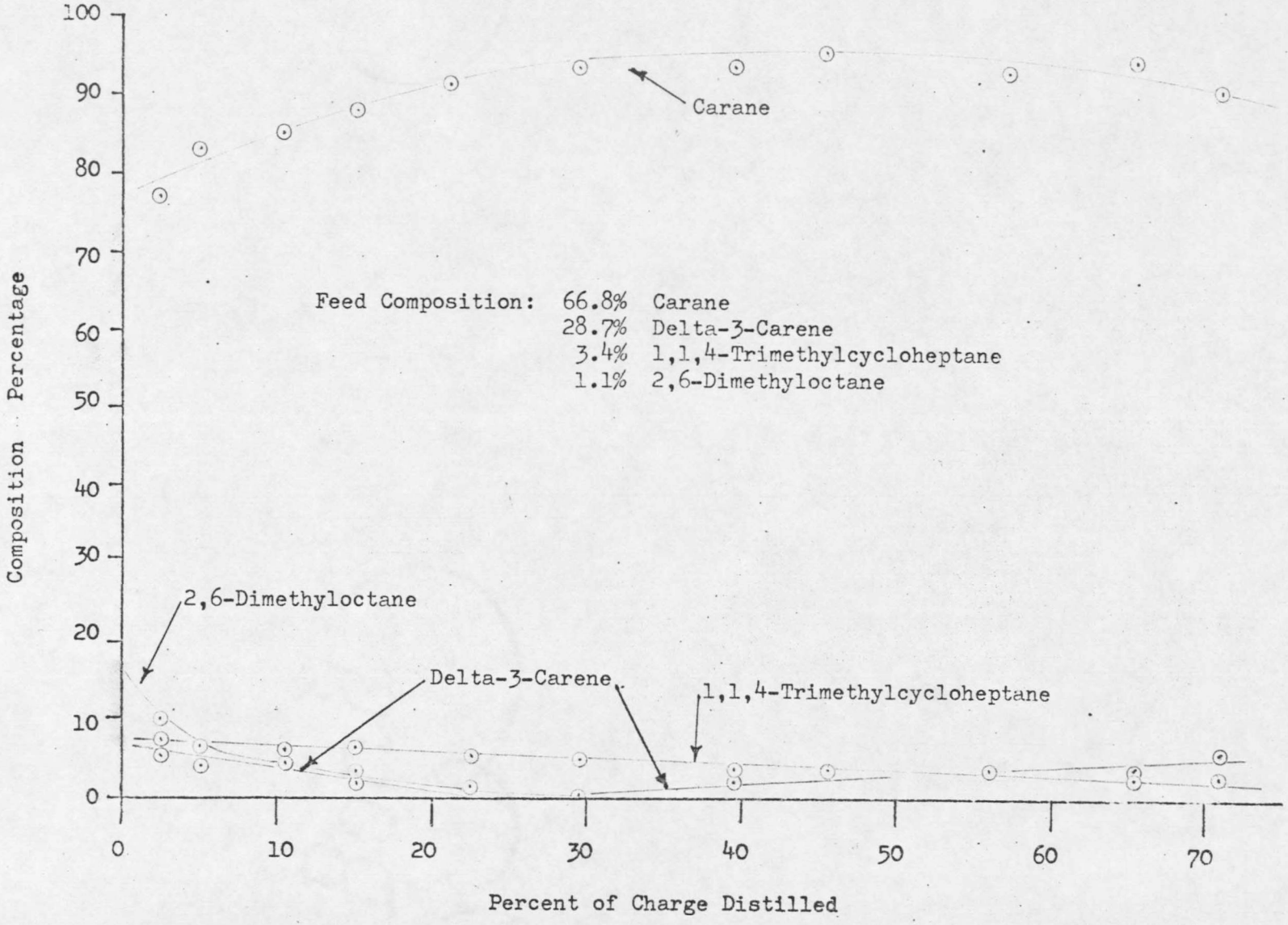


Figure 25. Distillation 4.

LITERATURE CITED

1. Cocker, W., Shannon, P. V. R., and Saniland, P. A., Chemical Communications, No. 12, 254-255, 1965.

2. Doss, M. P., "Physical Constants of Principal Hydrocarbons," 4th Edition, The Texas Company, New York, 1943.

3. Hannah, M. A., Ph.D. Thesis, Montana State University, Bozeman, Montana, 1966.

4. Isaacson, W. B., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1963.

5. Lange, Norbert Adolph, "Handbook of Chemistry," 8th Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952.

6. Morrison, R. T., and Boyd, R. N., "Organic Chemistry," Allyn & Bacon, Inc., Boston, 1959.

7. Shreve, R. N., "The Chemical Process Industries," 2nd Edition, McGraw-Hill Book Company, Inc., New York, 1956.