Continuous isomerization of hexenes
by Walter J Luke

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

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Analysis of the product was accomplished by hydrogenation followed by precision fractionation of the resulting paraffins.

The hydrogenated product was found to be 50% 2-methyl-pentane , 15% 3-methylpentane and 15% 2,3-dimethy!butane.

This indicates an olefin product composed of 50% 2- and 4-methylpentenes, 15% 3-methylpentenes and ethylbutenes and 15% 2 , 3-dimethylbutene-l.

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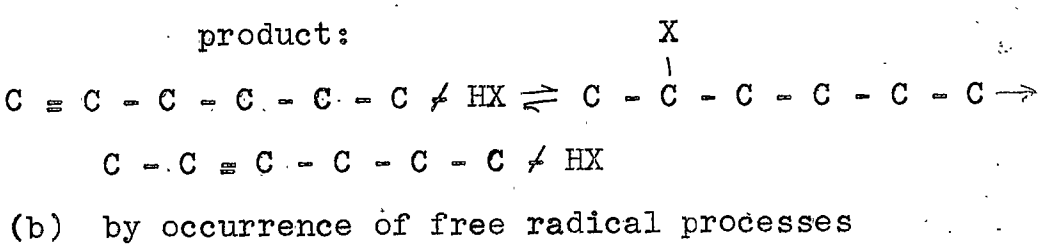
I INTRODUCTION

The purpose of this investigation was the evaluation of alumina activated with anhydrous hydrogen fluoride as an isomerization catalyst to convert hexene-1 to branched chain hexenes in a continuous system.

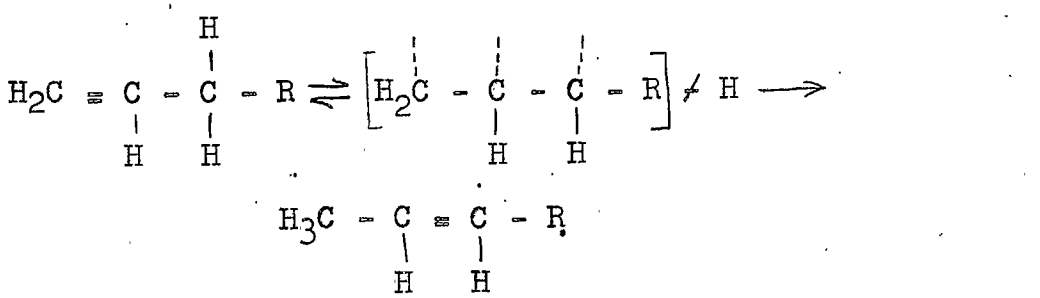
The double bond contained in unsaturated hydrocarbons is labile and, as a result, isomerization reactions are easily accomplished. The isomerization of olefins according to Egloff, Hulla and Komarewsky (1) may proceed in several directions as:

1. Shift of the double bond in one or more ways:

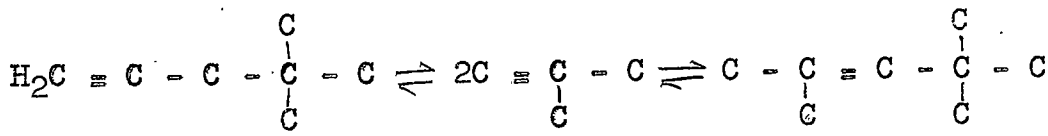
   (a) by formation of an unstable intermediate product:



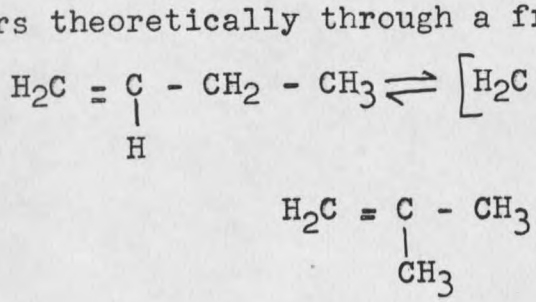
   (b) by occurrence of free radical processes



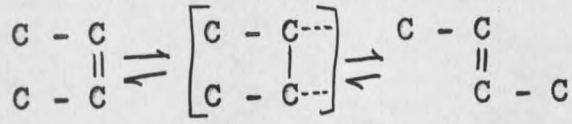
   (c) by depolymerization plus polymerization (both hypothetical reactions)



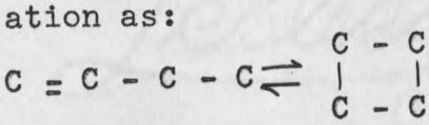
2. Isomerization by change in chain branching along occurs theoretically through a free radical exchange, e.g.



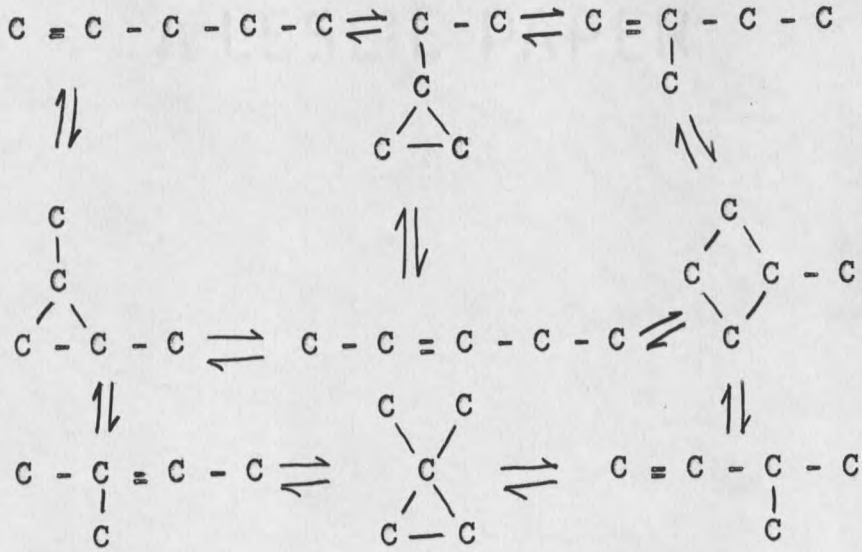
3. Isomerization by interconversion of cis and trans isomers:



4. Isomerization by cyclization or "internal" cyclization as:

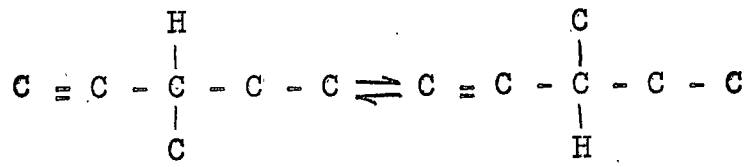


5. Isomerization by hydrogen transfer plus cyclization followed by decyclization and hydrogen transfer as:



6. Isomerization by polymerization plus intermediary isomerization of polymer plus depolymerization. According to the authors, these reactions seem quite probable, but have not been studied to date.

7. Isomerization by change in arrangement of the four different groups about an asymetric carbon atom, as:



The alkenes (olefins) are characterized by a tendency to polymerize, which must be taken into account in isomerization processes. The conditions of isomerization and the catalysts applied are preferably mild in order to avoid the formation of polymers, but the temperatures used in catalytic isomerization are near those at which olefins crack and are also near the temperatures at which the olefins polymerize.

The isomerization of the lower olefins (butenes, pentenes) has been studied in great detail (1). Catalysts used were: zinc chloride, benzenesulfonic acid and perchloric acid, pure phosphoric acid with or without diatomaceous earth, bauxite, silica, titania, difficultly reducible metal oxides, neutral borates, neutral phosphates, neutral silicates, aluminum phosphate on pumice, and aluminum sulfate. These catalysts favor double bond shift, principally. n-Butenes were isomerized to isobutene in presence of steam using such

catalysts as aluminum sulfate, Glukhov clay, "floridin" or phosphoric acid dried either on charcoal or "silicate" related to Chamotte (1).

Isomerization of pentene-1 to pentene-2 was accomplished by the following catalysts under suitable conditions (1): Activated alumina, silica alumina, silica, alumina and thoria, calcined alumina (2) or sodium permutite (3) convert n-pentenes to 2-methylbutenes at temperatures of 400-450°C. Norris and Reuter (4) passed pentene-2 over alumina, phosphoric acid, and aluminum sulfate at 425°C. and found pentene-2 remained unchanged but isopropylethylene (3-methylbutene-1) was extensively converted to trimethylethylene (3-methylbutene-2) under the same conditions. Egloff, Morrell, Thomas and Bloch (5) found activated silica-alumina catalysts to isomerize n-butenes, n-pentenes, n-octenes, and cetene at 375-600°C. Reactions of this type play an important part in the catalytic cracking of gas oils to make high octane gasoline (6).

Hexene-1, heated in the presence of five per cent of molybdenum trisulfide and under hydrogen pressure, yielded significant amounts of hexene-2 and some hexene-3 but no isohexenes at 300°C. (7). Polymerization began at 350° and was considerable at 400°. More extensive isomerization of hexene-1 and heptene-1 in contact with alumina or thoria at 400°C. was observed by Goldwasser and Taylor (8), into several branched chain isomers but the method of identifying the isomers

was found to be very questionable (9). Treatment of highly branched hexenes like 3,3-dimethylbutenes with catalysts such as phosphorus pentoxide on silica gel at 300°C. gave fifteen per cent of 2,3-dimethylbutene-1, 30 per cent of 2,3-dimethylbutene-2 with trace of 3,3-dimethylbutene, and a considerable amount of a polymerized product (10). Similar treatment with sodium permutite at 310°C showed almost complete conversion into 2,3-dimethylbutenes-1 and -2 (11). Activated alumina at 350°C was without action on 3,3-dimethylbutene, but anhydrous aluminum sulfate at 275° gave 29.7 per cent of 2,3-dimethylbutene-1, 55.5 per cent of 2,3-dimethylbutene-2 together with 3.8 per cent of 3,3-dimethylbutene (12).

Alumina activated with anhydrous hydrogen fluoride was used by Kindschy (13) as a catalyst for dealkylating alkylbenzenes at 500°C. He reported that if pressure and space velocity were held constant dealkylation will increase with increase in temperature while alkylation will decrease with increase in temperature.

Since many of the more highly branched isomers have a much higher octane value and are more volatile than the straight chain isomers, it is desirable to separate these isomers in order to raise the octane value of olefinic naphtha in the gasoline range. Thus, if hexene-1, having a C.F.R. research octane number of eighty (15), is isomerized to 2,3-dimethylbutene-1, the octane number would be increased to 95

or better. Berg, Sumner, and Montgomery (14) improved the octane number of olefinic gasolines by treatment at 380-420°C. with alumina activated with anhydrous hydrogen chloride. The octane number of the olefinic gasolines was brought by catalytic isomerization to that estimated for equilibrium mixtures of olefins of the same boiling range. The greatest improvement in octane number was obtained with the normal hexenes, whose octane number was raised from 36.8 to 75.0. Isomerization of this sort would be of great value in reforming Fischer-Tropsch naphtha which contains a large proportion of hexene-1 and other straight chain olefins. Oblad and Messinger (16) used alumina impregnated with hydrogen fluoride as an isomerization catalyst in converting straight chain olefins from a light naphtha cut from Fischer-Tropsch synthetic hydrocarbon product containing pentenes and hexenes to an equilibrium mixture containing high percentages of branched chain olefins.

Hexene-1 was chosen for this study because it is a common constituent of cracked gasolines and of Fischer-Tropsch naphtha. It has a boiling range such that it may be easily handled at atmospheric pressures without extensive vapor losses and the hydrogenated product, hexanes, has few enough isomers that identification of them is not rendered too difficult.

II EQUIPMENT, METHODS AND MATERIALS

A. Equipment

The equipment used in this investigation consisted of the reaction system shown in Figure 1. In addition, the following equipment was required: potentiometer, a precision rectification column, Corad distilling head (constant reflux type), distillation flasks, two glass stem thermometers, Harvard triple beam balance, a refractometer, eight autotransformers, Parr hydrogenation bomb with heating jacket and rocker powered by an electric motor and a catalytic reaction system for the dehydration of hexanol-1.

The reactor was made from a piece of three inch standard mild steel pipe 24 inches long. The pipe was threaded at both ends with the bottom end capped and the top and fitted with a flanged head for easy removal. The thermowells were made from pieces of 1/8 inch standard pipe 4-3/4 inches long and sealed at one end. The lower thermowell was placed two inches from the bottom of the reactor. The middle and upper thermowells were spaced at four inch intervals above the lowest one.

The catalyst bed extended from just below the bottom thermowell to the top thermowell. Holes, 13/32 inch in diameter, were drilled in the reactor at these points and the thermowells, when welded to the reactor wall, extended into the center of the catalyst space. The iron-constantan

thermocouples were inserted into these thermowells and connected to a Leeds and Northrup potentiometer with built-in cold junction. The potentiometer is calibrated so that the temperature may be read directly. It may be used to measure temperatures up to 1200°C.

Two 3/8 inch low carbon steel rods, 13 inches long, were welded on the reactor opposite the thermowells to be used as supports for the reactor. The reactor was mounted by clamping these rods to the equipment rack.

The reactor was wrapped with asbestos tape. Over this tape was wound 75 feet of Nichrome wire with a resistance of 1.079 ohms per foot. This winding drew 2.95 amperes from a 220 volt autotransformer. After covering this winding with asbestos tape, another resistance winding 33 feet long was placed over it and was connected to a 110 volt autotransformer and drew about seven amperes. Another 33 feet length of this resistance wire was wrapped around the upper portion of the reactor to act as a preheater. It was also connected to a 110 volt autotransformer. Both of these 33 foot windings were covered with asbestos tape and a one inch layer of magnesia was placed over the winding and tape.

The malleable iron caps at the top and bottom of the reactor were drilled and tapped to take 1/2 inch short nipples. The upper nipple was fitted with a 1/2 inch malleable iron cross and reduced to 1/8 inch, while the bottom one was

reduced directly to 1/8 inch. Feed was admitted to the top of the reactor from 1000 ml. graduated separatory funnel through a Merkle-Korff type bellows pump operating on 110 volt A.C. and connected to the reactor through 1/8 inch flexible copper tubing. To the bottom outlet was fitted 1/8 inch flexible copper tube which led directly to an 8 inch hard glass test tube having a side arm near the top and at whose bottom a stopcock was sealed. This test tube, so constructed, acted as a water and tar trap. To cool and condense the vapor from the reactor, a 3/8 inch standard mild steel iron pipe, 11 inches long with rubber stoppers on each end, was placed around the 1/8 inch copper tube to act as a condenser. Two 1/8 inch standard mild steel nipples, 3-1/2" long, were inserted in holes drilled in the pipe, and were brazed on to serve as an inlet and outlet for the cooling water. This is shown in Figure 1.

Through the side arm on the 8 inch test tube, the overflow of the liquid was led into a packed fractionating column as shown in Figure 1. This column is divided into two sections, one above and one below the feed point. The top section had 48 inches of packing and calibrated about 30 theoretical plates while the bottom section had 23 inches of packing and calibrated about 14 theoretical plates.

These sections were constructed of three concentric glass tubes. The innermost tube was 33 mm inside diameter

and was packed with 1/8 inch Fenske stainless steel helices. A thermometer was fastened on the outside surface of the inner tube halfway between the top and bottom of the section. This was done for both sections. The second or middle section was wrapped with Nichrome resistance wire which was connected to a 110 volt transformer to provide heat for the column. This was done for both sections also. The outer tube acted as an outside jacket. On the top of the column was mounted an adjustable reflux head with a cold finger condenser as well as a wall condenser. A precision thermometer was placed in the head so that vapor temperature could be recorded. On the bottom of the top section the feed plate was welded directly on the end of the innermost glass tube. The bottom of the feeder plate was connected to the top of the bottom section by means of a tapered ground glass joint.

The stillpot was of the continuous type with a side arm for takeoff (see Figure 1). It was connected by sealing the neck of the stillpot to the bottom of the innermost glass tube of the bottom section of the column. The stillpot was wound with Nichrome resistance wire and covered with asbestos tape for insulation. The resistance wire was connected to a 110 volt autotransformer to furnish heat to the stillpot.

The bottoms material in the stillpot was recirculated to the feed by connecting the side arm of the stillpot to a 1/8 inch copper tube which led to another bellows pump. The

bottoms product passed through a condenser made of 3/8 inch malleable iron pipe, 36 inches long, fitted similarly to that on the bottom of the reactor and thence to the feed receiver. This condenser cooled the recycle material in order to eliminate any vapor loss from the feed receiver.

Attached to the outlet on the head was a water condenser and water cooled receiver where liquid product was drawn off. The non-condensible gases were withdrawn through an outlet in the receiver which led to a dry ice condenser and a "Precision" Wet Test meter connected in series as shown in Fig. 1.

The dry ice condensers used to trap the highly volatile material which was not condensed in the water condensers in the head were composed of Dewar thermos flasks in which dry ice was dropped into acetone to give a better cooling medium. The glass trap was immersed in the dry ice-acetone mixture in the Dewar flask.

The precision rectification column used to fractionate the hydrogenated product was a batch column with a Corad head, a 48 inch packed section of 1/8 inch Fenske stainless-steel helices and calibrated 30 theoretical plates. The heater used for this column was made of a ceramic base supporting Nichrome coils in a concave depression into which the distilling flask was placed. The coils were connected to a 110 volt autotransformer. Refractive index determination was made on an Abbe type Valentine capable of reading to five significant

figures. All refractive indices were read at 20 ± 0.1°C.

The autotransformers were Superior Electric Company powerstats. The 110 volt Powerstats had a voltage range of 0 to 135 volts and were fused at seven amperes; the 220 volt Powerstats had a voltage range of 0 to 260 volts and were fused at 3 amperes. The Parr hydrogenation bomb was the 250 cc. size fitted with a pressure gage which read from 0-10,000 pounds per square inch. The bomb fitted into an insulated jacket with built-in heating coils which was supported by rocker which was rocked by an electric motor. An iron constantan thermocouple fitted in the bottom of the bomb and led to a Brown potentiometer. The heat in the jacket was controlled by an autotransformer.

The reactor used to dehydrate hexanol-1 was of similar construction to that used in the isomerization unit except that only two heating wires of 33 feet and 75 feet respectively, were employed. Nine hundred cc. of Harshaw 1/8 inch activated alumina pellets were used as catalyst, which were the same as those used in the isomerization reactor except that, of course, they were not activated with hydrogen fluoride. The hexanol-1 was introduced to the reactor from a 1000 cc. graduated separatory funnel by means of a bellows pump through 1/8 inch flexible copper tubing to the top of the reactor. The vapor from the reactor was condensed by a water condenser fitted on the bottom of the reactor.

B. Methods

1. Preparation of Catalyst:

The reactor was filled with Berl saddles to a point about 1/8 inch below the bottom thermowell. Fifteen hundred mls. of Harshaw 1/8 inch activated alumina pellets were placed in the reactor over the Berl saddles. The reactor was then completely filled with additional Berl saddles which acted as a preheat section.

The method of catalyst activation was similar to that outlined by Berg, et al (14). The catalyst was first dried by heating to 250°C. and holding that temperature for two hours. The reactor was then capped with a calcium chloride drying tube and allowed the reactor to cool to room temperature. Anhydrous hydrogen fluoride was passed through reactor at room temperature for an hour, then the reactor was heated to 400°C. and held there for an hour while the hydrogen fluoride was still passing through. The catalyst was then purged with nitrogen to sweep out any excess hydrogen fluoride. During activation any excess hydrogen fluoride that flowed through the reactor was bubbled through kerosene and out through a blow-down line.

2. Isomerization:

The reactor was heated until the temperature of the preheat section (top thermowell) reached 350°C., then the reactor was purged with nitrogen. By this time, the temperature

of preheat section having reached 380°C., the feed line was connected to the reactor and feed introduced by starting the pump which was connected to the feed chamber. Two hundred to three hundred ml. of feed was usually kept in the chamber. The column heats, as well as the stillpot heater, were turned on after enough material had collected in the stillpot to reach the side arm leading to the recycle pump. The recycle pump was also started at this time. The system then was allowed to run until material was condensing in the head and the column and the reactor temperatures were constant showing that equilibrium conditions had been reached. The temperatures of the reactor were 300-318°C. in the preheat section, 375-390°C. in the middle thermowell, and 370-390°C., in the bottom thermowell. The temperature of the vapor condensing in the head was 49-52°C., with temperatures of 54-58°C. in the top section of the column, 67-71° in the bottom section of the column, and 71-74° in the stillpot.

Material balances for the system were determined after first lining out the system as described above. After noting the feed level in the 1000 cc. graduated feed chamber, a weighed amount of the hexene, generally about 100 grams, was added. At the same time, the reading on the gas meter was noted and a new condenser was inserted in the dry ice trap. When the feed level in the graduated separatory returned to the original feed level (the level before the weighed amount

of hexene-1 was added), the total product collected in the water cooled receiver and the dry ice trap was weighed. The density of the gas was estimated at one gram per liter. The sum of the weights was then compared with that originally added. The unit was kept in continuous operation by merely adding more feed to the feed chamber.

To shut down the system, the reactor was purged with nitrogen for fifteen minutes. The oily material was blown out and collected in a suction flask which acted as a blow-out bottle. The effluent gases were withdrawn through a side arm on the blow-out bottle. The reactor was then capped with a calcium chloride drying tube on one end and the other was completely shut off from contact with air.

3. Analysis of Product:

The product was hydrogenated in order to simplify the identification of products by distillation. Hydrogenation decreases the number of possible isomers but still shows the degree of branching as all the cis-trans and double bond migration type of isomers are converted to one corresponding paraffin.

Hydrogenation was carried out by placing 100 ml. of olefin product in the 250 cc. Parr hydrogenation bomb with 5-10 ml. of Universal Oil Products hydrogenation catalyst. The bomb was then pressurized by connecting with high pressure tubing to a hydrogen cylinder at a pressure of 1800-2000

pounds per square inch. The valve on the bomb was then closed, the tubing disconnected and the bomb placed in the rocker and the thermocouple inserted. The rocker was started and heat was applied to the bomb by means of the heating jacket. When the temperature reached 80-100°C (usually required about 10-15 minutes) the heat was turned off. The temperature continued to increase due to the heat of the reaction to about 150°C., then decreased indicating that the reaction was complete. The bomb was allowed to rock until the temperature decreased to 100°C., or lower to insure complete reaction. The bomb was cooled to room temperature by removing it from the rocker and heating jacket and placing it in cold water. Next, the hydrogen was bled off in a hood by means of the valve on the bomb and then the head was removed. The liquid product in the bomb was poured out leaving the catalyst in the bomb. Another charge of olefin was added and the process repeated.

The accumulated hydrogenated product was then weighed and placed in a one liter distillation flask with 100 grams of cumene as a chaser. The precision fractionation was carried out batchwise. The column was run at total reflux and flooded to wet the packing. This was done by merely applying enough heat to the stillpot. After flooding, the heat was reduced. The reflux was set at 30-1 by means of the Corad head and the stopcock on the head was opened to

allow the product to be withdrawn. Cuts were taken from the overhead, the size of which depended upon the range of temperature increase during the cut. When at a plateau, the cuts were large; while during a midfraction, the cuts were small. This was done to define the distillation curve more clearly. The refractive index of each cut was taken. The results are plotted in Figure 2.

A sample of the bottoms or recycle stock was collected, hydrogenated and analyzed in a similar manner (Figure 3).

4. Catalyst Burn-Off and Reactivation:

As the catalyst was used, a deposit of carbonaceous material and tar was laid down upon its surface thus reducing the activity of the catalysts and necessitating periodic burn-offs. The catalyst was burned off after 15-18 hours use indicating that the deposit per unit time was slight but never-the-less building up.

Burn-off was accomplished by passing air through the reactor while maintaining the temperature below the sintering point of the catalyst (570°C.). The burn-off need not be done immediately after the completion of isomerization runs. The air for burn-off was regulated by a needle valve as only a small stream of air could be allowed to pass over the catalyst. The oil and carbon ignited readily and heated the reactor very rapidly to above the catalyst sintering point unless great care was taken in the control of the admission of the air.

It was found that the reactivation of the catalyst with hydrogen fluoride after use and burn-off was unnecessary, but rather it seemed to retain its activity despite long use and numerous burn-offs.

5. Preparation of Hexene-1:

The hexene-1 was prepared by heating the reactor containing the alunina catalyst to 400°C. and introducing the hexanol-1. The effluent from the reactor was condensed and collected. The water was decanted off and the remainder collected in a large distillation flask. The hexene-1 was separated from the remaining water and unreacted alcohol by fractionation in a precision column. The material boiling at 58-61°C. was collected as the olefin product. The refractive index of the product was 1.3920 as compared to 1.3880 for pure hexene-1 (15) indicating that some hexene-2 and -3 possibly was present due to the isomerizing action of the alumina.

C. Materials

Material	Source
One-eighth inch Activated Alumina Pellets	Harshaw Chemical Co.
Anhydrous Hydrogen Fluoride	Matheson Company
Hydrogenation Catalyst	Universal Oil Products Company
Hydrogen	Air Reduction Company
Hexanol-1	Carbide and Carbon Chemicals Company

III RESULTS

Twenty-two isomerization runs were made with cycle times varying from three to eighteen hours. Poor material balances (60-85 per cent recovery) in early runs resulted because the vapor tended to leak around the spherical ground glass joints originally used to connect the feed plate and the stillpot to the packed sections of the column. The hot hexene tended to dissolve the silicone stopcock grease used to seal these joints. This type of joint was subsequently eliminated by sealing the column section together. The resulting material balance after the leaks had been eliminated is presented in Table I.

The composition of the overhead product could be controlled by adjusting the reflux ratio in the head. If run at a very high reflux ratio, a poorer material balance results but a more volatile product was obtained. The accumulated overhead product, which was hydrogenated and precision fractionated, was taken off at a temperature range of 49-54°C. with an average of 52-53°C. at 637 mm and an R.I. of 1.3810-1.3840.

Figure 2 shows the fractionation curve of the hydrogenated product. The boiling points and refractive indices for the hexane and hexene isomers are listed in Table II.

As seen from Figure 2, the overhead product is composed of about 18 per cent lights, which were probably butenes and pentenes in the olefin product, and the remainder were hexenes.

At 637 mm pressure, the boiling range for the hexane fraction is 51 to 63°. The curve approaches a plateau in the range of 53.2 to 55.4. From this and the refractive index of this fraction, it is evident that the plateau was composed of 2,3-dimethylbutane and 2-methylpentane. The remainder was a mixture of 2- and 3-methylpentane and possibly n-hexane.

A sample of the bottoms or recycle stock was collected from the still pot and feed chamber after the completion of several runs. The precision fractionation of this hydrogenated material is shown in Figure 3. The bottoms was composed of about 68 per cent hexane mixture and the remainder a complex mixture of higher condensation products.

The formation of the olefin condensation product or polymer increased the density of the recycle stock from 0.674 to 0.704. This could cause an error of up to 3 per cent in the material balance. After the unit was in operation, the amount of polymer did not increase, but seemed to attain an equilibrium.

Hexene-1, separated from Fischer-Tropsch naphtha, was used for one run and gave a product identical with that obtained from hexene-1 produced by the dehydration of hexanol-1.

IV DISCUSSION

The distribution of isomers in the equilibrium mixture where an olefin such as hexene-1 is isomerized depends upon the temperature at which the equilibrium is established. Usually, the equilibrium mixture contains appreciable quantities of most or all the isomers and rarely do any one or two isomers predominate. This is especially the case in the isomerization of an olefin such as hexene-1 which has a large number of isomers. The distribution of isomers in the equilibrium mixture at any desired temperature may be calculated by chemical thermodynamics. This has been done by Berg, et al (17) for the hexenes. They state that the validity of the conclusions drawn is dependent only on the correctness of the thermodynamic data employed in the calculation. The results at 400°C. are shown in Table III.

From this Table it may be concluded that equilibrium isomerization results in a product composed of a mixture of all the isomers. The significant thing about the overhead product, secured by the use of a continuous fractionation of the isomerized product as it is removed from the reactor, is the concentration and resulting high yield of 2,3-dimethylbutene-1 and 2-methylpentene-1 far above that obtainable by batchwise establishment of equilibrium. From the fractionation curve of the hydrogenated overhead product (Figure 2) the following composition was estimated.

18% pentane and lighters

15% 2,3-dimethylbutane

50% 2-methylpentane

15% 3-methylpentane

trace n-hexane

Which corresponds to the following olefins:

19% pentenes and lighter (1% estimated lost in hydrogenation)

15% 2,3-dimethylbutene-1

50% 2- and 4-methylpentenes

15% 3-methylpentenes and ethylbutenes

trace of n-hexenes

This indicates that hexene-1 was converted predominantly to the 2- and 4-methylpentenes. It is interesting to note that the most volatile isomer, 3,3-dimethylbutene-1, was not indicated as being present in the overhead. However, according to Wachter (18), the 3,3-dimethylbutene-1 (neohexene) is very difficult to prepare and if it is formed, it tends to revert to the 2,3-dimethylbutenes.

The fraction of Fischer-Tropsch naphtha refined by azeotropic distillation methods so that it was composed chiefly of hexene-1 was charged to the unit under the same conditions as before, and the resulting product was identical as that obtained from the hexene-1 prepared from hexanol-1. Therefore, it is indicated that a process of this sort could be used

for upgrading the anti-knock properties of olefinic naphtha from the Fischer-Tropsch synthetic hydrocarbon process.

The losses not accounted for in the material balance may be attributed to carbon laydown on the catalyst, the change in density of the feed due to influx of more dense recycle, and vapor losses due to evaporation.

It was found by experience that the optimum reactor temperature seemed to be in the range 375-395°C. If the temperature in the reactor exceeded 395°C., extensive gas formation was noted. If the temperature was lower, the degree of isomerization was less as noted by vapor temperature and refractive index of the overhead product.

An analysis by means of the infrared spectrum method was made on the overhead product after hydrogenation by the Analytical Group of the Phillips Petroleum Company of Bartlesville, Oklahoma. Their report on the composition of the hexanes present was as follows:

2,2-Dimethylbutane	0.6	volume	present
2,3-Dimethylbutane	16.0	"	"
3-Methylpentane	18.6	"	"
2-Methylpentane	63.2	"	"
n-Hexane	1.6	"	"

V CONCLUSIONS

1. Alumina activated with anhydrous hydrogen fluoride may be used as an isomerization catalyst in the temperature range of 375-395°C. to convert hexene-1 to the branched chain isomers in a continuous system with better than ninety per cent of the charge being recovered as product.

2. The feed for this process may be either hexenes obtained from Fischer-Tropsch naphtha or prepared from hexanol-1.

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TABLE I

Material Balance of Isomerization of Hexene-1

Charge: Hexene-1	
Charge Weight	459.5 grams
Charge Volume:	675 ml.
Time of Run:	4.5 hours
Feed Rate to 1500 ml. of Catalyst:	16 ml./min.
Volume passed over Catalyst:	4320 ml.
Average Reactor Temperature:	
Upper (preheat) Section	306°C.
Middle Section	385°C.
Lower Section	396°C.
Average Column Temperature, °C. at 640 mm.	
Head	52.0
Section above Feed Plate	58.5
Section below Feed Plate	71.5
Stillpot	74.0
Product, gms.	
Liquid Overhead from Column	421.1 grams
Liquid condensed in Dry Ice Trap	5.2 grams
Non-condensible Gases	3.0 grams
Total Weight Recovered:	429.3 grams
Total Volume Recovered:	625 ml.
Weight Per Cent Recovery:	93.6 per cent
Volume Per Cent Recovery:	92.7 per cent

TABLE II

Physical Properties of the Hexanes (15) and the Hexenes

Isomer	Boiling Point (corrected for 637 mm.)	Refractive Index
n-Hexane	63.5°C	1.3750
2-Methylpentane	55.5°C	1.3715
3-Methylpentane	57.0°C	1.3766
2,3-Dimethylbutane	53.2°C	1.3750
2,2-Dimethylbutane	44.0°C	1.3688
Hexene-1	58.7°C	1.3880
cis-Hexene-2	63.2°C	1.39538
trans-Hexene-2	62.5°C	1.39348
cis-Hexene-3	61.9°C	1.39338
trans-Hexene-3	62.5°C	1.39377
2-Methylpentene-1	56.7°C	1.3921
3-Methylpentene-1	48.6°C	1.3855
4-Methylpentene-1	48.8°C	1.3825
2-Methylpentene-2	62.3°C	1.4005
cis-3-Methylpentene-2	61.0°C	1.3994
trans-3-Methylpentene-2	62.9°C	1.4002
cis-4-Methylpentene-2	53.0°C	1.3885
trans-4-Methylpentene-2	49.7°C	1.3881
2-Ethylbutene-1	61.5°C	1.3940
2,3-Dimethylbutene-1	50.6°C	1.39022
3,3-Dimethylbutene-1	36.2°C	1.37604

TABLE II (Continued)

Isomer	Boiling Point (corrected for 637 mm.)	Refractive Index
2,3-Dimethylbutene-2	68.2°C	1.4121

TABLE III

Thermodynamic Equilibrium of the Hexenes at 400°C. (17)

Isomer	Equilibrium Mol Fraction in per cent
Hexene-1	8.89
cis-Hexene-2	11.83
trans-Hexene-2	16.85
cis-Hexene-3	7.12
trans-Hexene-3	12.51
2-Methylpentene-1	22.85
3-Methylpentene-1	8.84
4-Methylpentene-1	4.83
2-Methylpentene-2	1.49
cis-3-Methylpentene-2	1.21
trans-3-Methylpentene-2	1.21
cis-4-Methylpentene-2	0.32
trans-4-Methylpentene-2	0.50
2-Ethylbutene-1	0.46
2,3-Dimethylbutene-1	0.44
3,3-Dimethylbutene-1	0.16
2,3-Dimethylbutene-2	0.44
	100.00

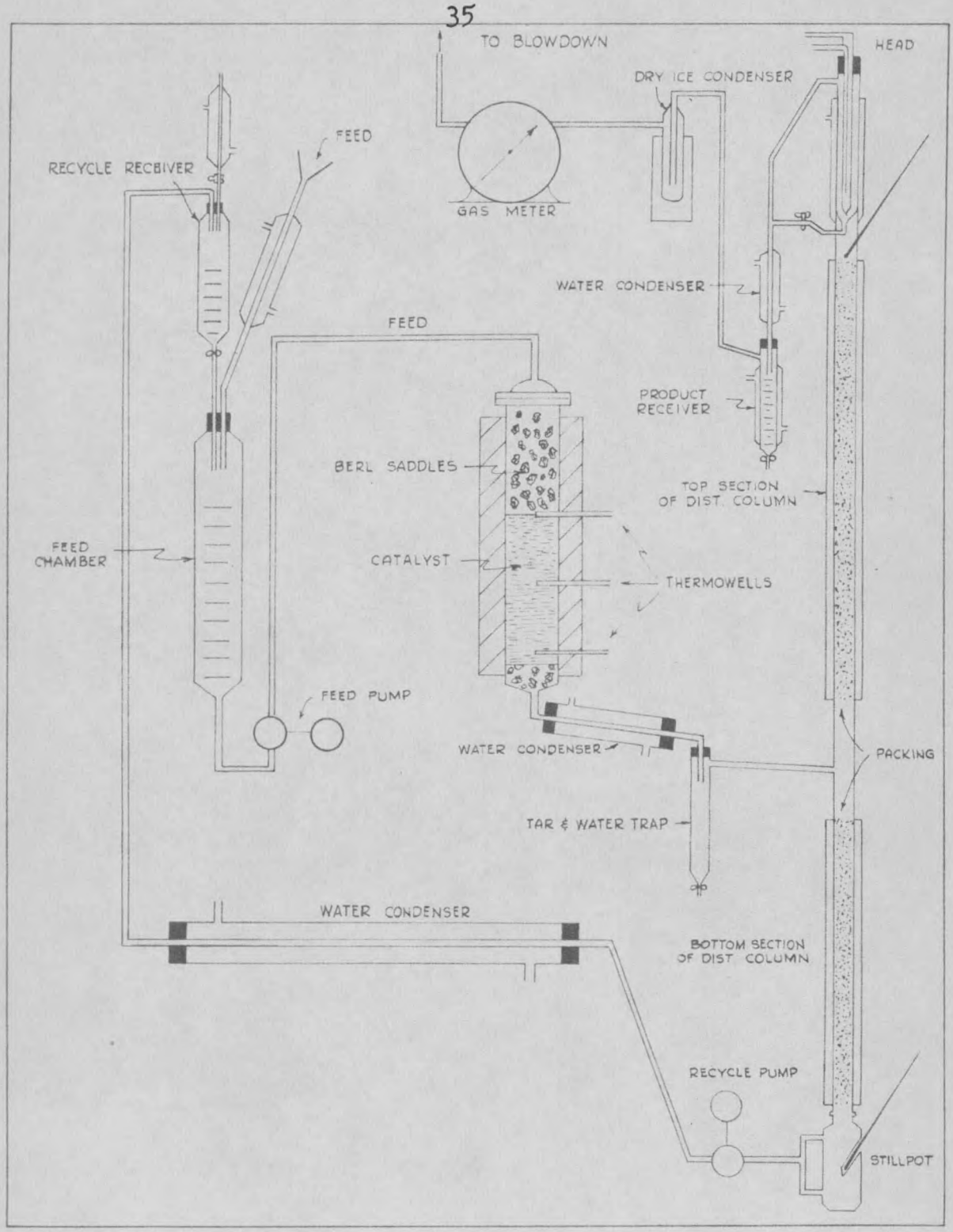

Figure 1. Diagram of Equipment

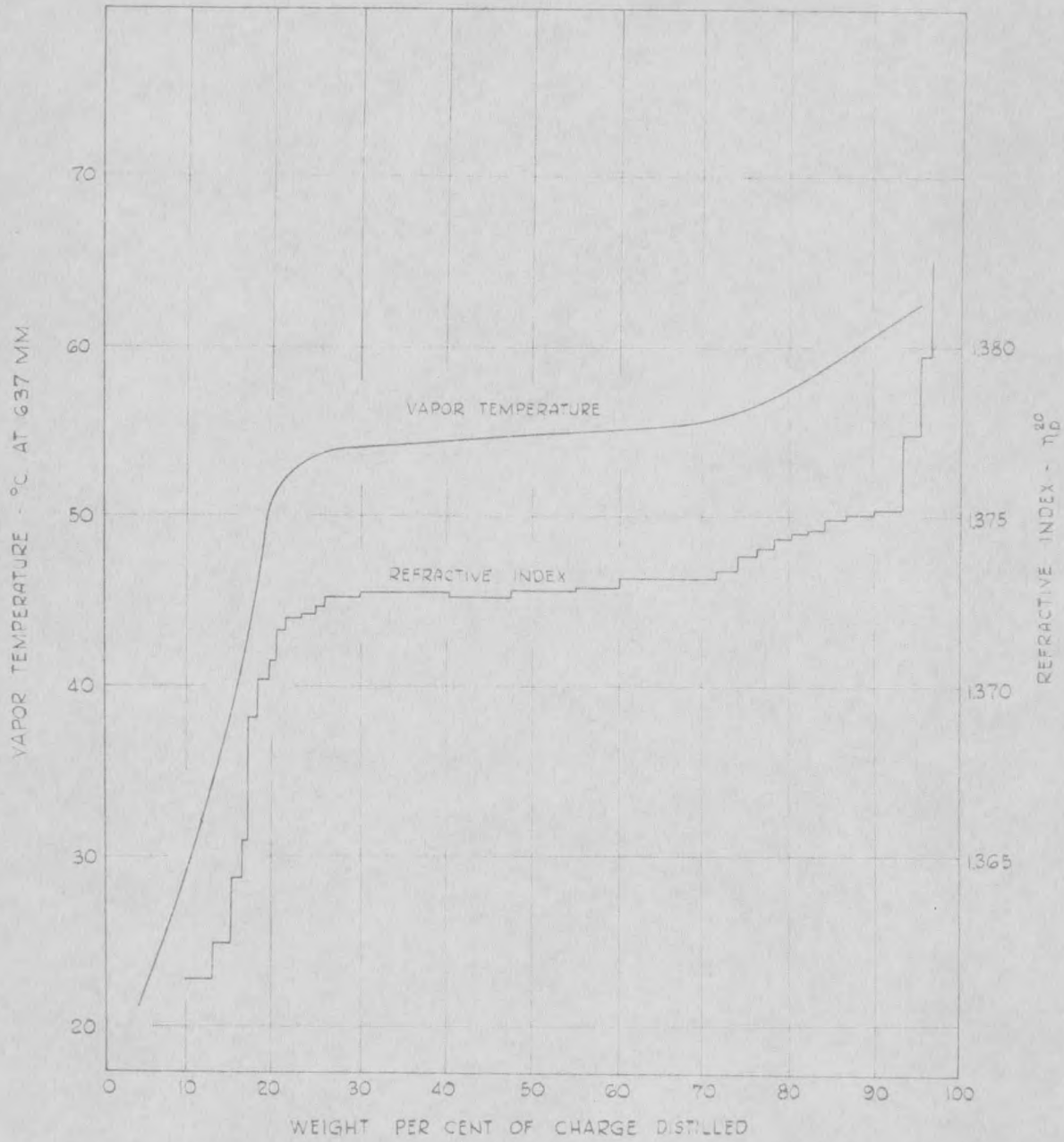

Figure 2. Analysis of Hydrogenated Overhead Product

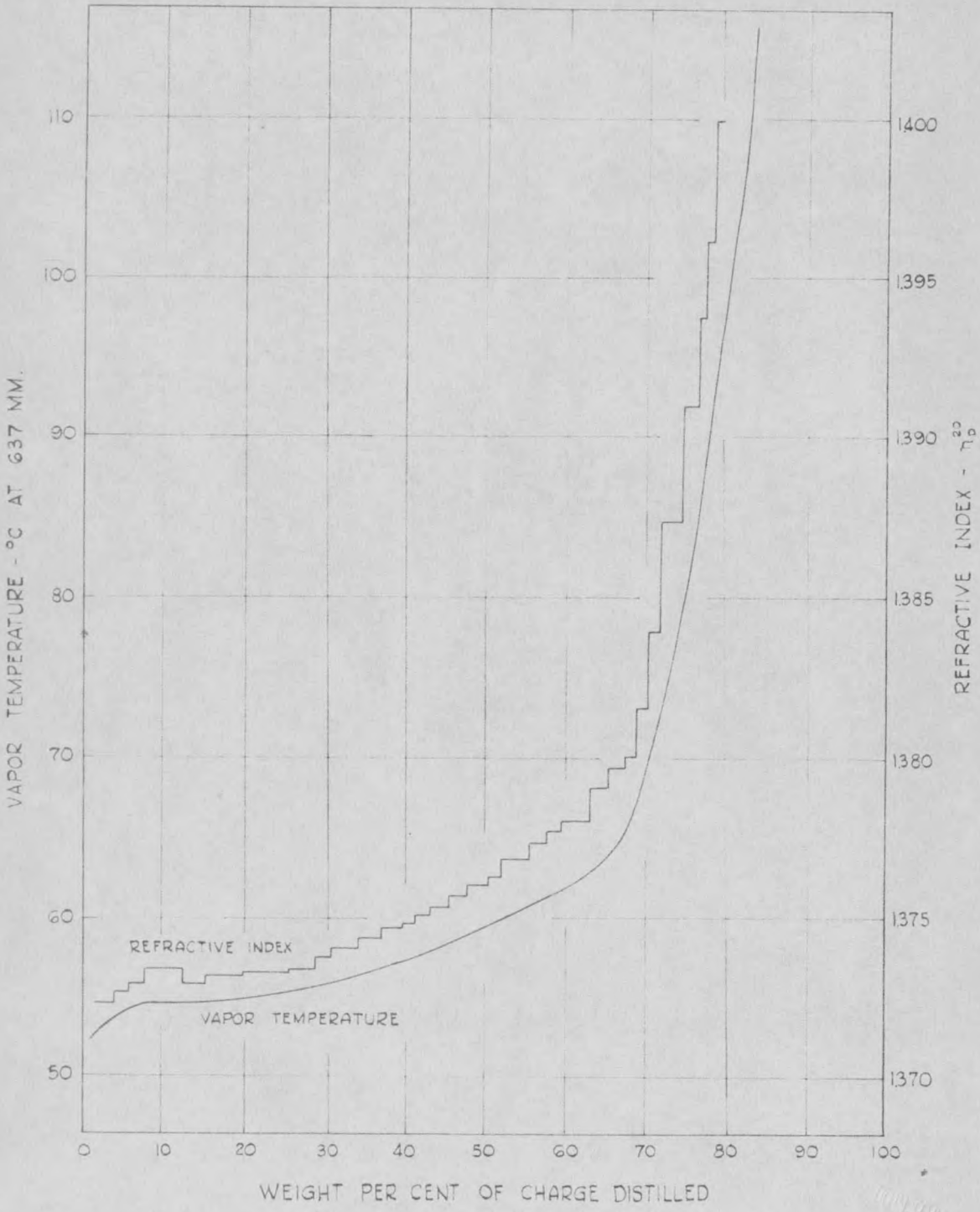

Figure 3. Analysis of Hydrogenated Recycle

NAME AND ADDRESS