



## Reactions in a distilling column by Paul R Hippely

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering  
Montana State University  
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### Abstract:

Work of an exploratory nature has been done using apparatus which allows catalytic and other reactions to be carried out concurrent with fractionation. Only reactions in which the product is lower boiling than any of the reactants can be carried out in this apparatus since successful operation depends upon continuous removal of the product as formed.

The apparatus consisted of a glass distilling column to which a removable catalytic chamber could be fitted. The chamber, which consisted of a ten inch length of 48 mm. Pyrex tubing wound with a Nichrome heating element, was attached to the bottom of the distilling column by means of ground glass spherical joints and the still pot was attached to the bottom of the reactor, also by spherical joints. Thus, vapors rising from the still pot could pass over the catalyst and on up the column, where any low boiling product could be removed, and the unreacted, higher boiling substances returned via the reflux to the still pot for further reaction.

The still pot was provided with a gas inlet tube to allow gases (e.g, hydrogen) to bubble through the liquid in the still pot.

The following reactions were studied; isomerization of paraffins, using "Isocel", an aluminum chloride impregnated, activated bauxite; isomerization of naphthenes, also using "Isocel"; hydrogenation of di-isobutylene, mesityl oxide and ni-tropropane, using a Universal Oil Products hydrogenation catalyst; and esterification of acetic acid with ethyl alcohol, normal propyl alcohol, isobutyl alcohol and isoamyl alcohol.

No catalyst was used the esterifications and hence no catalyst chamber was necessary. All reactions took place at the boiling points of the reagents and were run under atmospheric pressure (average; 635 mm.).

The paraffin isomerizations produced some branched chain products, but, in general, equilibrium was re-established too slowly to enable the product to be taken off with any degree of rapidity. Catalyst life for paraffin isomerization was short. Naphthenes isomerized readily and the isomerized product could be taken off rapidly enough to suggest commercial development of the process.

The hydrogenation reactions, necessarily limited in scope because of the low temperatures and pressures used, proceeded with ease to produce good yields of high purity product. Highly exothermic hydrogenations, such as nitro-propane to propylamine, cannot be carried out successfully in this apparatus.

Results of the esterifications show that, in each case studied, no catalyst was necessary to produce a high yield of very pure product. The reactions depend upon the ester-water azeotrope formed being the lowest boiling substance in the system. The acetates of most of the lower primary and secondary alcohols do form low-boiling water azeotropes and can be produced successfully in this manner. The

n-propyl alcohol -acetic acid esterification was carried out continuously for approximately 24 hours, the product showing a refractive index very close to that given in the literature.

The results indicate that a number of the reactions could be investigated more thoroughly along lines of commercial development. The simplicity of the apparatus and the fact that two operations, usually carried out consecutively, can be run simultaneously, indicate attractive industrial possibilities.

REACTIONS IN A DISTILLING COLUMN

by

PAUL R. HIPPELY

A THESIS

Submitted to the Graduate Committee

in

partial fulfillment of the requirements

for the degree of

Master of Science in Chemical Engineering

at

Montana State College

Approved:

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Bozeman, Montana  
August, 1947

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Graduate Committee

## ABSTRACT

Work of an exploratory nature has been done using apparatus which allows catalytic and other reactions to be carried out concurrent with fractionation. Only reactions in which the product is lower boiling than any of the reactants can be carried out in this apparatus since successful operation depends upon continuous removal of the product as formed.

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The following reactions were studied: isomerization of paraffins, using "Isocel", an aluminum chloride impregnated, activated bauxite; isomerization of naphthenes, also using "Isocel"; hydrogenation of di-isobutylene, mesityl oxide and nitropropane, using a Universal Oil Products hydrogenation catalyst; and esterification of acetic acid with ethyl alcohol, normal propyl alcohol, isobutyl alcohol and isoamyl alcohol. No catalyst was used in the esterifications and hence no catalyst chamber was necessary. All reactions took place at the boiling points of the reagents and were run under atmospheric pressure (average: 635 mm.).

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The hydrogenation reactions, necessarily limited in scope because of the low temperatures and pressures used, proceeded with ease to produce good yields of high purity product. Highly exothermic hydrogenations, such as nitropropane to propylamine, cannot be carried out successfully

in this apparatus.

Results of the esterifications show that, in each case studied, no catalyst was necessary to produce a high yield of very pure product. The reactions depend upon the ester-water azeotrope formed being the lowest boiling substance in the system. The acetates of most of the lower primary and secondary alcohols do form low-boiling water azeotropes and can be produced successfully in this manner. The *n*-propyl alcohol - acetic acid esterification was carried out continuously for approximately 24 hours, the product showing a refractive index very close to that given in the literature.

The results indicate that a number of the reactions could be investigated more thoroughly along lines of commercial development. The simplicity of the apparatus and the fact that two operations, usually carried out consecutively, can be run simultaneously, indicate attractive industrial possibilities.

## INTRODUCTION

In the course of a study of catalytic isomerization of olefins, the problem of equilibrium-yield proved to be the decisive factor, so decisive that, because of the low yield of the particular isomer desired, the study was abandoned. A portion of the problem dealt with the isomerization of normal heptene to produce 2,3,3, tri-methyl-butene-1. Thermodynamic calculations indicating a one per cent yield of this isomer were substantiated by an actual laboratory run in which the yield obtained was almost exactly that computed.

The problem then became one of continuously upsetting and re-establishing equilibrium so that, eventually, all, or at least a considerable fraction, of the normal heptene would be converted to 2,3,3 tri-methyl-butene-1. One method of accomplishing this, of course, is to remove the desired isomer as it is formed. In the particular case cited, the fact that 2,3,3 tri-methyl-butene-1 has a lower boiling point than the other heptene isomers indicated continuous fractionation of the reacting mixture during the isomerization process. Thus, because of its lower boiling point, the 2,3,3 tri-methyl-butene-1 would be continuously removed as formed, and the remaining isomers returned via the reflux to the reaction chamber for further isomerization.

Thus was suggested a new research topic. The problem would be to investigate a number of contact catalytic reactions wherein the product was lower boiling than any of the

reactants and to develop a suitable apparatus for carrying out such reactions so as to remove the product as formed.

Reactions which take place at approximately the boiling points of the reagents would require the least elaborate equipment, and from reactions of this kind, typical examples were chosen for study. Since olefins isomerize at temperatures greatly in excess of their boiling points, olefin isomerization was not included in the work.

A search of the literature revealed that isomerization of paraffins had been accomplished, using similar methods, by several investigators. Robertson (11) used a 5 ft., thirty plate, carborundum-packed distilling column in the still pot of which were placed n-heptane and ten weight per cent aluminum chloride. The product boiling below n-heptane was continuously removed. Similarly, n-butane was isomerized to isobutane in 85 per cent yield using 25 weight per cent aluminum chloride and 40 lb./sq. in. hydrogen chloride gas circulating in the system. Sweeney (13) isomerized paraffins using an aluminum chloride impregnated catalyst as column packing. The central portion of a distilling column contained the catalyst, and above and below it was space for fractionation. The aluminum chloride could be used in slurry form and allowed to flow down a series of baffle plates and recycled. Ross and Pezzaglia (12) simultaneously isomerized and separated cycloparaffins from acyclic paraffins using a liquid hydro-

carbon - aluminum chloride complex run counter current to the vapor stream in a distilling column. The column was kept at isomerization temperature and hydrogen chloride gas introduced near the bottom. Upham (15) isomerized paraffins using an aluminum chloride sludge activated with hydrogen chloride and simultaneously alkylated the isomerized product with low boiling olefins. The product, a stabilized liquid, branched-chain, saturated hydrocarbon, was withdrawn from the stripping section of a distilling column in which the reactions took place. Loy (10) isomerized hydrocarbons in a distilling column using aluminum chloride dissolved in liquid sulfur dioxide. A catalytic hydrogenation of azines was carried out simultaneously with distillation by Beregi (1) who noted that by displacing the equilibrium by distillation of primary amine in proportion to its formation, the product of the alzadines can be made to favor, exclusively, the primary amines.

Groggins (6), in his discussion of esterification, covers the literature up to 1936 rather thoroughly. All the reactions discussed require the use of some form of catalyst. Wade (16) investigated a continuous esterification scheme very similar to the one employed in this work, consisting of adding alcohol and acid continuously to sulfuric acid in a flask kept at 130°C. The sulfuric acid as a catalyst was necessary, however, and the distillate appeared as a ternary azeotrope of ester-water-alcohol. Groggins reports in some

detail Wade's results and those of later investigators of the process. In all cases the process is characterized by use of inorganic acids as catalysts and the formation of the ternary azeotropes.

The purpose of the present work was to investigate a number of reactions which might profitably be carried out concurrent with fractionation, the characteristic of each reaction being that the desired product is lower boiling than any of the reactants. Thus could be combined into one operation and one piece of equipment a process usually involving two separate and consecutive operations. No attempt was made to obtain exhaustive data on conditions and yields or ways and means of improving yields. Likewise, it was not within the scope of this work to explain theoretically some of the rather unusual behavior noted. Sufficient data were not taken on each reaction to validate positive conclusions as to mechanism, reaction rate, optimum conditions, or the effects of changing the process variables.

The scope, then, was to present an essentially new apparatus which, it is demonstrated, will enable two operations to be combined into one. Basic operating characteristics of the apparatus are described and the quality and quantity of yield in each case presented and discussed. Adaptability of the apparatus to commercial production is treated in the final section of the paper.

No work of exactly this nature, that is, combining all the features of equipment and process herein presented, has been reported in the technical literature. However, as previously noted, various features of the apparatus have already been reported and, in some cases, similar reactions studied. As noted, Robertson carried out a heptane isomerization in which the catalyst was placed directly in the still pot. This necessitates batch operation in which the catalyst must be changed with each new charge. The Sweeney catalyst-packed column is superior in this respect; however, every change of catalyst necessitates repacking the distilling column, a not inconsiderable labor. The investigations involving liquid catalyst, while essentially different from the method of this work, are useful from the standpoint of continuous operation, since the catalyst can be constantly recycled.

Apparently, little published work on hydrogenating distillation exists. The work of Beregi does not encompass a study of the process used but deals principally with the materials. Similarly meagre are data on the role played by gases in distilling columns. Brown and Lockhart (2) state that, except for very low velocities, the overall column efficiency is relatively independent of mass vapor velocities, with maximum efficiency at the maximum allowable vapor velocities. Whether this statement holds when a gas other than the distilled vapors passes through the column cannot be said.

Some interesting deviations from normal distillation routine occurred during the hydrogenating runs which indicated that there is much room for new work of a theoretical nature in this field.

Esterifications have for some time commonly been carried out in some form of reflux apparatus. However, since the fractionating column is a comparatively recent development, not a great deal of work has been done on precision separation of the ester, or its water azeotrope, as formed. Horsley (8) produced isobutyl acetate in 1927, removing the ester as an ester-water-alcohol ternary azeotrope, but in 1927, no precision fractionation equipment of the type used here in existed. Patents have been issued (3, 4, 17) for esterifying apparatus which incorporate simple distillation, but there is apparently none for precision fractionation-esterifications.

## MATERIALS AND EQUIPMENT

As indicated by the title of this work, the apparatus used consisted mainly of a distilling column to which could be attached a reaction chamber containing catalyst. The column used was a four foot Pyrex tube of one inch inside diameter, packed with either 1/8 inch stainless steel helices (Fenske) or 3/8 inch glass helices. The column was double jacketed to minimize heat transfer to the surroundings, the inner jacket being wound with 34 feet of #22 Brown and Sharpe gauge Nichrome wire as a heating element. A Variac or Powerstat was used to control the temperature of the jacket. The column calibrated about 30 theoretical plates with a test mixture of toluene - methylcyclohexane at total reflux. The bottom of the column ended in a ground-glass 35/25 spherical fitting to which the reactor was attached by means of the spherical joint and a "C"-clamp.

The reactor was a ten inch length of 48 mm. Pyrex tubing fitted with ground-glass, spherical fittings, female at the top and male at the bottom. The catalyst was supported in this reactor by means of a 20 mesh, stainless steel screen, bent in the shape of a cone and forced into the bottom of the reactor. The reactor was wound with a layer of asbestos tape, a spiral heating winding of 13 feet of #22 B & S gauge Nichrome wire, and another layer of tape. When plugged into a 110 volt Variac, a temperature of about 300°C. was obtain-

able in the reactor at maximum amperage (5 a.) and voltage (70 v.) A relative temperature reading in the reactor was obtained by placing a mercury thermometer between the asbestos-tape windings and the reactor. The reactor was easily removed for catalyst change or inspection, and air could be excluded from the interior of the chamber merely by inserting rubber stoppers in both ends of the reactor as soon as it was removed from the column.

To the spherical joint at the bottom of the reactor the still pot was attached. The pot was heated by an electric coil, ceramic stove constructed to fit round-bottom flasks. The heat applied to the stove is regulated, as above, with a 110 volt Variac.

Refractive indices of the products were measured on a Valentine refractometer manufactured by Industro-Scientific Co. Sample weights were taken on a Harvard triple-beam balance of Cenco manufacture.

#### ISOMERIZATION

For the isomerization runs, apparatus essentially as just described was used. A one liter, Pyrex, round-bottom flask with a 35/25 spherical ground-glass fitting served as a still pot. The condenser was a simple cold-finger reflux condenser, the reflux being adjusted by means of a stopcock in the take-off line. The distillate was collected in a 50 cc.

side-arm Erlenmayer flask, the side-arm of which was connected to a dry-ice trap.

#### HYDROGENATION

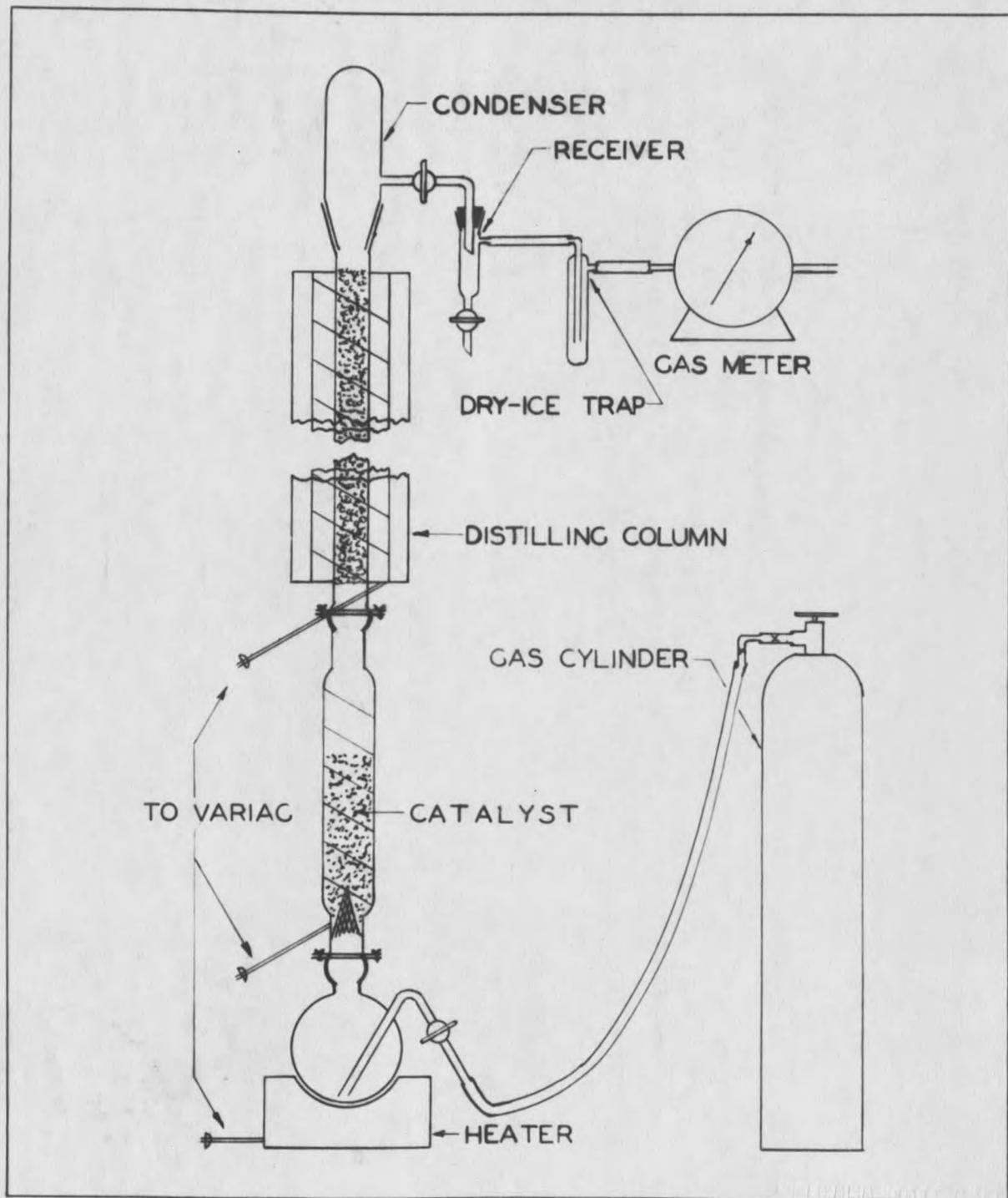
The setup of hydrogenation was the same as for isomerization except for the still pot, the distillate receiver and the catalyst. A one liter, Pyrex, round-bottom flask was a spherical fitting and a sampling tube was used as a still pot. The sampling tube extended inside nearly to the bottom of the flask so that hydrogen could be bubbled through the liquid in the flask. The distillate receiver was a ten inch, side-arm test tube with a stopcock at the bottom. Excess hydrogen and uncondensed vapors were removed via the side-arm to a dry-ice trap and thence to a "Precision Wet Test Meter" (Precision Scientific Co.) By means of the stopcock in the receiver, samples could be taken without stopping the hydrogen flow or allowing hydrogen to escape into the room. As a hydrogen supply a Portland Oxygen and Hydrogen Co. cylinder at 2000 psi was used. The cylinder was fitted with a two-stage reducing valve with a needle valve outlet, providing a very fine adjustment in flow rate. Hydrogen delivery pressure was from four to five pounds. The cylinder was connected to the gas inlet tube in the still pot by means of rubber tubing. The stopcock in the inlet tube was left completely open and the flow rate regulated by means of the needle-valve on the cylinder.

## ESTERIFICATION

The apparatus used in the esterification reactions was simply a distilling column such as previously described, packed with 3/8 inch glass helices and provided with a Corad constant reflux distilling head and a distillate receiver such as used in the hydrogenations. The receiver side-arm led to a dry-ice trap and thence to the blow-down line. Hydrogen chloride gas could be admitted to the still pot through a sampling tube. For continuous operation, a small Merkel-Korff stainless steel bellows pump was used to pump the acid-alcohol mix into the still. Feed was placed in a 250 cc. graduated separatory funnel which was attached to the pump inlet by neoprene tubing. The pump outlet was attached to the still pot via another length of neoprene tubing and a side-arm inlet at the top of the still pot. The pump rate was adjusted until 50 cc. were pumped into the still pot in the same length of time that 50 cc. came off overhead. Once set, the bellows pump would deliver liquid at a constant rate indefinitely.

## REAGENTS AND CATALYSTS

A list of reagents and catalysts will be found in Tables I and II.



Schematic Diagram of Equipment

TABLE I  
REAGENTS AND CATALYSTS

<u>Run No.</u>	<u>Reagent</u>	<u>Catalyst</u>
1,2,10*	Normal pentane; Phillips Pure 99% B.p: 30.9°C @ 638 mm; $n_D^{20}$ 1.3577	A
3,4,5,6, 7,8,9	Normal hexane; Phillips Tech, 95% B.p.: 63°C. @ 638 mm.; $n_D^{20}$ 1.3750	A
11,12	Cyclohexane, Dow, Tech; B.p.: 77.6°C. @ 627 mm.; $n_D^{20}$ 1.4262	A
13,14	Methylcyclohexane, Dow, Tech; B.p.: 97.7°C. @ 627 mm.; $n_D^{20}$ 1.4230	A
15	Normal heptane, Westvaco, C.P. B.p.: 98.44°C. @ 760 mm.; $n_D^{20}$ 1.3878	A
16	Normal octane, Conn. Hard Rubber Co. B.p.: 118.8°C. @ 640 mm. $n_D^{20}$ 1.3977	A
17	Cyclohexanol, Eastman Kodak Co. C.P.	B
18	Normal hexene, Dehyd. of n-hexanol B. range 57.7-58.8°C @ 636 mm.	C
19,21	Di-isobutylene, Shell	D
23,24	Above, heart cut 94.6-96.5°C. @640 mm.	D
20,22	Mesityl oxide, Shell B.p.: 120°C. @ 639 mm.; $n_D^{20}$	D
25	1-Nitropane, Commercial Solvents B.p.: 122.8°C. @ 637 mm.; $n_D^{20}$	D
26 - 34	Acetic Acid, glacial; Merck, 99.5%	(E)
35	Acetic Anhydride; Carbide & Carbon Chemicals Corp; Prac.	None
26,27,28	Ethyl Alcohol, 95%; $n_D^{20}$	(E)
29,30	Normal propyl alcohol; Eimer & Amend, C.P.	None
31,32	Isobutyl alcohol; Eastman Kodak Co. C.P.	"
33,35	Isoamyl alcohol; Eastman Kodak Co. C.P.	"
34	Tertiary butyl alcohol; Eastman K. Co. C.P.	"

\* 4-8 mesh catalyst

Note: Where no boiling points are given, the reagents were used just as they came from the container.

See Table II for description of catalysts.

## TABLE II

## CATALYSTS

- A: Isocel, 6-14 mesh or 4-8 mesh; Porocel Corp.
- B: Alumina, pellets, 1/8 inch; Harshaw
- C: Catalyst "B" activated with anhydrous hydrogen chloride
- D: Hydrogenation catalyst; Universal Oil Products;  
Nickel on Kieselguhr
- E: Anhydrous hydrogen chloride gas; Mathieson  
(Used in runs 26 and 27 only.)

## PROCEDURE

A basic procedure, common to all reactions, was followed throughout the investigation. This will be outlined first and followed by a discussion of the variations in technique used in the individual runs.

A weighed amount of the reacting liquid was charged cold to the still pot in which were two 1/2 inch Berl saddles used as boiling chips. The reactor was partially filled with a weighed amount of the desired catalyst, the ground-glass joints greased, and the apparatus assembled with the charge and the catalyst already in place. The ground-glass joints were secured with "C"-clamps or screw clamps manufactured for this purpose. An effort was made to have the reactor as nearly vertical as possible, to prevent the refluxing liquid from channeling down over only a portion of the catalyst. When the equipment was in order, the Variacs controlling the pot, reactor and column heats were adjusted to the proper settings for the material being investigated. In general, the temperature halfway up the heated jacket was maintained six to ten degrees higher than the temperature of the overhead, this being the condition providing most nearly adiabatic conditions in the column itself. When possible, the column was flooded and the pot heat adjusted to a value just below that which caused flooding. In most cases it was necessary to have the pot heater on full to cause flooding. After the

proper Variac settings had been determined by observing flooding and the column and overhead temperatures, the system was allowed to run at total reflux until the temperature of the overhead remained constant. This required from one to three hours, depending on the rapidity with which equilibrium was established. When the temperature had reached a constant value, take-off was begun, the samples being collected in 50 cc. bottles. The size of the sample depended upon the changes in overhead temperature, it being endeavored to keep the temperature range of each sample as small as possible. Thus, when the temperature rose fairly rapidly, the individual samples were small. The bottles containing the distillate samples were labeled as to temperature range, numbered chronologically, weighed, and the refractive index of each sample taken.

No attempt was made to isolate pure compounds from any of the samples, and no chemical or physical treatment other than washing or drying was accorded any of the products. The reaction was continued until the overhead temperature and/or refractive index indicated that no further product of value was being obtained. The system was then shut down, the catalyst chamber removed and closed off to protect it from air, and the residue in the still pot weighed and, in some cases, its refractive index taken. If the results of the run were positive, an attempt was made to reproduce them in a subsequent run or runs.

### Isomerization

The first isomerization runs were carried out with the reactor not externally heated. Some difficulty was experienced in obtaining sufficient throughput in the column without causing the reactor to flood over the catalyst bed. The catalyst used was 6-14 mesh Isocel, and its irregular shape caused it to pack to some extent, making it difficult for the reflux to flow down through it. Dispersing the catalyst by mixing it with 1/2 inch Berl saddles or 1/8 inch helices, or by layering these materials alternately, was of no help, nor did filling the four-inch free space at the top of the catalyst bed with Berl saddles improve operation. When the reactor was wound with a Nichrome heating element and heated to approximately the boiling point of the material in the still pot, throughput was more satisfactory, although flooding was still experienced at temperatures below that which would have given optimum reflux. Even at reflux ratios as low as 5:1, the rate of take-off was comparatively small. A control run using 1/8 inch alumina pellets, which had no catalytic action at the low temperature used, showed a throughput superior to that obtainable with the Isocel. Unfortunately, Isocel catalyst is not available at present in pellet form. A small quantity of the 4-8 mesh size was available. It showed characteristics superior to the 6-14 mesh catalyst, but not as good as the pellets. Since

aluminum chloride is quite deliquescent, air was excluded from it as much as possible by closing off the ends of the reactor with rubber stoppers when not in use. A portion of catalyst was used until it no longer caused isomerization to take place.

It was necessary to run the paraffin isomerizations at very high reflux ratios in order that the product not be taken off faster than formed. Normal pentane isomerized rapidly enough for a reflux ratio of about 30:1, normal hexane required about 40:1, and normal heptane and normal octane isomerized too slowly at the temperature of their boiling points to enable isomerized product to be taken off at any reasonable reflux ratio.

If the temperature appeared to be rising too rapidly, it was possible to cause it to decrease again by allowing the system to run at total reflux for a time; that is, equilibrium was allowed to re-establish itself while no product was being taken off. When the temperature again reached a constant value, take-off was re-commenced at a higher reflux ratio.

The naphthenes isomerized comparatively readily and pure product could be obtained with a reflux ratio of 20:1.

An attempt was made to isomerize normal hexene using 1/8 inch alumina pellets activated with anhydrous hydrogen chloride. However, with the reactor at the olefin-isomerization

temperature of 350-400°C., downcoming liquid was immediately revaporized and none of the reflux could re-enter the still pot. Thus the column eventually would have filled up with liquid.

### Dehydration of Alcohols

For reasons similar to those given for the failure of the olefin isomerization, an attempt to dehydrate cyclohexanol over 1/8 inch alumina pellets also failed. Normal dehydration temperature is 350-450°C., again too hot to allow the reflux to return to the still pot. At the boiling point of cyclohexanol, which is relatively high, no appreciable dehydration took place, although a few drops of cyclohexene were obtained.

### Hydrogenation

The procedure for hydrogenation involved bubbling hydrogen through the material in the still pot, otherwise it was the same as the isomerization procedure. In the first hydrogenation run attempting to reduce di-isobutylene to "isooctane", the system was allowed to run at total reflux for an hour before passing in the hydrogen. The reactor heat was then turned on and hydrogen flow started. After several hours, no hydrogenation had taken place. It was found that the catalyst needed to be "activated" by passing hydrogen over it at 200-250°C. before beginning the boil-up. This was accomplished by bubbling the hydrogen through the reagent in

the still pot for an hour with no heat applied to the pot, but with the reactor heat on full. The reactor was allowed to cool to the boiling point of the reagent and, with hydrogen still flowing into the system, the pot heat was turned on and the system run at total reflux until the temperature reached a constant value. The hydrogen delivery pressure was kept constant at about 4 psi and the rate of flow adjusted by observing the bubbles created by the gas passing through the reactant. Too high a gas rate caused the column to flood in the condenser or at the top of the packing, but little difficulty was experienced in this respect and throughput was excellent. Considerable liquid was entrained by the hydrogen; this was recovered by a dry-ice trap.

The hydrogenation catalyst used was very active and it was necessary to take precautions to prevent its prolonged contact with air. Air would spontaneously oxidize the catalyst, causing considerable heat to be given off. Catalyst so treated could not be re-activated at temperatures and pressures available to the investigators.

#### Esterification

The first two esterifications runs were made using anhydrous hydrogen chloride gas as a catalyst. Molecular combining proportions of ethyl alcohol and glacial acetic acid were weighed out and charged cold to a still pot fitted with

a sampling tube. The still pot was attached directly to a distilling column such as previously described. The column was packed with glass helices because of the corrosive action of acetic acid on stainless steel. A Corad constant reflux distilling head was used because some of the products were two phase. The cold finger condenser used in the other reactions allowed the overhead to separate into layers before being taken off, and when take-off was begun, only the lower layer came off.

The hydrogen chloride was bubbled through the reacting mixture for a time before the heats were applied; then, with pot heat on full, the column was flooded and the pot head adjusted to that just below the flooding heat. The system was allowed to come to equilibrium a matter of about an hour, then take-off at 20:1 reflux ratio begun. The product came off steadily at nearly constant temperature until practically all of the liquid had boiled out of the still pot. Hydrogen chloride in considerable quantities was dissolved in the product and it was necessary to wash with dilute sodium hydroxide before taking a refractive index.

The third esterification run was intended to be a control run and was made without use of hydrogen chloride. Previous to the run, the column was washed out with 500 cc. of concentrated nitric acid, several gallons of water and dried with acetone and air to remove any trace of hydrogen chloride

that might be adhering to the packing or other portion of the column. When this control run revealed that esterification was as rapid and complete without catalyst as with it, all subsequent runs were made without use of hydrogen chloride.

Ethyl acetate and water form a single-phase azeotrope boiling lower than any of the reactants or their water azeotropes. The other acetates studied, normal propyl, iso-butyl, and iso-amyl, all produce ester-water azeotropes which are two-phase and hence easily separable by decantation. For normal propyl acetate, the amount of water produced by the esterification was approximately equal to the amount of water required to azeotrope with the ester produced.(9). Therefore, no water was added to the mix. For the other acetates, water had to be added in excess of that produced in order that all of the ester formed would azeotrope and thus be removed by virtue of the azeotrope's low boiling point. A sample calculation showing how the amount of water necessary was computed appears in the following section. In addition to the water necessary to azeotrope with the ester, sufficient water was added to act as a chaser in the batch runs. About 100 grams additional were used for this purpose.

The product was allowed to separate into two layers, the ester decanted, dried with anhydrous calcium chloride and its refractive index taken.

For purposes of computing the theoretical yield of ester















































