



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 Hichrome 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

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A THESIS

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

HYDROGENATION

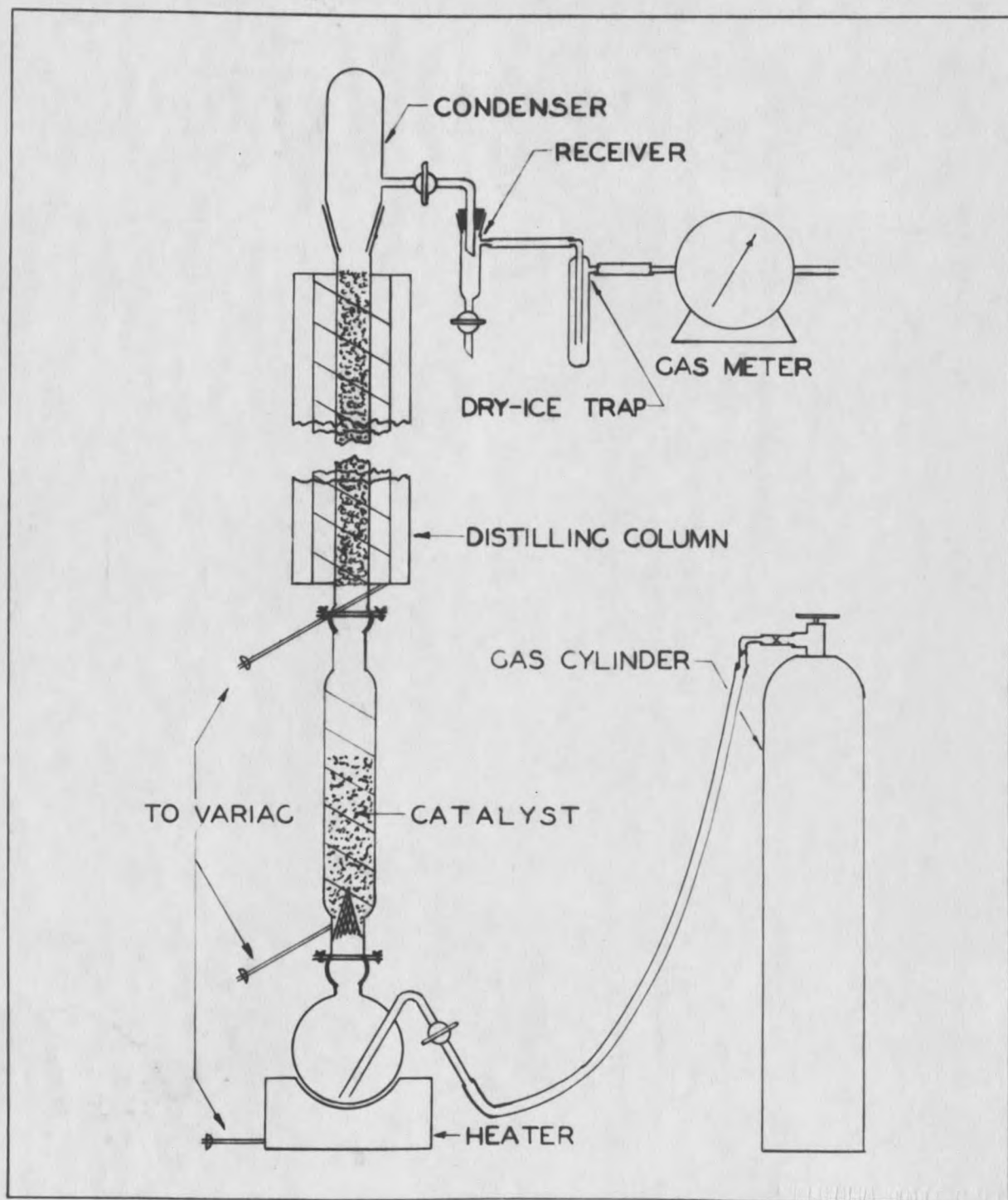
The setup of hydrogenation was the same as for isomerization except for the still pot, the distillate receiver and the catalyst. A one liter, Pyrex, round-bottom flask was a spherical fitting and a sampling tube was used as a still pot. The sampling tube extended inside nearly to the bottom of the flask 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 "iso-octane", 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, isobutyl, 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

produced, the per cent water in the azeotrope was taken from the table of azeotropic data compiled by L. H. Horsley (9). The weight of water-free ester was not computed directly for these runs.

Propyl acetate was produced in continuous operation by using a small bellows pump to pump feed continuously from a graduated separatory funnel into the still pot. In this case it was necessary to calculate quite closely the percentage water in the azeotrope because an excess of either water or ester would soon build up in the system if either component appeared in the wrong proportions. For this computation, a quantity of the ester-water azeotrope was produced, the volume of water and ester noted, and, using their specific gravities, the weight per cent of water present computed. Because of the slight mutual solubility, this method of calculation was not exact, but it was thought more accurate than the Horsley data since the latter were compiled for sea-level atmospheric pressure.

The rate of feed of the bellows pump was adjusted, by changing the amount the bellows was compressed, so that the rate of feed just equalled the rate the distillate was being taken off.

It was found that a certain amount of charge had to accumulate in the still pot before take-off was begun in order to give the reaction sufficient contact time. Assuming the

first molecule entering the system to be the first molecule leaving, this contact time was computed to be approximately 75 minutes, that is, enough charge had to be added to the still pot batch-wise for 75 minutes of batch operation before the continuous operation could proceed indefinitely. The contact time was determined as follows: Having determined the take-off rate at 20:1 reflux ratio for the system being investigated, the pump was set to pump in at this rate and allowed to pump the alcohol-acid mix into the system for 80 minutes. Then take-off was commenced, with the pump still running at the original rate. After these conditions were established the system operated indefinitely. The procedure was repeated with a 75 minute interval of pumping previous to take-off. The results were the same. For a 70 minute pumping interval, however, the system operated normally for about two hours, at the end of which time, the overhead temperature began to rise and the material condensing in the head became one-phase, indicating that the product was being taken off faster than formed. Thus 75 minutes, or 140 cc. was judged to be about the minimum allowable lag.

SAMPLE CALCULATIONS

Run Number 35



Molecular weights:

$$\text{Ac}_2\text{O} = 102.1$$

$$\text{iAmOH} = 88.15$$

$$\text{iAmOAc} = 130.18$$

$$\text{H}_2\text{O} = 18$$

Theoretical yield of iso-amyl acetate = X:

$$\frac{100}{102.1} = \frac{x}{260.36} \quad x = 255 \text{ gm}$$

Theoretical yield of water = y:

$$\frac{100}{102.1} = \frac{y}{18} \quad y = 17.6 \text{ gm}$$

Total yield of azeotrope = 376.5 gm

% water in azeotrope = 35.1%

Wt. water in azeotrope = $376.5 \times 0.351 = 132 \text{ gm}$ Wt. ester in azeotrope = $376.5 - 132 = 244.5 \text{ gm}$ Per cent yield = $\frac{244.5}{255} \times 100 = 94\%$ Theoretical yield of azeotrope = $\frac{255}{0.649} = 393 \text{ gm}$ Water in theoretical yield of azeotrope = $393 - 255 = 138 \text{ gm}$

Water formed by reaction = 17.6 gm

Excess water required to azeotrope all of ester =

$$138 - 17.6 = 120.4 \text{ gm}$$

TABLE III
Results: Isomerization

Run No.	1 & 1A	2	10	3	5	6	8	9	11	12	13
Charge	n-Pen- tane	n-Pen- tane	n-Pen- tane	n-Hex- ane	n-Hex- ane	n-Hex- ane	n-Hex- ane	n-Hex- ane	Cyclo hexane	cy- clo- hexane	Methyl cyclo hexane
Wt (gm)	203.6	234.9	179.9	216.8	193.3	234.4	226.5	100 R ³	295.7	100 R ³	214.6
B.P. (640mm)	30.9	30.9	30.9	63.2°					74.8°	74.8°	99.7°
R.I.	1.3577	1.3577	1.3577	1.3750					1.4262	1.4262	1.4230
Catalyst ¹	6-14 mesh	6-14 mesh	4-8 mesh	From 2	6-14 mesh	From 5	6-14 mesh	From 8	6-14 mesh	From 11	6-14 mesh
Wt. (gm)	230.9	266.9	220	"	270.4	"	268.4	"	257.8	"	269
Product											
Total Wt.	67.8	56.7	66.3	18.3	46.8	38.8	64.3	29.7	142.3	123.5	89.1
Boiling Range	25.7° 30°	24.5° 30.2°	2 24.5°	54.8° 60°	45.6° 54.8°	53.2° 60.4°	43.6° 58°	56.8° 60.2°	63.8° 66°	64.8° 66.2°	80.8° 88°
R.I.	1.3551	1.3538		1.3630	1.3694		1.3648	1.3734	1.4077	1.4101	1.3988
Range	1.3566	1.3556	1.3540	1.3732	1.3713	1.3740	1.3735	1.3742	1.4101	1.4106	1.4130
Percent Yield	33.3%	24.1%	36.9%	8.5%	24.3%	16.6%	28.4%		(48.2%) ⁴	67.2%	41.5%

1. Catalyst in all cases is Isocel
2. Collected as dry-ice condensate
3. Residue from preceding run plus 100 grams fresh reagent
4. Run 11 continued as Run 12

TABLE IV
RESULTS: HYDROGENATION

Run Number	19	20	21	22	23-4
Charge	Di-iso-butylene	Mesityl-Oxide	Di-iso-butylene	Mesityl-Oxide	Di-iso-butylene
Wt. (gm)	240.3	358.7	200.0	430.9	165.3
Boiling Pt.	93.6	120°	93.6°	120°	94.6°
n _D ²⁰	1.4095	1.4450	1.4095	1.4450	1.4095
Catalyst ¹	Fresh	From 19	Act'd from 20	From 21	From 22
Product					
Total Wt.	36.9 ²	124.0	121.9	276.1	79.5
Distillate 1 ³	12.9 gm	51.0 gm	61.5 gm	73.5 gm	26.1 gm
n _D ²⁰	1.4090	1.3597 - 1.3599	1.3910 - 1.3915	1.3597 - 1.3935	1.3933
B.P.	91° - 91.4°	50.3°	85.8° - 86.6°	50° - 106.4°	88.2° - 91.2°
Distillate 2	10 gm	30.5 gm	41.6 gm	202.6 gm	33.4 gm
n _D ²⁰	1.4090	1.3591	1.3918 - 1.3921	1.3951 - 1.3959	1.3924
B.P.	91.4° - 91.6°	50°	86.6° - 87.8°	103.7° - 106°	66.4° - 88.2°
Distillate 3	14 gm	42.5 gm	18.8 gm		20.0 gm
n _D ²⁰	1.4090	1.3624 - 1.3658	1.3929 - 1.3937		1.3943
B.P.	91.6° - 94.4°	50° - 70.5°	87.8° - 88.2°		88.2° - 88.5°
Per Cent Yield	0 ²	34.7%	61%	64.2%	48.1%

1. Catalyst in each case is 238.5 gm of U.O.P. Hydrogenation Catalyst.
2. No hydrogenated product.
3. Distillate 1 includes dry-ice condensate.

TABLE V
RESULTS: ESTERIFICATION

Run No.	26	27	28	29	30	31	32	33	35
Acid	Acetic	Acetic	Acetic	Acetic	Acetic	Acetic	Acetic	Acetic	Acetic Anhydride
Wt.	150	100.2	75	100	200	100.3	100	100	100
Alcohol	Ethyl	Ethyl	Ethyl	n-Propyl	n-Propyl	Isobutyl	Iso- butyl	Iso- amyl	Iso- amyl
Wt.	122.5	81.8	60.5	102	210	197	125.6	150.6	177.5
Wt. Water							20.9	100.5	220.4
Dist. 1 n _D ²⁰	82.1gm 1.3725- 1.3729	35.7gm 1.3727	45.0gm 1.3725	45.5gm 1.3825	146.1gm 1.3844	43.8gm 1.3909	87.8gm 1.3909- 1.3911	87.6gm 1.4020- 1.4025	45.7gm 1.4020
B.P.	58.3°- 62°	63.5°	65.3°	66.9°- 77.5°	77.4°- 78.4°	83.4°	82.4°- 82.5°	88.5°	88.4°
Dist. 2 n _D ²⁰	34.1gm 1.3745	50.2gm 1.3728	24.4gm 1.3720	40.4gm 1.3844	64.3gm 1.3847- 1.3850	25.2gm 1.3929	82.5gm 1.3913- 1.3914	143.4gm 1.4030- 1.4033	43.8gm 1.4034
B.P.	58.4°	63.3°	65.5°	77.5°- 78°	81.7°- 86.5°	94.3°	82.8°- 82.9°	88.6°- 88.9°	88.5°
Dist. 3 n _D ²⁰	84.3gm 1.3723- 1.3729	54.2gm 1.3728- 1.3729	11.0gm 1.3700	21.7gm 1.3873	104.5gm 1.3861- 1.3873	87.7gm 1.3996- 1.4011	30.0gm 1.3922	88.4gm 1.4047- 1.4048	231.0gm 1.4040- 1.4044
B.P.	59.4°- 65°	63.7°- 64°	66.3°	78°- 82°	86.7°- 104.5°	87.6°- 100.9°	83.2°	89.3°- 94°	88.7°- 89.5°
Total Product	200.5	140.1	80.4	107.6	310.9	156.7	200.3	319.4	320.5
Total Ester	183.3	128.0	73.6	94.1	272.1	126.3	161.2	207.4	208.3
Per Cent Yield	84.1%	87.1%	67.5%	55.3%	80.0%	65.2%	83.3%	95.4%	81.7%

DISCUSSION OF RESULTS

As indicated in the introduction to this thesis, the nature of the work precludes reaching any but the most general conclusions about the nature of the individual reactions and how various factors affect them. However, a number of interesting results were obtained which are valuable in themselves or provide a basis for further investigations of the particular reactions.

Paraffin Isomerization

The paraffin isomerizations were generally the least satisfactory of those investigated. Normal pentane, the easiest to isomerize of the paraffins studied, gave a greater total per cent yield of isoparaffins at a greater rate than obtainable with hexane or heptane. The product of the pentane isomerization showed a boiling range of 24.5° - 30.2°C . at approximately 640 mm. atmospheric pressure. The boiling point of pure normal pentane at this pressure is 31°C . and that of isopentane is 22.9°C . The refractive index of the product ranged from 1.3538 to 1.3568, while the refractive indices of normal and iso-pentane, respectively, are 1.3576* and 1.3539*. Thus it appears that the product is a mixture of iso- and normal pentane. No neo-pentane was detectable.

* Data for all pure hydrocarbons were taken from Doss (5). Data for pure organic compounds other than hydrocarbons come from the Chemical Rubber Handbook (7).

The hexane isomerizations showed similar characteristics with the additional feature of noticeable catalyst deactivation. It was found that a given weight of Isocel kept in the reactor for several runs would produce a certain weight of the neo-hexane isomer and no more, even if fresh normal hexane were charged. After this weight of neo-hexane was removed, a certain amount of iso-hexanes could be produced and after these fractions had been removed, no further isomerization would take place. This cycle was fairly short, taking about two volumes charge per volume catalyst to "use up" the catalyst. Of course, the fact that a small amount of catalyst was used (250 cc.) and the fact that the catalyst chamber had to be exposed to air more often than in a normally operating plant, cut down on the catalyst life. It was found that when unusual precautions were taken to protect the catalyst from the atmosphere, an improved yield was obtained.

The product of the hexane isomerizations apparently contained all the hexane isomers, including neo-hexane. The refractive index range of the product was 1.3630 to 1.3742, while the refractive index of normal hexane is 1.3750 and of neo hexane 1.3688. As in all of the reactions studied in this work, no attempt was made to isolate pure compounds from the products. However, an examination and comparison of the boiling points and refractive indices of the products and of the pure compounds that might be expected was usually sufficient

to indicate to what extent and to what end the reaction had proceeded. The fact that the hexane isomerization product showed a refractive index range which extended below that of the lowest hexane isomer indicated, then, that a certain amount of pentanes was also formed.

As stated in the procedure, difficulty was experienced in getting sufficient throughput with the shapes of catalyst used. The free space above the reactor would fill up with liquid when the pot heat got too high, and the reflux would be very slow. With this small reflux and the necessarily high reflux ratio required, the rate of take-off was very slow, about 15 grams of distillate per hour for the 6-14 mesh catalyst. The results using the 1/8 inch pellets indicate that use of a catalyst in some regular shape, such as the pellets, would improve the throughput and flooding characteristics of the system and consequently improve the yield, since the longer the reaction takes the greater the losses will be.

A few drops of water were added to the catalyst in run number seven and blown through the catalyst bed with air. The result was a complete loss of catalytic activity. The amount of moisture present in the atmosphere is sufficient to activate the catalyst, and more water will ruin its activity.

Normal heptane and normal octane isomerized too slowly to allow the product to be taken off as formed. At other

than extremely high reflux ratios (50:1) the product taken off was pure normal compound.

Olefin Isomerization

As indicated in the procedure section, olefins cannot be isomerized using this system because of the high temperature required. Normal hexene, the compound studied, undergoes no noticeable isomerization at its boiling point, the usual isomerization temperature being approximately 400°C. At the latter temperature no reflux could return to the still pot, all of it having been re-vaporized as soon as it reached the hot reaction zone.

Naphthene Isomerization

The isomerization of cyclohexane was a rapid and comparatively easy process. The product was almost entirely methylcyclopentane of high purity (refractive index range 1.4084 - 1.4101) The refractive index of pure methylcyclopentane is 1.4098. The yield was comparatively high, 67%, and the catalyst seemed to retain full activity after two volumes cyclohexane had been charged per volume catalyst.

A similarly easy isomerization was that of methylcyclohexane. The product, however, was so mixed that it was impossible to say definitely which isomer appeared in preponderance. The refractive index of the product ranged from 1.3988 to 1.4160, with the bulk of the product within the range

1.4120 to 1.4140. This would indicate 1,1- and 1,2-dimethyl cyclopentane, but probably all the possible isomers are present to some degree.

Alcohol Dehydration

The alcohol dehydration run on cyclohexanol was unsuccessful for reasons similar to those for the failure of the olefin isomerization. At the boiling point of cyclohexanol no appreciable dehydration takes place, although a few drops of cyclohexene and water were obtained. After these few drops were removed, only cyclohexanol came off overhead. The temperature of dehydration using the alumina catalyst is 350 - 450°C. If the pressure on the system could be increased sufficiently to cause cyclohexanol to boil at 350°C. or above, it seems reasonable to expect that dehydration would proceed nicely and cyclohexene of high purity be obtained directly from the system.

Hydrogenation

The hydrogenations proceeded readily to give products of a high degree of purity. The first hydrogenation run on diisobutylene was unsuccessful because, as previously explained, it was found necessary to activate the catalyst before it came in contact with the liquid. Subsequent runs, in which hydrogen was passed over the hot catalyst for a time before beginning reflux, were quite successful.

Di-isobutylene was reduced in excellent yield 61% to "iso-octane" (2,2,4-tri-methylpentane) of high purity. The lower yield of runs 23-4 was caused by a partial oxidation of the catalyst (see below). The great heat evolved by this spontaneous oxidation caused large quantities of gas to be produced. Since the dry-ice trap could not condense vapors in such rapid flow, some product was lost via the blow-down line. The remainder of the loss of yield can be accounted for by the fact that only a portion of the catalyst was acting. The boiling range of the product was 88.2 - 85.8°C. and the refractive index range 1.3929 - 1.3910. Corresponding values for pure 2,2,4-tri-methylpentane are 92° and 1.3914. It is interesting to note that the boiling point decreased as the run progressed, as did the refractive index. It should also be noted that the hydrogen passing through the column acted to reduce the overhead temperature three to six degrees. When the hydrogen flow was stopped, the temperature rose immediately, even at total reflux. The product was contaminated by mesityl oxide which had been absorbed on the catalyst from a previous run. This fact probably accounts for the decrease in temperature of the overhead, the temperature gradually going down as the higher boiling contaminant was removed.

The contamination of the product due to absorption of other liquids on the catalyst, while something of a problem in this research where a number of different materials are

passed consecutively over the same sample of catalyst, would be no problem in actual practice where a charge of catalyst is used for only one reagent.

The hydrogenation of mesityl oxide yielded a product of boiling range $103.7 - 106^{\circ}\text{C}$. and refractive index range $1.3951 - 1.3959$. This corresponds well to the boiling point and refractive index of the expected compound, methyl isobutyl ketone which are, respectively, $108 - 112^{\circ}\text{C}$. and 1.3957 .

After the second mesityl oxide run, it was noticed that the catalyst spontaneously became very hot on contact with air. Until that time, no especial precautions had been taken to keep air away from the catalyst. An inquiry sent to Universal Oil Products, manufacturer of the catalyst, yielded the information that the freshly reduced, as well as the used, catalysts are pyrophoric upon exposure to air and that if the oxidation is allowed to proceed uncontrolled, loss of activity will result. Catalyst so treated cannot be reactivated. The company suggested essentially the same activation procedure as herein described, and stated further that after a run the catalyst should be cooled in a stream of hydrogen and stored in alcohol. (14).

A run was made on 1-nitropropane to attempt reduction to propylamine. During this run, with no air in the system, the temperature of the reactor rose spontaneously to nearly 300°C . making it necessary to abandon the run. Examination

of the catalyst showed that the portion nearest the still pot had crumbled to a black powder. This result, coupled with the outcome of the mesityl oxide run, led to the conclusion that the catalyst was not fitted for reduction of oxygenated compounds, particularly those possessing more than one oxygen atom per molecule. The manufacturer, however, states that the catalyst can be used for the reduction of mesityl oxide successfully if care is taken to exclude air from the catalyst region. He also states that nitroparaffins can be reduced using this catalyst if the temperature is kept at 20°C. and the reactants are liquid. Hydrogen pressure of 50 psig is recommended (15). The equipment as set up for this investigation had no provisions for pressurization or heat removal, therefore reduction of nitroparaffins was not studied further.

The effects of the hydrogen gas in the distilling column on the distillation characteristics present an interesting topic for further research. A large amount of liquid was collected in the cold trap during each run indicating that the hydrogen was entraining considerable liquid. The effects of this entrainment on column efficiency were not determined, although in the mesityl oxide run, number 22, 155 grams of product were taken off within a refractive index range of two in the fourth decimal place, indicating good separation. Entrainment was very apparent if the hydrogen rate was too high, in which case the column would flood, beginning in the head

and progressing downward. It is interesting to note that the entrained liquid collected by the dry-ice trap showed a refractive index approximately equal to that of the lowest boiling distillate in the range through which it was collected. It might be suspected that some of the higher boiling unsaturates would also be entrained and show up in the dry-ice condensate.

As in the isomerization, too rapid take-off caused a premature temperature rise. Allowing the system to run at total reflux for a time would cause the temperature to return to the proper value. Take-off rate was much faster than for the isomerizations, however.

The hydrogen rate, as measured by the wet test meter, averaged about 20 liters per hour.

Esterification

The products of the esterifications were, on the whole, very pure and the yields exceptional. The percentage yields have been computed using the azeotrope compositions listed by L. H. Horsley (9) although, as previously mentioned, these compositions do not necessarily prevail at other than 760 mm. atmospheric pressure. A sample calculation for theoretical yield appears in the calculations section.

The acid-catalyzed runs to produce ethyl acetate show a theoretical yield averaging 85.5% with a refractive index

range of 1.3727 to 1.3729. The refractive index of pure ethyl acetate is 1.3722. In all cases, the refractive index recorded here for the product is that of the decanted (when possible) ester dried over calcium chloride. The non-catalyzed ethyl acetate run shows only 67.5% yield and the first non-catalyzed propyl acetate run a yield of only 55.3%. Further data indicate that the low yield was probably due to experimental technique rather than an inherent quality of the reaction.

The refractive indices of the products show a total range that is rather large. However, the bulk of the product in each case was ester having a refractive index fairly close to that of the pure compound. Thus, the refractive index of the propyl acetate ranged from 1.3825 to 1.3873, but fully three-fourths of the product had a refractive index of 1.3843-4, that of the pure compound being 1.38438. The main portion of the iso-butyl acetate produced shows a refractive index of from 1.3909 to 1.3914, that of the pure compound being 1.3911. The iso-amyl acetate range is 1.4020 to 1.4044 while the refractive index of pure iso-amyl acetate is 1.4017.

Acetic anhydride was also used successfully with iso-amyl alcohol to produce iso-amyl acetate in approximately the same purity and yield as the acetic acid iso-amyl alcohol run. Two molecules of ester are of course produced from one molecule of anhydride, but otherwise no difference in reaction characteristics was apparent. Enough water was added to the

reactant mixture to azeotrope with all the ester produced, plus an additional 100 grams to act as a chaser. The last sample taken in the run was one-phase, being almost entirely water with a small amount of ester dissolved in it. The total amount of water in the samples was weighed, and, using the weight of ester found by subtracting this weight of water from the total weight of azeotrope, the yield was computed to be 85% of theoretical. Using Horsley's percentages to compute theoretical yield gave 81.7%.

By operating continuously, essentially 100 per cent yield can be obtained. The continuous run made using acetic acid and normal propyl alcohol was operated for 24 hours. The pump rate was adjusted to be equal to the take-off rate at 20:1 reflux ratio. Molecular proportions of acid and alcohol were used to make up the charge, with enough water added to give, with the water of esterification formed, just sufficient water to azeotrope with all the ester produced. The percentage of water in the azeotrope was found by actual weight of a portion of the product. If too much or too little water is added to the charge, either water or ester will build up in the still pot; so, for large scale operation, an accurate azeotrope percentage should be determined experimentally.

The total amount of ester-water azeotrope formed was 2468 grams, of which 334 grams, or 13.5%, were water. Horsley lists 12.5% water for this azeotrope. The ester was decanted,

washed with pure water, dried over calcium chloride and the refractive index of the total yield taken. This refractive index was 1.3948, which indicates excellent purity, the refractive index of the pure propyl acetate being 1.3944. The loss in weight of ester in the water-washing process was 79.5 grams, or 3.2%

After the run lined out, the temperature varied less than one-half degree, and the refractive index range was less than five in the fourth place. Approximately one hour was needed for the charge in the still pot to come to equilibrium. When equilibrium was reached and the pump started, an additional half hour passed before the temperature became constant. After this time, the reaction was entirely self-sustaining. The system was shut down overnight; take-off could begin again in the morning as soon as the charge had come to a vigorous boil.

As indicated in the procedure section, a certain reaction time had to be allowed for by starting out with a portion of charge in the still pot. This portion amounted to about 140 cc. for propyl acetate, giving a reaction time of 75 minutes.

Groggins (6), in his discussion of esterification, describes a similar process developed by Wade (16) for producing acetates azeotropically and continuously. The reactions were catalyzed by sulfuric acid, however, and the ester came off

as a ternary azeotrope of ester, water and alcohol. As noted, the product in the esterifications studied in this work is a binary azeotrope of ester and water. The percentages listed by Groggins for the propyl acetate ternary are: 59.5% ester, 19.5% alcohol, and 21% water. As noted above, the product of this system was approximately 13.5% water and 86.5% ester. When the ester was water washed, a decrease in weight of only 3.2% was noted, far less than would have resulted if alcohol had been present in quantities approaching 19.5%. The ternary exists as one phase, also, whereas the product here was two-phase.

Considering the relatively small amount of data taken on these reactions, it would be idle to speculate on the reasons for the absence of the ternary. Examination shows only three major differences in the operations of Wade, et al. and the present investigators. They are: (1) lack of a catalyst; (2) use of a precision fractionating column; and (3) glass helix column packing. Whether any one or all of these is responsible for the lack of a ternary cannot be said definitely at this time.

CONCLUSIONS

An examination of the results of the isomerization process reveals that, for the paraffins, equilibrium was not established fast enough to make rapid take-off possible. Thus, the particular value of this scheme would appear to be less for commercial production than as a research tool in the comparatively easy and inexpensive production of small quantities of pure compound. Since a number of good isomerization processes are in commercial production today, further development of the paraffin isomerization scheme herein described along commercial lines seems unjustifiable.

The naphthenes, on the other hand, isomerize rapidly enough to merit development, should a market for one of the producible isomers arise.

The hydrogenation reactions present an excellent field for further study and development. The ease with which "isooctane" was obtained in high purity using this scheme indicates that the process would be attractive to the petroleum industry. Proper design of equipment would make this scheme applicable to the more difficult hydrogenations, also. Thus, if provisions were made for pressurization and removal of the large excess of heat, nitorparaffins could be reduced to amines with comparative ease. Bearing in mind the fact that the products appear in good purity and yield directly from the hydrogenation equipment, it would seem that a considerable

cost saving could be effected by using apparatus of the basic design herein described. The simplicity of the equipment makes it readily adaptable to an economic development of a plant-size process.

The esterification study reveals that esters can be produced in quantity and with excellent purity without the use of catalysts. The process yields ester by simple decantation and drying of the product. No complicated scheme for separation of the components of a ternary azeotrope need be used. There would appear to be no problem of equipment design for commercial production, since plant-size, packed distilling columns of similar precision have been in operation for some time. A thorough investigation of ternary production, or lack of it, and of the various factors affecting formation of the binary azeotrope, as well as the effects of different kinds of column packing and different sizes of equipment, should of course be made before any large scale development begins.

It can be concluded that each of the processes and the equipment in general merits further study, and, as noted, possible commercial development. Although all the variables have not been investigated, sufficient data were collected to determine whether and to what extent the apparatus applied to some typical reactions. The results of the investigation were, on the whole, very favorable.

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Reactions in a distilling column.

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