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Production and some reactions of furfuryl alcohol

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NOTE TO USERS

PRODUCTION AND SOME REACTIONS OF FURFURYL ALCOHOL

by

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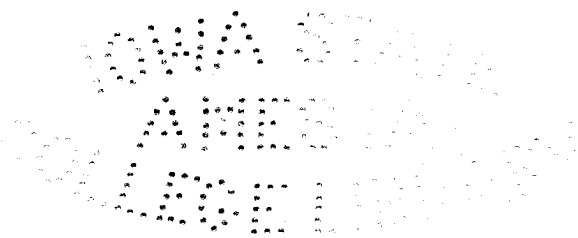

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TABLE OF CONTENTS

I. INTRODUCTION

In recent years there has been a growing interest in the industrial development and utilization of our agricultural by-products. Such a program merits continued attention from the standpoint of efficient utilization of our available resources.

A related program which meets with considerable disapproval from some sources is the conversion of edible food materials into commercial chemicals. In times of world shortage such disapproval is understandable. A logical solution to the problem would seem to involve maximum production at all times and the diversion of surplus materials into industrial use.

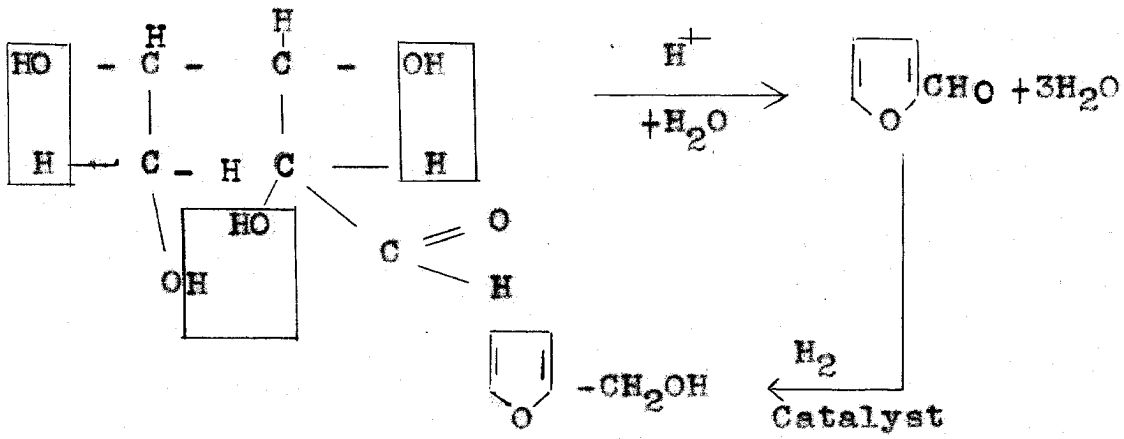
Essentially there are three principal sources of organic chemical raw materials: (1) coal, (2) petroleum, and (3) plants (animal products being considered as secondary to plants). At the present time a major portion of our chemical industry is based largely on the utilization of petroleum as a source for organic chemicals. There is already some concern over our rapid utilization of the petroleum supply, and thought is being given to the idea of using coal and other sources (e. g. Fischer-Tropsch reaction) as a means of stretching our liquid fuel reserve.

Although cultivated crops and natural vegetation were the first sources for a large number of chemicals - consider the dye and pharmaceutical industries - the ready availability of petroleum has overshadowed these original sources in recent years. In spite of this fact one can easily see the wisdom of a long range research program designed to utilize the products of our soil to supplement the coal and petroleum supply. Such a development should also tend toward the stabilization of our farm economy by the creation of a steady demand for farm crops.

To be of economic importance in the chemical industry a compound must be readily available from reasonably cheap raw materials and must offer some desirable physical or chemical property which makes it of practical interest. Hence the development of our agricultural resources as chemical intermediates must of necessity follow these two lines of study: (1) the design of practical methods of production of chemical compounds and (2) the study of their properties to determine the potential value of the compounds to industry.

The present investigation was undertaken to study two compounds along the lines mentioned above, said compounds being furfuryl alcohol and 2- valerolactone. These substances although not structurally related have quite a lot in common. Both are obtained by the reduction of products

obtained in the acid hydrolysis of carbohydrates, the furfuryl alcohol being ultimately derived from the pentose fraction while the lactone originates from the hexose fraction. The steps necessary to produce furfuryl alcohol from a pentose sugar are sketched in below.

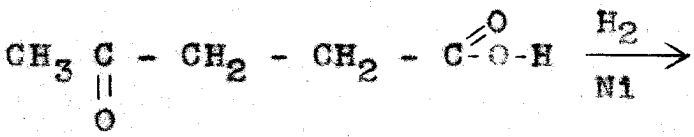


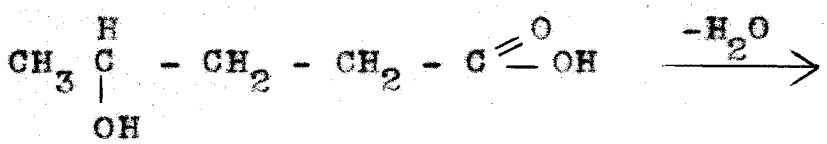
A number of various mechanisms have been proposed for the formation of levulinic acid from the hexose sugars (or materials which can be hydrolyzed to hexoses). The molecular reaction is known to be:

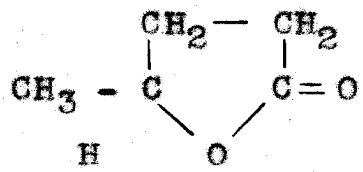
$$CH_2(OH)CH(OH)CH(OH)CH(OH)CH(OH)CHO \xrightarrow[(H_2O)]{H^+}$$

$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2CH_2COOH + HCOOH + H_2O$$

Reduction of the keto group in levulinic acid with subsequent dehydration leads to the formation of 2-valerolactone.







Further reduction of furfuryl alcohol and 2-valerlactone (followed in the latter case by additional dehydration) leads to the production of 2-methyl tetrahydrofuran in both instances.

The two parent compounds in this series, furfural and levulinic acid, are at present obtained respectively by the dilute acid hydrolysis of corn cobs and corn starch. An industry based on the first is thus dependent on waste products for its raw material while the second utilizes one of the world's principal cereal grains. The cost of the furfural raw material is thus chiefly the cost of collecting and shipping the bulky wastes. In contrast to this the corn starch is obtained from a grain whose price fluctuates widely in accordance with world demand. It is this instability in the price of agricultural products which a long range research program might hope to correct. A combination of the two industries might well be utilized

to advantage with the bulk of production being shifted from one to the other depending on the relative cost of the raw materials.

As part of the overall program the present investigation was undertaken to provide practical, economical processes for the production of furfuryl alcohol and 2-valerolactone. In addition some of the reactions of furfuryl alcohol and closely related compounds were investigated on an exploratory basis with the hope that grounds for additional study along these lines might be established. Such studies should eventually result in commercial outlets for the new compounds prepared.

II. MATERIALS AND SPECIAL APPARATUS

The furfural used for this investigation was a technical grade supplied through the courtesy of the Quaker Oats Company. In each case the product was distilled at reduced pressure in a nitrogen atmosphere, the first 10% and the last 20% of the material being discarded. Tetrahydrofurfuryl alcohol and furfuryl amine also supplied by the Quaker Oats Company were used without further purification.

Chemicals for the preparation of the copper chromite catalyst were reagent grade supplied by the General Chemical Company.

Raney nickel was prepared by a standard procedure from the powdered alloy.

Activated charcoal for the catalyst support was 4-10 mesh norite A (American Norite Company, Inc.) or nuchar (West Virginia Pulp and Paper Company).

Glass beads, also used as a catalyst support, were smooth Kimble Brand solid beads, 6 mm. size.

The apparatus used in the vapor phase hydrogenations is described in detail below and is shown in Figures 1 and 2. Liquid phase hydrogenations for the most part were made in a 500 ml. rocking bomb of standard design (Parr

Instrument Co.). A motor driven booster pump (American Instrument Co.) enabled one to use pressures higher than those encountered in commercial hydrogen cylinders. A 3.85 liter rocking bomb with a copper lining was used for the production runs in the 2-valerolactone studies. Standard practices were followed in the liquid phase hydrogenations. Some details are given in connection with the individual experiments for points not adequately covered by the above explanations.

Chemicals used in the reaction studies with the furan derivatives were either reagent grade or suitably purified technical materials.

Levulinic acid was obtained as a technical grade from Eastman Kodak Company. In some experiments it was found necessary to purify this material by distillation at reduced pressure.

Melting points were taken with the aid of a Fisher-Johns micro block. All values given are uncorrected.

III. PRODUCTION OF FURFURYL ALCOHOL

In the course of his studies on the production of 2-methylfuran, Holdren (1) noted that measurable quantities of furfuryl alcohol were formed after a given sample of catalyst had been in use for several days. However, the yield of both methylfuran and furfuryl alcohol then dropped off rapidly and the catalyst was rather quickly deactivated. The formation of furfuryl alcohol in this study may be explained by assuming that the catalyst at the top of the bed became completely deactivated by the high surface temperature resulting from the reaction. The effective bed length was thereby decreased. Undoubtedly this "burning out" of the top layer of catalyst was accompanied by a decrease in the activity of the rest of the catalyst down the tube with a consequent reduction in surface temperature of the catalyst film. Hence both the contact time and the reaction temperature were decreased with a resulting increase in the yield of furfuryl alcohol.

Since the procedure now used for the commercial production of furfuryl alcohol involves a batch process and the use of high pressure equipment, it was of interest to follow up this lead mentioned in Holdren's previous work. A research program was set up to provide a continuous

vapor phase process which could be operated at atmospheric pressure. Such a procedure would eliminate the need for expensive high pressure equipment, enable one to use low pressure hydrogen and require less rigid supervision than the liquid phase method. All these factors are important in determining the cost of producing furfuryl alcohol.

A. Historical

1. Vapor phase hydrogenation

A great number of workers have interested themselves in the hydrogenation of furfural. Careful study of the outstanding papers on the subject, however, shows that the problem was in many cases complicated by the variety of products obtained and also in some instances by incomplete conversion of the furfural. Much of the earlier work in these hydrogenation studies was patterned after the procedure of Sabatier (2) both as to the nature of the apparatus used and the preparation of the catalyst. This is of course understandable in the light of the enormous amount of work which this great pioneer contributed to the field of catalytic hydrogenation.

Padoa and Ponti (3) used a reduced nickel catalyst to obtain a product consisting principally of furfuryl alcohol and small quantities of more highly hydrogenated derivatives. The reaction temperature was about 190° C. At a reaction temperature of 270° C. the furfural vapor was converted to furan and carbon monoxide.

A patent issued to Ricard and Guinot (4) claims the use of a metallic copper catalyst supported on asbestos,

pumice, silica or the like to produce methylfuran and furfuryl alcohol. With a fresh catalyst at 140° C. these investigators state that methylfuran is formed to the extent of about 10 to 20% of the furfuryl alcohol yield. They separated the methylfuran by distillation, steam distilled the unreacted furfural and recycled in order to obtain complete conversion. A kilogram of copper was reported to retain its activity for several days of continuous operation. Excess hydrogen was recommended, and the yield of methylfuran increased with the temperature.

Furfuryl alcohol was the only reduction product isolated when furfural vapor and excess hydrogen were passed over a reduced nickel catalyst at 200° C. or over finely divided copper metal at 215° C. (5). The maximum yield of furfuryl alcohol (5%) was obtained with the nickel catalyst.

Lazier (6) has patented the use of a reduced nickel chromate catalyst for the vapor phase hydrogenation of furfural. The abstract of this patent does not mention the products obtained.

Tetrahydrofurfuryl alcohol has been prepared in yields ranging from 60 to 95% by the vapor phase reduction of furfural in the presence of a large excess of hydrogen and in the optional presence of an inert material (e. g. alcohol). The catalysts mentioned were Ni, Cr and Cu (7).

Small amounts of amyl alcohol and 1,5-pentanediol were identified as by-products of the reaction.

Lazier (8) has also patented a process for producing tetrahydrofurfuryl alcohol using a reduced copper chromate catalyst at 70 to 300° C. and several atmospheres pressure. The material was thought to be gaseous at the moment of reaction.

In a more recent patent (9) Rittmeister has disclosed a rather extensive study of a variety of catalysts including nickel, nickel-chrome, nickel-copper and copper-chrome with or without carrier. These catalysts were tested with furfural in the vapor phase at temperatures of 130 to 230° C. in the presence of 20 to 500 times the theoretical amount of hydrogen. Furfuryl alcohol, tetrahydrofurfuryl alcohol and pentanediols were the products obtained - the amounts of these three components varying with the catalyst and the temperature of the reaction. Note the large excess of hydrogen used to remove the heat of the reaction.

Copper chromite and related types of catalysts have been the subject of a series of patents claiming the hydrogenation of a number of organic compounds (10, 11, 12).

An I. G. Farbenindustrie patent (13) claims the production of a 79% yield of furfuryl alcohol from technical furfural using a metallic copper catalyst at atmospheric

pressure. Unreacted furfural was recovered in 3% yield and cyclopentane compounds made up 11.5% of the product. The presence of the cyclopentane fraction is undoubtedly due to impurities in the furfural as it is difficult to understand its formation from furfural. The report indicates that catalysts derived from other metals are soon deactivated under the conditions of the experiment.

2. Liquid phase hydrogenation

From the standpoint of yield of furfuryl alcohol obtained in the processes described in the literature the liquid phase procedures offer the best method of reducing furfural. This can be partially explained by the fact that surface temperatures are readily controlled in the liquid phase while such is not the case in the vapor phase, particularly when the reaction is carried out at elevated temperatures. Consequently, the vapor phase reduction generally proceeds beyond the furfuryl alcohol stage. The unsaturated ring may also be attacked under the more drastic conditions especially if a nickel catalyst is used. These factors contribute to the formation of a variety of products with a resulting decrease in the yield of furfuryl alcohol. The fact that furfuryl alcohol is now made commercially by a liquid phase high pressure process is further testimony to the fact that the vapor phase procedures

previously described have not been too satisfactory.

A rather large number of references are available for the liquid phase reduction of furfural to furfuryl alcohol. Mention will be made only of those investigations in which furfuryl alcohol was one of the principal products obtained.

Using a platinum oxide catalyst and stopping the reaction when one molecular equivalent of hydrogen had been absorbed, Kaufmann and Adams (14) were able to obtain almost quantitative yields of furfuryl alcohol. Further reduction saturated the ring and subsequent cleavage resulted.

A German patent (15) claims the production of high yields of tetrahydrofurfuryl alcohol with a supported nickel catalyst at 40 to 100 atmospheres of hydrogen pressure and temperatures of 100 to 150° C.

Furfuryl alcohol and 4-5% butyl alcohol (16) are listed as the principal products obtained by reduction with a nickel catalyst at 130 to 150° C. Further reduction of the furfuryl alcohol gives di- and tetrahydrofurfuryl alcohol and finally tetrahydrofuran, methyltetrahydrofuran and butyl alcohol (17).

One of the more practical procedures for making furfuryl alcohol in the liquid phase involves the use of a copper chromite catalyst. Connor and Adkins (18) report a quantitative conversion to furfuryl alcohol at 100

atmospheres of hydrogen pressure and a temperature of 150° C. A similar process has also been used as the basis for a small plant designed to produce furfuryl alcohol (19). The effect of decomposition temperature on the activity of the catalyst is pointed out in this article.

A comparison of several types of catalysts - including metals and metal oxides - showed that the Adkins chromite catalyst was the better of the group tested for the hydrogenation of furfural. The conditions for this study involved an initial hydrogen pressure of 100 atmospheres and a maximum reaction temperature of 200° C. (20).

Menzel (21) made a study of the comparative activity of a number of metal oxides for the catalysis of hydrogen absorption by furfural. Apparently no distinction was made between hydrogen which reacted with the aldehyde group and that which entered the furan nucleus. (However the nature of the catalyst used would indicate initial attack of the carbonyl group.) The greatest total amount of hydrogen was absorbed with a copper-chromium oxide catalyst prepared from the precipitated carbonates.

A copper catalyst supported on zinc oxide has been tested by Graves (22) for the reduction of furfural to furfuryl alcohol. Examples given in this patent indicate yields of furfuryl alcohol ranging from 53.5% to 70.5%

with 5% to 7.3% of the furfural being recovered unchanged. Furfuryl alcohol and 9.6% unchanged furfural were obtained when a nickel-cobalt alloy is used as a catalyst for the reduction of furfural at high pressure. The catalyst was activated by the customary procedure used for Raney nickel (23).

Recently a comparative study was made with a series of metals, metal alloys and metal oxides as catalysts for hydrogenation of the carbonyl group as well as the furan nucleus (24). For the hydrogenation of both functional groups nickel proved to be the best catalyst tested. Nickel-cobalt and nickel-iron alloys were also effective in the reduction to methylfuran and tetrahydromethylfuran. Copper chromite at high temperatures gave a mixture of glycols.

Lefrancois (25) has compared the effect of various promoters and stabilizers on a cuprous oxide catalyst used in the reduction of furfural to furfuryl alcohol. He reports that the mixture Cu_2O - Cr_2O_3 - C_aO was more active than copper chromite (Cf. Adkins) for the production of furfuryl alcohol. A recent patent claims the production of high yields of water white furfuryl alcohol using a cuprous oxide catalyst with activated alumina as a promoter (26).

Cobalt, chromium or molybdenum enhance the activity of Raney nickel for the hydrogenation of furfural according to

Paul (27). A concentration of 3 to 10% of the added metal was sufficient to produce a highly active catalyst.

In the light of the above survey it can be seen that a wide variety of catalysts and conditions have been tested for the hydrogenation of furfural. In general, the nickel catalysts may initiate reaction at the aldehyde group or in the ring - in the sequence given or simultaneously depending on the conditions of the experiment. The various copper catalysts are a little more selective in nature particularly if the reaction temperature is not too high. One could expect that a selective catalyst which would be effective at moderately low temperatures would be the ideal to strive for in the production of furfuryl alcohol.

In addition to the lack of selectivity pointed out above, nickel catalysts possess the disadvantage of being sensitive to atmospheric oxygen and trace amounts of impurities (e. g. mineral acids and their salts). Since copper chromite is easily prepared, stable in air and not readily poisoned and since a lead had already been obtained by Holdren's previous work, it seemed wise to explore all the possibilities of using this catalyst before attempting a general catalyst survey.

B. Experimental

1. Vapor phase hydrogenation of furfural

a. Description of the hydrogenation apparatus. The apparatus used was a modification of that described by Holdren (1). A sketch of the unit is shown in Figure 1 and an actual photograph in Figure 2. The numbers used in describing the apparatus in this section refer to the photograph in Figure 2. Furfural was added from the feed unit[1] to the vaporizer[2] where it was mixed with the hydrogen gas stream and led into the reactor tube.[3] This chamber, heated by a surrounding furnace, was 40 cm. in length and 31 mm. in outside diameter. A thermometer placed into the catalyst bed (prior to filling) indicated the average temperature. Two other thermometers showed the temperature of the heating jacket 10 cm. from either end of the furnace. From the reactor tube the product and excess hydrogen passed through the water cooled condenser[4] where most of the product was condensed. The gas stream continued through the dry ice-acetone trap[6] where the small amounts of methylfuran and water were removed. A small diaphragm pump,[9] using a pair of ground glass check valves,[7] was used to circulate the excess hydrogen. Rate

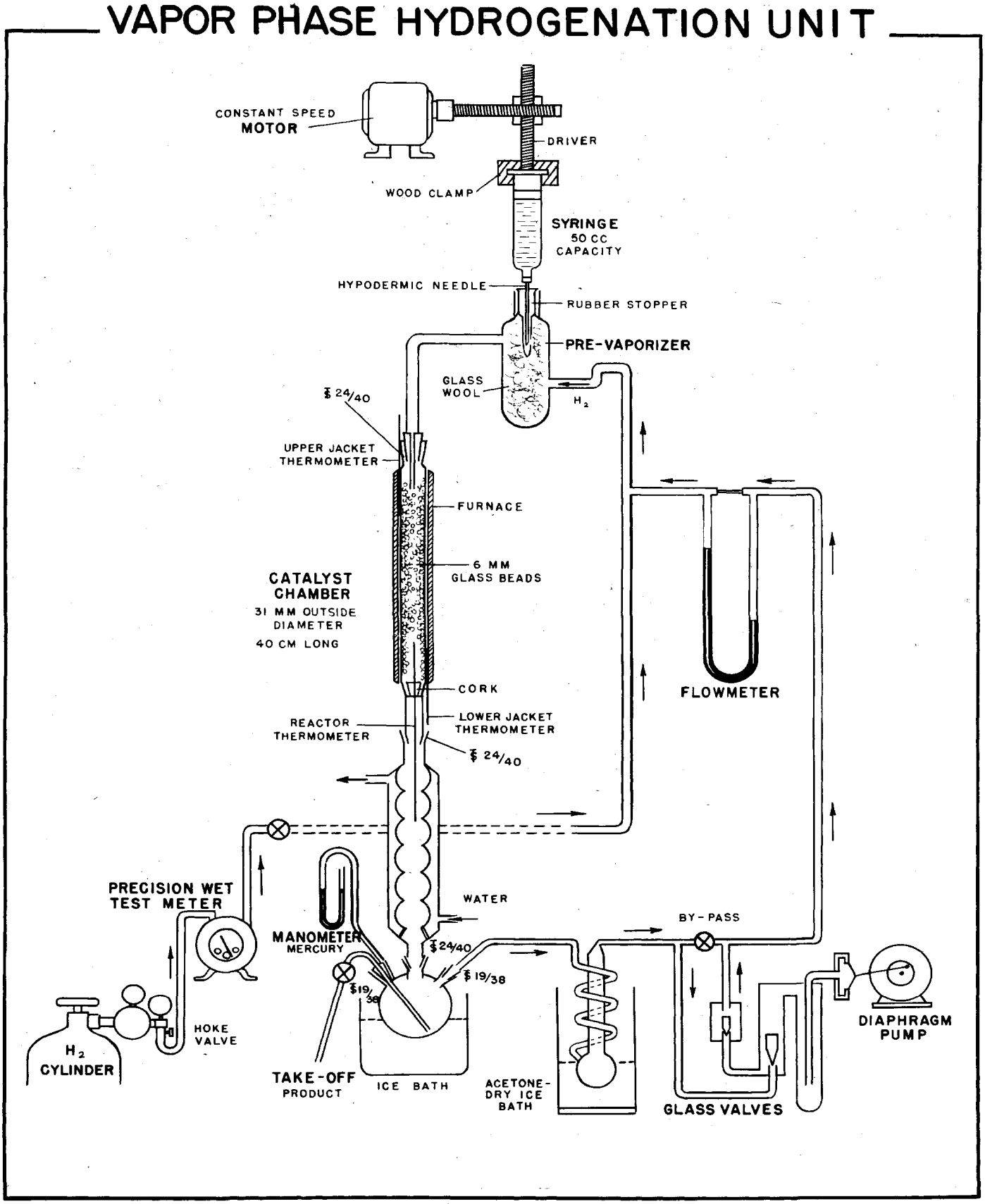


Figure 1.
Sketch of Laboratory Hydrogenation Unit

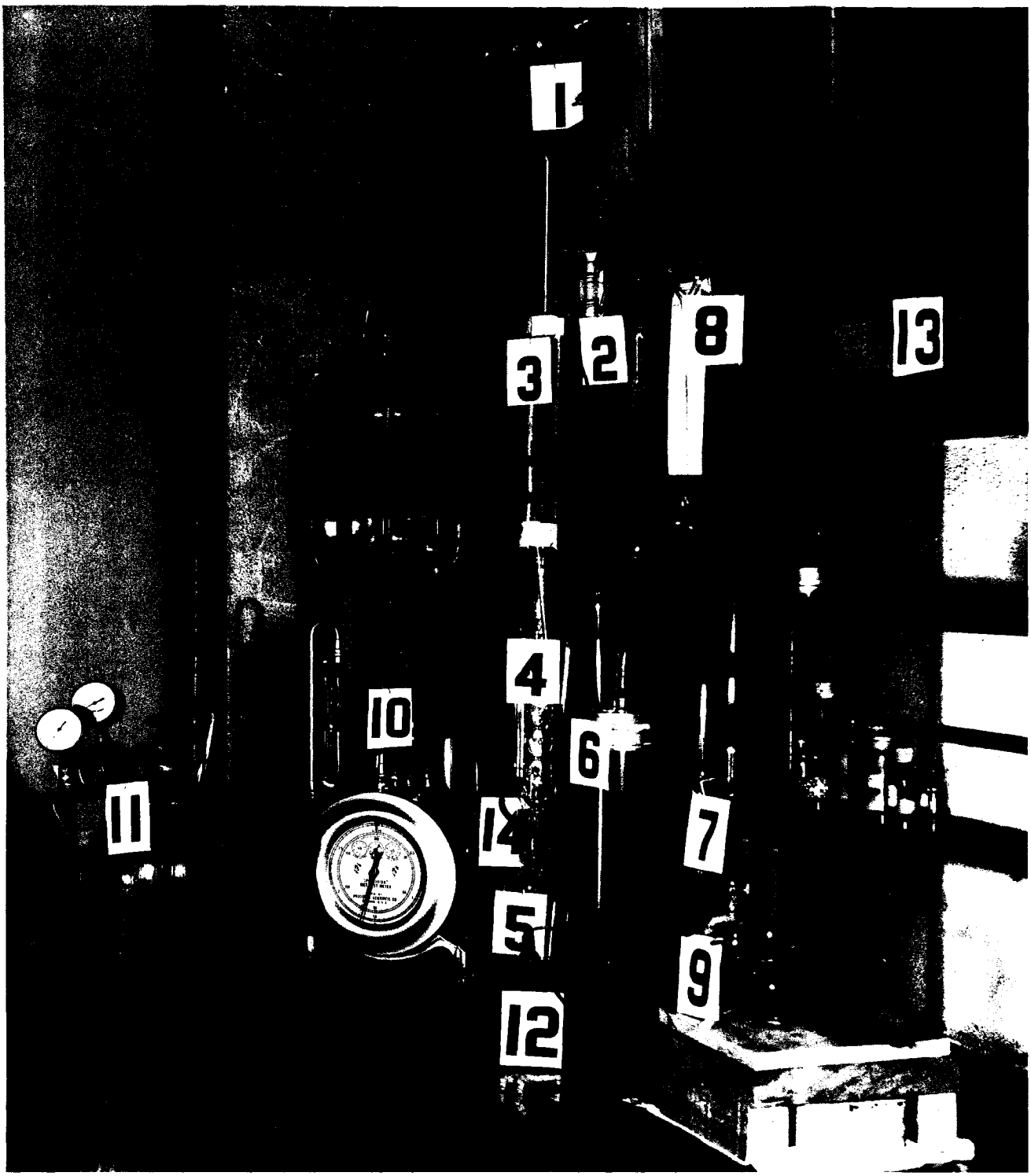


Figure 2. Laboratory Hydrogenation Unit.

of circulation was indicated by a capillary flow meter.[8] Hydrogen consumption could be determined by the difference in readings taken from the meter[10] which connected to the hydrogen supply through a Hoke valve.[11] A by-pass valve[7] enabled one to change the rate of gas circulation with a fixed length of stroke by the pump.

The feed unit[1] was constructed from a synchronous motor which through a series of changeable gears drove the ground-glass plunger of a 50 ml. "B-D Yale-Lok" syringe (Becton, Dickinson & Co.) downward at a constant rate. Changing the gear ratio gave a series of constant feed rates which could be varied at will.

The vaporizer[2] was constructed from a piece of pyrex tubing 31 mm. in outside diameter. Nichrome resistance wire was used to heat the central portion of the tube. Prior to sealing off the lower end of the furnace the portion to be heated was packed with glass wool. A hydrogen inlet near the bottom of the glass wool allowed the gas to be pre-heated before contacting the furfural which dripped onto the upper surface of the wool. A 2 cm. section at the bottom of the tube was left empty and uncovered in order to be able to detect the presence of any furfural which was not swept out by the hot gas stream. For a feed rate of 23.1 grams per hour it was found that a temperature of 140-150° C. in the upper part of the glass wool was

sufficient to completely vaporize the furfural as it entered. A 3 cm. section of 8 mm. pyrex tubing was sealed to the upper portion of the vaporizer. A hole was blown into the side of this tube (prior to the making of the ring seal) and the lower end was sealed off and pulled out to give a small rod-like projection which touched the upper surface of the glass wool. The hypodermic needle was led into this small tube through a rubber stopple and the tip of the needle extended into the small pool of furfural. This prevented the formation of gas bubbles in the needle (from the pump strokes). As the furfural overflowed down the tiny rod it was spread onto the large surface area of the glass wool and immediately vaporized. An exit tube near the top of the furnace carried the mixed vapors of hydrogen and furfural into the catalyst tube.

Alternate but less satisfactory modifications of the unit shown in Figure 1 involved: (1) the use of a dropping funnel to introduce the furfural directly onto a 10 cm. layer of glass beads at the top of the catalyst bed (or directly onto the catalyst when glass beads were the carrier used); (2) the use of two 20 liter bottles to introduce the hydrogen by water displacement. It should be noted in passing that introduction of the furfural directly into the catalyst bed without preheating offers an advantage in that the vapor-liquid equilibria gives a cooling effect

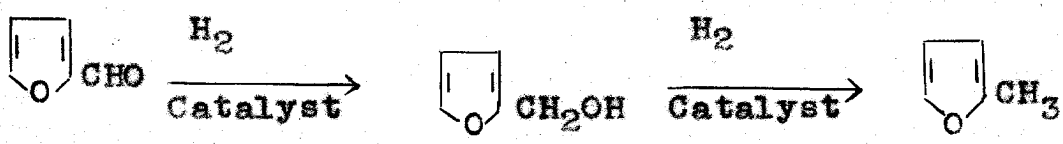
near the top of the bed. It is here that deactivation of the catalyst by high surface temperatures is most likely to occur.

b. Preparation of the catalyst. As indicated above it was desirable in this study to obtain a very active catalyst so that the reaction could be carried out at the lowest possible temperature. Since the catalyst prepared by Holdren appeared to be quite active at the beginning of each run it seemed advisable to start out with his general procedure and then introduce any modifications that might become necessary. From previous work (28) it was known that the use of calcium as a stabilizer, precipitation of the complex chromates from a neutral solution and decomposition at a controlled temperature (19) all tend to enhance the activity of a chromite catalyst. Hence particular attention was paid to these points in the preparation.

A large batch of catalyst which was used for many of the experiments to be described below was prepared in the following manner. A solution of 522 g. of $Cu(NO_3)_2$ $3H_2O$ and 62 g. of $Ca(NO_3)_2$ $4H_2O$ in a total volume of 1800 ml. of aqueous media was heated to 80° C. and added with stirring to an equal volume of solution containing 302 g. of $(NH_4)_2 Cr_2 O_7$ and 400 ml. of concentrated

ammonia. (A test with the ammonia at hand showed this to be the volume necessary to leave the mother liquor at a pH of 7- as indicated by test with Hydrion paper). The complex chromates were filtered off and dried at about 75° C. for 24 hours. The material was then pulverized and decomposed in a rotary kiln, previously described by Holdren (1). Decomposition temperature was read from a thermometer the bulb of which was placed in the catalyst at the point in the kiln where maximum decomposition occurred (about 10 cm. from the upper end of the kiln). For maximum activity of the catalyst the temperature as read in this manner should not rise above 350° C. and is preferably kept as near to 300° C. as is possible and still allow for decomposition of most of the chromate in one pass. After one pass through the kiln the brown powder was placed in a porcelain crucible in 50 gram portions and heated in an air bath until the temperature in the powder rose to 190-200° C. Leaching with 1200 ml. of 10% acetic acid, washing thoroughly with water and drying at ca. 105° C. completed the preparation of the catalyst. When dry the catalyst was thoroughly pulverized with the aid of a mortar and pestle (this step is quite important when the glass beads are used as a carrier). The yield of dry catalyst was 288 grams.

c. Testing of the catalyst activity. The hydrogenation of the aldehyde group in furfural proceeds in two steps which is normal for the reduction of aldehydes in general:



Each of these reactions is highly exothermic and this fact combined with the elevated temperatures employed in much of the earlier work resulted in the formation of considerable quantities of methylfuran. In the early part of this investigation it was essential to have some means of estimating the activity of a given catalyst for the reduction of furfural. The production of high yields of methylfuran under the conditions described by Holdren (1) was taken as the best measure available. It was then reasoned that with high catalyst activity the operating conditions could be made less drastic (low temperature and shorter contact time) and the reaction stopped at the furfuryl alcohol stage.

Several small batches of catalyst were prepared from the procedure given above. These all gave good yields of methylfuran at a temperature of 230-250° C. with a contact time greater than one second and a hydrogen to furfural ratio greater than 25 to 1. Then the large batch of

material described above was prepared and tested for methylfuran production.

In the first test with this sample of catalyst a 30 cm. bed of the charcoal supported chromite (ratio of catalyst to carrier 1.5/1) was covered with a 5 cm. layer of glass beads. The measured void space was 103 cc. (62% of the bed volume). Two runs were made with this packing and each time the water layer smelled strongly of amyl alcohols. The addition of furfural to the fresh catalyst caused a 40° C. rise in the center of the bed. These facts and the fair yields of methylfuran obtained were indicative of the desired activity. Table 1, Columns 1 and 2, summarizes the results of these two tests.

After the above experiments were completed the reaction tube was emptied and refilled with fresh catalyst

Table 1

Catalyst Activity as Evidenced by Methylfuran Production

Furfural added gms.	Feed Rate g./hr.	Contact time in sec.	H_2/furfural ratio	Catalyst temp. (center of bed) ° C.	% Yield Methyl-furan
1-50	10	10	11/1	230-40	70.5
2-39	11.2	1.7	76/1	220	77.2
3-23	5.8	0.97	111/1	180-5	82.8

to a depth of 15 cm. (52.4% voids) and covered with a 10 cm. layer of glass beads. A 23 gram sample of furfural was hydrogenated to give the results in Table 1.

d. Analysis of reaction products. Since the ultimate aim of this investigation was to develop a process which would be suitable for adaptation to commercial production of furfuryl alcohol a practical method of control and assay was needed. Early in the study it was decided that the proper goal to strive for was complete conversion of the furfural - with the production of small quantities of methylfuran if necessary. A glance at the physical properties of furfural, furfuryl alcohol and methylfuran immediately shows the wisdom of this choice. The boiling point of furfural is 161.7° C. while furfuryl alcohol boils at 170.2° C. Methylfuran, of course, is a much lower boiling product (63° C.). Hence if complete conversion is obtained the small amount of methylfuran can easily be separated, and the residue can be sold as a technical product without a distillation. If the separation of furfural from furfuryl alcohol by distillation becomes necessary an efficient column is needed (29). Presumably small quantities of furfural could be "blown off" with steam but this heating would be expected to result in

some darkening of the alcohol and would also involve a drying process to remove the excess water.

The above discussion emphasizes the need for a method of assay for small quantities of furfural. A number of procedures have been worked out: (1) electrometric titration of an aqueous solution with bromine in presence of HCl and $HgCl_2$ (30); (2) measurement of the refractive index of a distilled mixture of furfural and furfuryl alcohol (29); (3) reaction with excess bisulfite and back titration with a standard iodine solution (31); and (4) reaction with aniline, etc. to mention a few of the more reliable methods. Two of these procedures were combined for this study. In all of the 50 g. runs the ultimate analysis was accomplished by distillation of the furfural-furfuryl alcohol fraction in a nitrogen atmosphere at reduced pressure and measurement of the refractive index with an Abbe refratometer. The percent furfural could then be read directly from a graph (29). This procedure gives a low recovery due to mechanical loss but is relatively accurate and has the advantage of giving a practical "in hand" value.

In the large runs (e.g. No. 4 in series F, and No. 14 in series F-109-161) weighed aliquots were periodically removed for bisulfite iodine titration since this procedure has

the advantage of being faster. The combined fractions were later distilled and corrected for the aliquots removed for titration.

Mechanical losses are greatest in the first run of a given series of experiments. The apparatus was cleaned and dried before the beginning of each series and since the product was removed simply by siphoning off from the trap there was a considerable loss here (estimated by washing the condenser and traps with a solvent to be 2-3 grams maximum). In the subsequent runs of a given series the loss due to hold up in the apparatus becomes much smaller. A relatively constant loss is encountered in all the runs in the distillation. From 15 distillations picked at random the average weight of residue left in the distillation flask was 2.1 grams. An additional gram (estimated) would be held up in the Vigreux column and the condenser. For a fifty gram sample of furfural this represents a mechanical loss of furfuryl alcohol of 6.2%.

In order to compare the two methods of furfural assay, three samples were picked covering a wide range of furfural content. After distillation the refractive index was read and the furfural content taken from the graph mentioned above. The three samples were then sent to the Chicago Laboratory of The Quaker Oats Company and bisulfite-iodine titrations were made. The results obtained are compared

below in Table 2.

Table 2

Analysis of Furfural-Furfuryl Alcohol Mixtures

Sample	% Furfural as shown by: Refractive Index	Bisulfite-iodine Titration
Series E No. 2	0.0	0.40
Series E No. 3	5.2	5.26
Series C No. 3	29.0	28.51

These values and others obtained in this laboratory show that the bisulfite-iodine titration tends to give slightly higher results for furfural content than the refractive index measurement. This is particularly true when the furfural content is low (2% or less).

The methylfuran fraction obtained in these studies was separated by distillation of the wet material through a Claisen head. Thus the results reported for this constituent will also be somewhat low due to mechanical loss in the distillation. In the course of duplicating this work in the Quaker Oats Research Laboratory it was noted that methylfuran recovery from a dry synthetic mixture of furfural, furfuryl alcohol and methylfuran is quite low*.

*Private communication with Mr. Samuel Swadesh, Quaker Oats Research Laboratory, Chicago 16, Illinois.

(It should be noted in passing that all the samples in this investigation were distilled wet - 2-3 g. of H_2O per 50 g. sample). Due to the high intersolubility and the wide difference in boiling points the presence of some intermediate material is apparently needed.

In addition to the measurement of physical constants the furfuryl alcohol was further identified by conversion to the solid α-napthylurethan by a standard procedure (32). Recrystallization from alcohol gave a derivative melting at 129° C. The previously reported value is 133° C. (33).

e. Detailed description of a sample experiment. A complete experiment in the vapor phase hydrogenation of furfural will now be described (Run No. 4 in Series N). The catalyst tube had previously been packed in the following manner. A volume of glass beads (Kimble glass, 6 mm.) sufficient to fill the catalyst tube to a depth of about 37 cm. was boiled in a nitric-sulfuric acid mixture and thoroughly rinsed in distilled water. The wet beads were then spread out in a single layer in a large evaporating dish. As the catalyst was sprinkled over the beads in small amounts the beads were mixed with a spatula. This was continued with the occasional addition of small amounts of water (as necessary) until all of the desired catalyst

(30 g. in this experiment) had been added. At the end of this procedure the catalyst should contain just sufficient water to hold it to the beads - an excess results in loss of catalyst. The material was then transferred to the reaction tube which contained the catalyst thermometer, supported by a notched cork to allow gas passage. Drying of the catalyst in a hydrogen atmosphere gives a catalyst preparation ready for use. The system was then placed under about 1.5 cm. of hydrogen pressure as indicated by the mercury manometer; the circulation pump was started and dial settings were made on the several variacs to give the approximate temperature readings desired (about 100° C. in the catalyst bed and 140° C. in the top section of the vaporizer for this experiment).

A 50 gram sample (0.521 mole) of freshly distilled furfural was placed in the syringe and then all joints were paraffined to make the system gas-tight. Gear ratios from the 10 r.p.m. synchronous motor were set to deliver 23.1 g. of furfural per hour to the vaporizer. The traps were cooled with their respective media (ice for the furfuryl alcohol trap and dry ice-acetone for the methylfuran trap). When equilibrium had been established in the circulating gas stream readings were taken on the several thermometers, flowmeter, gasometer, etc. and the motor on

the feed unit was started. Table 3 shows the various readings taken during the course of the experiment. Furnace temperatures were taken from thermometers with tips 10 cm. from the top and bottom of the jacket, and the thermometer in the catalyst bed was 15 cm. from the bottom of the 38 cm. bed of catalyst. Hydrogen circulation during the course of the experiment was maintained at 3500 cc. per minute.

Table 3

Operation Data for Sample Experiment in the Vapor Phase Hydrogenation of Furfural

Time	Furnace T. °C. Top	Furnace T. °C. Bottom	Catalyst T. °C.	Furfural level in Syringe cc.	Hydrogen meter readings in liters
3:48	98	97	99	44	13.75
3:55	102	101	109	41	14.55
4:15	100	101	115	35	16.2
4:35	96	96	112	28	18.3
4:50	97	98	111	24	19.8
5:15	100	100	113	15	22.2
5:35	100	101	115	8	24.3
6:02	-	-	-	0	26.75
6:20	-	-	-	-	26.85

The traps were emptied at the close of the experiment and 53 g. of material was obtained (a little water is carried over from the meter). Distillation of the product was started through a 42 cm. Vigreux column* at atmospheric pressure. No fraction was obtained boiling below 65° C. (hence no measureable quantity of methylfuran was produced). The remainder of the distillation was made at reduced pressure in a nitrogen atmosphere. At a pressure of 23 mm. a product fraction b.p. 77-81° C. was obtained weighing 47.8 g. Five readings on an Abbe refractometer gave an average N_D^{20} 1.4881 equivalent to a furfural content of 2.5% (29). A residue of 1.4 g. was left in the distilling flask and a fore-run of almost 2 cc. (water) was obtained. These data lead to the following yields, calculated as "in hand":

Methylfuran - - - -	Negligible
Unreacted furfural -	2.4%
Furfuryl alcohol - -	91.4%

At the end of the series of experiments 94 cc. of water was required to fill the void space in the catalyst bed. For a circulation rate of 3500 cc/m. this gives a contact time of

$$94 \text{ cc} \times 60 \text{ sec/min} \times \frac{1}{3500 \text{ cc/min.}} = 1.6 \text{ sec.}$$

*Since the volume of hydrogen absorbed indicated that little or no methylfuran could have been formed the usual distillation through the Claisen head was not attempted.

for the experiment described above.

Assuming an average temperature of 25° C. and a barometric pressure of 720 mm. (corrected for aqueous tension) the moles of hydrogen circulating per hour may be found from:

$$3500 \text{ cc/m} \times 60 \text{ m/hr} \times \frac{273^\circ \text{ A}}{298^\circ \text{ A}} \times \frac{720 \text{ mm.}}{760 \text{ mm.}} \times \frac{1}{22{,}400 \text{ cc/mole}} =$$

8.15 moles H_2 per hour.

This value divided by the furfural feed rate gives the mole ratio:

$$\frac{8.15}{0.241} = \frac{33.6}{1}$$

f. Summary of vapor phase hydrogenation runs. In the pages that follow a description will be given of the various experiments carried out in an effort to find the optimum conditions for the continuous vapor phase hydrogenation of furfural to furfuryl alcohol. The individual experiments are listed as part of a series, those experiments in a given series having all been made with a given catalyst packing in the sequence listed in the table for that series.

Series A through E were made using charcoal as the carrier with a constant ratio of catalyst to carrier (1.5/1) in all the fillings. In this group (A-E) the furfural was added to the reaction chamber from a dropping funnel and the

hydrogen was measured into the unit from a 20 liter bottle. In series F glass beads were used as the carrier - this being the only change in the set up from that used in A-E. Beginning with Series G and throughout the rest of the investigation the unit shown in Figure 1 was employed.

In none of the experiments did the catalyst ever become completely inactivated. Fresh catalyst was used for each series merely to give a better comparison in the studies on bed length, contact time, gas to feed ratio, etc. Using a fresh sample of catalyst for the individual series serves to eliminate any doubt due to possible deactivation.

Unless otherwise indicated all of the experiments were made with a 50 gram (0.521 mole) sample of freshly distilled furfural.

Series A. A sample of charcoal supported catalyst was prepared from 10.5 grams of Cu-Ca-Cr catalyst and 7.5 g. of charcoal. The 11 cm. bed had a void space of 40 cc. In the packing of this tube the thermometer tip was placed just slightly above the center of the bed. Addition of furfural to the fresh catalyst gave a 50° temperature surge in the center of the bed. This initial temperature rise amounted to only 20° in the second experiment and 10° in the third. The decrease may be accounted for either by the lower feed rate or by deactivation of the catalyst.

Table 4 gives the pertinent data for this series of runs.

Series B. A catalyst bed of 7.5 cm. length was prepared from 5 g. of charcoal and 7.5 g. of the Cu-Ca-Cr catalyst. A 10 cm. layer of glass beads was used to preheat the furfural. Void space in the bed amounted to 28.5 cc. The thermometer tip for this series was placed in the center of the bed. In the first experiment a 45° C. temperature surge was observed. To keep the temperature down to the level desired in this series low feed rates and high rates of gas flow were essential. Toward the end of the series the feed rate could be increased indicating a slight decrease in catalyst activity. Table 4 contains the pertinent data for the four experiments with this packing.

Series C. A catalyst sample prepared in the usual fashion was placed in the catalyst tube to a depth of 5.5 cm. (void space 16 cc. - 53%). Upon the initial addition of furfural a 40° rise in temperature was noted. By decreasing the contact time and lowering the temperature this series of experiments shows that the methylfuran production could be cut down to permissable values but a considerable quantity of furfural then passes through unchanged as the summary in Table 4 indicates.

In connection with the data in Table 4 there are several indications that are brought out by the results obtained with these scouting experiments. The temperature surge which came as the result of the addition of furfural at the beginning of an experiment was found to decrease in going down the series. This is very probably due to a decrease in activity of the catalyst caused by the high surface temperatures (a 40° C. surge within a 5 cm. bed of catalyst which is being "washed" with 4 liters of gas per minute must represent a phenomenal increase in temperature on the catalyst film). One should also note that although the contact time is quite short and the hydrogen to furfural ratio is high (for cooling effect) the yields of methylfuran are still appreciable in the temperature range 150-175° C. Although shortening of the bed length (in series B and C) decreases the yield of methylfuran it results in incomplete conversion of the furfural. Hence in the light of these points one must conclude that the relationship between feed rate, contact time, hydrogen to furfural ratio and bed length is quite complex at this range of temperature. Although by studying each of these variables independently of the others one might eventually hope to find a set of conditions which would selectively produce high yields of furfuryl alcohol the yields of

Table 4

Series A, B and C
Vapor phase Hydrogenation of Furfural

	Feed Rate g/hr.	Contact time in sec.	H_2 to furfural ratio	Temp. of Catalyst bed (center) °C.	Furfural Furfuryl Alc. mixture N_D^{20}	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl-furan	Furfuryl Alcohol
A.								
1	30	0.56	32.3/1	175±5	1.4864	0.0	49.8	25.5
2	25	0.56	38.8/1	190±2	1.4880	0.8	53.9	26.6
3	20	0.85	32.4/1	169-72	1.4906	6.4	Negligible	72.0
4	18.8	0.86	33.8/1	170-3	1.4930	9.2	9.4*	59.4
5	16.7	0.85	38.2/1	169-73	1.4920	6.5	25.8	53.2
B.								
1	10-15	0.61	42.5/1	165-75	1.4863	0	24.6	49.9
2	12.5	0.61	51/1	168-70	1.4878	1	12.9	65.6
3	14.3	0.42	65.4/1	168-72	1.4911	6.4	11.7	62.4
4	14	0.56	70/1	165-70	1.4950	12.4	8.8	59.7
C.								
1	9.1	0.22	107.5/1	160-2	1.4873	0.5	14	66.5
2	10.8	0.22	91/1	157-62	1.4961	16.8	7.3	66.7
3	8.4	0.44	61/1	155-61	1.5002	25.0	4.7	59.6
4	13.4	0.22	73.4/1	169-72	1.5011	28.0	9.4	58.0
5	13.3	0.22	73.5/1	178-84	1.4977	16.9	6.4	53.8

*Part of methylfuran sample lost in distillation.

methylfuran are still high at 155-160° C. Hence, the obvious inference is to lower the temperature and hope that the other factors will cease to be so critical. Note that this lowering of the temperature means decreasing the furfural content of the gas stream (if only one phase is maintained). However, since the hydrogen is recirculated this does not materially influence the economics of the process.

Series D. With the above thoughts in mind the catalyst bed was repacked with fresh catalyst to be tested at temperatures considerably below the boiling point of furfural. From a 22.5 gram sample of Cu-Ca-Cr catalyst and 15 grams of charcoal support a catalyst bed of 20 cm. depth was obtained (67% voids). As usual a 10 cm. layer of beads was placed on top of the catalyst. Since it was decided to test the activity at 135-140° C. equilibrium was established with the jacket temperature at this value. However, the addition of furfural at a feed rate of about 12 g/hr. caused a 20° temperature rise in the center of the bed.

In these and other similar experiments with the charcoal carrier below the boiling point of furfural it was noted that as much as 2-5 minutes elapsed between the time when furfural was dropped onto the glass beads (about the same temperature as the catalyst bed) and the

appearance of condensate on the walls of the condenser below the reaction tube. This indicated the need for a pre-vaporizer furnace and in conjunction with other data also showed that the contact time calculated on the basis of the vapor phase alone was not very reliable. Supposedly liquid furfural or liquid furfuryl alcohol was trapped within the pores of the charcoal and held there for considerable lengths of time, thereby resulting in the formation of more methylfuran than would otherwise be anticipated.

In run number 4 in this series about 0.5 gram of the catalyst was washed off into the product. This material was not filtered off prior to distillation. The catalyst (or some other material) caused considerable decomposition of the furfural-furfuryl alcohol fraction. When it became evident that the material was polymerizing the distillation was stopped. The 15 gram residue was a black viscous oil. Removal of the catalyst prior to distillation in later runs eliminated this difficulty.

It should be noted that lowering the reaction temperature to about 125° C. makes it possible to increase the contact time several fold and still obtain only relatively low yields of methylfuran (compare runs 3 and 5 in this series with Series C.).

Table 5 gives the remainder of the data needed to

Table 5

Series D and E

Vapor phase Hydrogenation of Furfural

	Feed Rate g/hr.	Contact time in sec.	H_2 to furfural ratio	Temp. of Catalyst bed (center) °C.	Furfural furfuryl alc. mixture N^{20}_D	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl-furan	Furfuryl Alcohol
D.								
1	11.75	1.12	82.5/1	136-53	1.4860	0	27.9	52.9
2	9.3	1.12	105/1	137-43	1.4865	0	11.5	82.6
3	10.0	1.69	64/1	128-31	1.4885	2.5	3.8	77.8
4*	9.4	1.12	105/1	126-34	1.4995	17.3	1.2	45.8
5	8	1.12	121/1	136-44	1.4895	4.4	1.2	83.0
E.								
1	8.6	1.54	113/1	122-31	1.4871	0.5	11.8	68.2
2	12.8	1.54	76/1	118-26	1.4868	0	9.2	88.2
3	13.6	1.54	71/1	112-15	1.4891	4.8	0.5	86.4
4	21.5	1.54	45/1	116-28	1.4919	10.4	0.5	82.0
5	16.7	1.54	58/1	126-31	1.4900	8.0	0.4	82.4

* See note above.

complete this series.

Series E. For this series of experiments a catalyst bed of 25 cm. was used with the customary layer of glass beads. The thermometer tip for recording the catalyst temperature was placed in the center of the bed. At the temperature selected for these runs the feed rate could be stepped up to 20 g/hr., without too great a temperature surge. However the data show that such a feed rate was too high for this bed length. (Probably some liquid furfural was flowing through the catalyst bed and acting as a "buffer" or coolant). In this connection note the data for runs 4 and 5. Run number 2 in this series was the first experiment to approach the goal set up at the beginning of the study - i.e. complete conversion of the furfural with yield of methylfuran not in excess of 10%.

See Table 5 for the data obtained from the five experiments with this sample of catalyst.

Effect of the catalyst carrier on furfuryl alcohol production. At this stage of the investigation considerable thought was given to the catalyst carrier. In addition to the matter of "hold up" within the pores of the charcoal mentioned above, the high rates of feed and hydrogen circulation (needed to cool the catalyst surface) began to remove measurable quantities of the chromite catalyst from the charcoal support. Since the results

were beginning to show promise the life of the catalyst and possible regeneration or recovery began to be of interest. Hence it was thought that the use of an impervious carrier might enable one to allow the catalyst to wash through, filter off the catalyst from the product, wash to remove adsorbed furfuryl alcohol and feed the catalyst back into the top of the bed - either as a suspension in the feed or as the dry material from a worm feed unit. A solid catalyst support would not introduce possible catalyst poisons or impurities and would permit flushing off the catalyst at will with a jet of water or methylfuran. If chosen with the proper care it would also afford better heat conduction than the charcoal and thus assist in the cooling of the catalyst surface. Glass helices, Rashig rings or glass beads were all considered as materials for use. A preliminary test was made with smooth 6 mm. Kimble glass beads, and it was found that by avoiding excess moisture the catalyst could be made to stick to the wet beads. Transfer of the heavy paste to the catalyst tube and subsequent drying gave an encrustation which adhered remarkably well so long as the tube was not shaken or flooded with liquid. As might be expected the particle size of the catalyst influences its adhesive properties.

The remainder of the experiments described below all

utilized the Kimble glass beads as a carrier. The data indicate that all of the proposed advantages mentioned above are gained thereby.

Series F. A 30 gram sample of the calcium stabalized copper-chromite catalyst was sprinkled over a sufficient volume of wet beads to give a catalyst bed 34.5 cm. deep. The thermometer tip was placed 10 cm. from the bottom of the bed. In this series the furfural feed was dropped directly onto the upper portion of the catalyst - no layer of glass beads was present to act as a preheater. The first 3 runs were made with 50 gram samples of furfural and the results shown in Table 6 are more or less self explanatory. Run No. 4 was made with a 400 gram sample of furfural over a continuous 24.25 hour period. The first 300 grams of material was almost quantitatively converted to furfuryl alcohol. Emptying the traps after this portion of the run was completed gave 291.5 grams of product (some hold up in system since machine was not stopped). Distillation gave 283 g. of furfuryl alcohol $b.p._{26}$ 78-84° C., N^{20}_{D} 1.4871. During the hydrogenation of the last 100 grams of furfural the feed rate increased to about 20 g/hr. (due to leakage around the stopcock), and the temperature was thereby lowered to 124° C. instead of the desired 130-4° C. Hence some furfural

passed through unchanged. The values shown in Table 6 are the average for the entire run.

Experiment No. 5 in the series shows that the catalyst was still active at a temperature considerably below the boiling point of furfural.

The rate of hydrogen circulation was the same for all of these experiments (about 4250 cc. per minute). With a void space of 94 cc. (measured at the end of the series) this gives a calculated contact time for the vapor of 1.32 seconds. However since the upper portion of the bed was actually used to vaporize the furfural the calculated value can be used only as a maximum for the vapor.

When the bed was filled with water to determine the voids it was noted that the catalyst surface was coated with a film of material not wet with water. This is undoubtedly a decomposition product or a polymer from furfural or furfuryl alcohol. Should this film become sufficiently thick to inactivate the catalyst washing with methylfuran or other solvent might become necessary.

Table 6 gives the data pertinent to this series of runs.

Use of pre-vaporizer unit. At this point in the investigation the apparatus was completely rebuilt to eliminate some of the mechanical difficulties that had been encountered in the previous studies. The catalyst tube

Table 6

Series F

Vapor phase Hydrogenation of Furfural

	Feed Rate g/hr.	Contact time in sec.*	H_2 to furfural ratio	Cat. Temp. (10 cm. from bottom of bed) ° C.	Furfural furfuryl alc. mixture N_D^{20}	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl-furan	Furfuryl Alcohol
1	15	1.32	64.8/1	124-7	1.4861	0	Negligible	89.2
2	15.4	1.32	63/1	122-30	1.4865	0	Ca.1	92.2
3	20	1.32	48.6/1	136-9	1.4869	Negligible	Negligible	87.2
4	16.5	1.32	58.8/1	124-34	*	2.4	0.4	94.6
5	12.5	1.32	77.7/1	142-6	1.4860	0	8.6	80.2

*See note above.

and furnace were lengthened to 40 cm., the small vaporizer unit was added and a "Precision" wet test meter was obtained to meter the hydrogen directly from a Hoke valve on the supply tank. The automatic feed unit was also installed. These changes gave the unit sketched in Figure 1 and this apparatus was employed throughout the remainder of the work.

Series G. The catalyst sample of 32 grams was supported on a volume of glass beads sufficient to give a bed depth of 39 cm. Two fifty gram portions of furfural were hydrogenated in the unit to "get the feel" of the apparatus. Hydrogen circulation was started at 4200 cc/min. with a feed rate of about 12 g/hr. Since the temperature was varied over a rather wide range and other variables were not held at a constant value the product from these two runs was not distilled. However, in each case more than the theoretical amount of hydrogen was absorbed.

In the course of these and later experiments it became evident that feed rates could be stepped up without appreciable temperature surges, and that so long as the temperature was kept down to 120-135° C. such variables as contact time and hydrogen to furfural ratio were not too critical.

Series F-109-161. At this point in the study thought was being given in the Chicago Laboratories of The Quaker Oats Company to the possible utilization of this process for commercial production of furfuryl alcohol. It was decided to build a larger unit there utilizing a metal reactor tube as the first step in the transfer to pilot plant operation. Since the validity of the test in metal as compared to glass involved the necessity for working with a catalyst of known activity and since it was of interest to the Ames Laboratory to know how easily the catalyst preparation could be duplicated, it was agreed that a catalyst sample would be prepared by the Chicago group and then tested in the Ames apparatus.

This series of experiments was made with Quaker Oats Laboratory catalyst sample F-109-161. A 30 gram portion of the material was suspended on a volume of 6 mm. glass beads sufficient to give a bed depth of 39 cm. in the reactor tube (31 mm. outside diameter). It should be noted that this length of catalyst bed represents a substantial increase over that used in the earlier experiments. Also the use of the vaporizer adds to the effective length since the top portion of the bed is not cooled by the vaporization of the furfural.

Several preliminary experiments with this catalyst

indicated it to be comparable in activity to the Ames catalyst. Hence it was used for a number of experiments to determine the optimum conditions for the production of high yields of furfuryl alcohol. Two large runs were also made to get an estimate of the catalyst life (Nos. 9 and 14). A total of 2050 grams of furfural was hydrogenated over this 30 gram sample of catalyst for a conversion ratio of 68 to 1. Experiment 14 (b) shows that the catalyst was still quite active at a temperature at least 10° C. below the boiling point of furfural (as evidenced by the complete hydrogenation of the furfural and the production of a considerable quantity of methylfuran).

Table 7 shows the summarized data for this series of experiments. The runs were all made in the sequence listed. Runs 1 to 5 inclusive are adequately described by the results in the table.

In experiments 6, 7 and 8, an attempt was made to determine the effect of contact time and hydrogen to furfural ratio on the temperature needed to completely hydrogenerate the aldehyde group to the alcohol. The hydrogen circulation was cut down so that the furfural feed entered the catalyst tube as a saturated vapor. During part of the time the top layer of catalyst (about 0.5 cm.) was

actually wet with furfural. Condensation occurred to some extent at the cork at the bottom of the bed indicating saturation of the exit gas stream. Note the unusually low temperature used in experiment 8.

Run No. 9 in this series was made over a continuous 35 hour period. The reaction was started with a catalyst temperature of 120° C. During the addition of the first 200 grams of furfural the temperature was gradually raised to about 128° C. since the theoretical amount of hydrogen was not being absorbed. As judged by hydrogen up-take, the reaction was apparently going to completion in the range 128-132° C. When the distillation was made, however, it was learned that this middle fraction, about 300 grams, contained about 6% unreacted furfural. During the last part of the run the temperature was set at 136-140° C. A tiny leak was later found in the diaphragm of the pump. The accumulation of inert gas in the circulating stream may have also been a factor. This inert gas could come from decomposition of the furfural, from nitrogen in the small air leaks or from impurities in the hydrogen gas (see note on experiment 13).

The next three experiments (10, 11 and 12) were run to determine whether or not the catalyst was losing its activity. As the data show a light increase in reaction temperature or contact time was sufficient to cause complete

conversion of the aldehyde.

Run No. 13 was made after the system had been thoroughly swept out with hydrogen. The operating conditions were then fixed to simulate as near as possible those noted in the latter part of 9 in this series. The unreacted furfural was negligible and a 2.6% yield of methylfuran was obtained.

A 650 gram sample of furfural was hydrogenated in experiment No. 14. Bisulfite-iodine titrations were used to monitor the reaction during the 29 hour period. These values for unreacted furfural were found to be slightly higher than those indicated by refractive index measurements subsequent to distillation - particularly when the concentration of furfural is 1% or less. This is in accordance with the findings of Dunlop and Trimble (31) that the method is least accurate for low concentrations of furfural.

The total recovery values for this run are a little lower than would be expected for this size sample due to the fact that the product was collected and distilled in several batches.

At the end of this and other series when the catalyst tube was taken down to measure the void space it was found that an organic film covered much of the catalyst surface.

Table 7

Series F-109-161

Vapor phase Hydrogenation of Furfural

No.	Size of run in grams	Feed Rate g/hr.	Catalyst Temp. °C.	Contact time in sec.	Hydrogen to furfural ratio	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl furan	Furfuryl Alcohol
1	50	12.6	125-31	1.46	77/1	Negligible	5.1	78.5
2	50	12.6	118-20	1.46	77/1	Negligible	Negligible	90.1
3	50	23.1	120-5	1.46	42/1	0	Negligible	92.1
4	50	22.3	118-21	2.35	27/1	0	1	88.3
5	50	23.4	120-30	2.92	20/1	0	15.4	76.5
6	50	23.1	105-9	2.92	20/1	Negligible	1.2	92.2
7	50	23.1	102-4	2.92	14/1	8.7	Negligible	85.8
8	50	12.8	98-101	4.37	25/1	0	Negligible	91.2
9	800	23.1	119-40	1.49	40/1	8.2	2.1	87.3
10	50	23.1	143-6	1.49	40/1	0	10.5	84.2
11	50	23.1	126-35	2.35	26/1	Negligible	3.2	58.8
12	50	23.1	134-8	1.75	38/1	Negligible	25.6	60.2
13	50	23.1	132-7	1.49	40/1	Trace	2.6	89.0
14a	550	23.1	137-43	1.49	40/1	0.33	8.25	88.2
14b	100	23.1	146-51	1.49	40/1	0	14.95	79.5

This was shown by the fact that the catalyst was not easily wet by water. The water which was drained from the tube (after measuring the voids) was acidic (pH 4.9 for the Series F-109-161). In the light of these facts it might become necessary in production runs to wash the catalyst with methylfuran (or other suitable solvent) after large quantities of furfural had been put through the unit. Such a procedure should remove the polymer or decomposition products responsible for the film.

Series H. A sample of calcium stabilized copper chromite catalyst which had been prepared by the author on July 23, 1943 was on hand in the laboratory. Although no attention had been paid to the pH of the mother liquor in the precipitation of the complex chromates the material had been rather carefully decomposed in small batches in a casserole. This catalyst was prepared for the liquid phase reduction of 2-valerolactone to pentanediol-1,4 and was noted to be quite active at that time. Hence it was of interest to test this material as a catalyst for the vapor phase hydrogenation of furfural.

A 30 gram portion of the catalyst was suspended on a volume of glass beads sufficient to give a bed depth of 38 cm. (thermometer tip 15 cm. from bottom of the bed). The particle size of this catalyst appeared to be somewhat

Table 8

Series H
Vapor phase Hydrogenation of Furfural

No.	Size of run in grams	Feed Rate g/hr.	Catalyst Temp. °C.	Contact time in sec.	Hydrogen to furfural ratio	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl furan	Furfuryl Alcohol
1	50	23.1	126-33	1.37	39.4/1	0	7.0	86.4
2	50	23.1	129-33	1.11	49.2/1	0	4.7	89.2
3	50	23.1	112-7	1.11	49.2/1	2.5	Negligible	93.5
4	50	23.1	109-15	1.61	33.6/1	2.4	Negligible	91.4
5	50	23.1	115-31	1.23	44.6/1	6.3	1.9	89.0
6	50	23.1	139-41	1.37	39.4/1	Trace	9.4	90.1

larger than the regular catalyst described above, and it was noted during the series of experiments that the material washed down a little more than usual.

Since nothing unusual was encountered during the series the data are shown in Table 8 without further comment.

Series I. This series of experiments was made with a sample of Hooker Chemical Co. catalyst dated April 4, 1945. Holdren has previously found that this catalyst was not satisfactory for the production of methylfuran (1). At the higher temperatures at which his studies were made the catalyst was reduced to the red cuprous state. In accord with previous studies this was assumed to be due to the absence of the alkaline earth constituent.

Several experiments were made with the Hooker chromite catalyst for the production of furfuryl alcohol (note Table 9). A 31 gram portion of the catalyst was placed on a sufficient volume of glass beads to give a bed depth of 38 cm. The thermometer tip was mounted 15 cm. from the bottom of the bed. All the experiments in this series were made with the feed rate, contact time and hydrogen to furfural ratio essentially constant. After the catalyst had been dried the first three experiments were made within a two day period. Then the catalyst stood in the reactor tube for 37 days at about 120° C. The system was closed

during this period but the hydrogen atmosphere was not renewed during this time. Gradually during this interval the lower half of the catalyst bed turned to an olive green color. This color was distinctly different from the customary reddish cuprous form of the reduced catalyst. However, experiment 4 shows that there was definitely a decrease in activity of the catalyst. During the course of this run (No. 4) the catalyst regained the brown color except for a small section of the tube at the lower end of the furnace. Test No. 5 showed a definite increase in activity over the preceding run.

In conclusion it may be said that although this catalyst is capable of catalyzing the hydrogenation of furfural it is definitely inferior to the catalyst described above, particularly with respect to stability and length of life. A slightly higher temperature is also necessary to give complete conversion of the furfural to furfuryl alcohol.

Series J. Throughout the course of this investigation it was noted that of the several variables involved the reaction temperature more than any other factor determined the ratios of the three products analyzed for: unreacted furfural, furfuryl alcohol and methylfuran. Hence it was of interest to compile a series of data with other variables constant and the temperature of reaction

Table 9

Series I

Vapor phase Hydrogenation of Furfural

No.	Size of run in grams	Feed Rate g/hr.	Contact time in sec.	H_2 to Furfural Ratio	Catalyst Temp. °C.	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl furan	Furfuryl Alcohol
1	50	23.1	1.7	39.4/1	140-4	0	4.2	72.5
2	50	23.1	1.7	39.4/1	144-6	0	4.7	92.0
3	50	23.1	1.7	39.4/1	139-48	0	3.5	92.1
4	48	23.1	1.7	39.4/1	132-50	11.8	3.5	78.0
5	50	23.1	1.7	39.4/1	143-53	3.8	Negligible	89.4
6	150	23.1	1.7	39.4/1	142-55	14.2	7.8	77.6

spread over the range chosen for study. Since the catalyst itself is one of the variables involved a series of runs was made with the same tube packing while the temperature was varied from about 105° C. to 160° C. during the course of study.

Preparation of the reactor tube was made in the following manner. Thirty grams of the standard chromite catalyst (cf. p. 23) was suspended on the glass beads in the usual manner to give a finished bed depth of 35 cm. After the catalyst had been dried in a hydrogen atmosphere the feed unit was set to deliver 23.1 grams per hour and the hydrogen circulation was adjusted to 4100 cc/min. These values were maintained for the entire series. Fifty gram samples of distilled furfural were used for the experiments. The reaction temperatures shown for the series were within 1 to 2° C. of the value listed - the two degree variation coming at the beginning of the run (if it varied to that extent).

Each of the product samples was worked up in the prescribed manner and the yields are thus the usual "in hand" calculation.

Table 10 and Figure 3 show that under the conditions chosen for these experiments the optimum reaction temperature would be about 135° C. A 10° C. increase in this

Table 10

Series J

Effect of Reaction Temperature on the Ratio of Products Formed in the Hydrogenation of Furfural

	Feed Rate g/hr.	Contact time in sec.	H_2 to furfural ratio	Catalyst Temp. °C. (Average)	% Furfural Recovered after Distillation as: Unreacted Furfural	Methyl furan	Furfuryl Alcohol
1	23.1	1.15	39.4/1	103	16.4	0	66.3
2	23.1	1.15	39.4/1	118	9.2	0	81.1
3	23.1	1.15	39.4/1	124	6.1	0	86.1
4	23.1	1.15	39.4/1	130	0.96	0.7	93.0
5	23.1	1.15	39.4/1	137	0	1.9	91.2
6	23.1	1.15	39.4/1	145	0	5.85	91
7	23.1	1.15	39.4/1	152	0	8.2	86.2
8	23.1	1.15	39.4/1	158	0	10.8	82.5

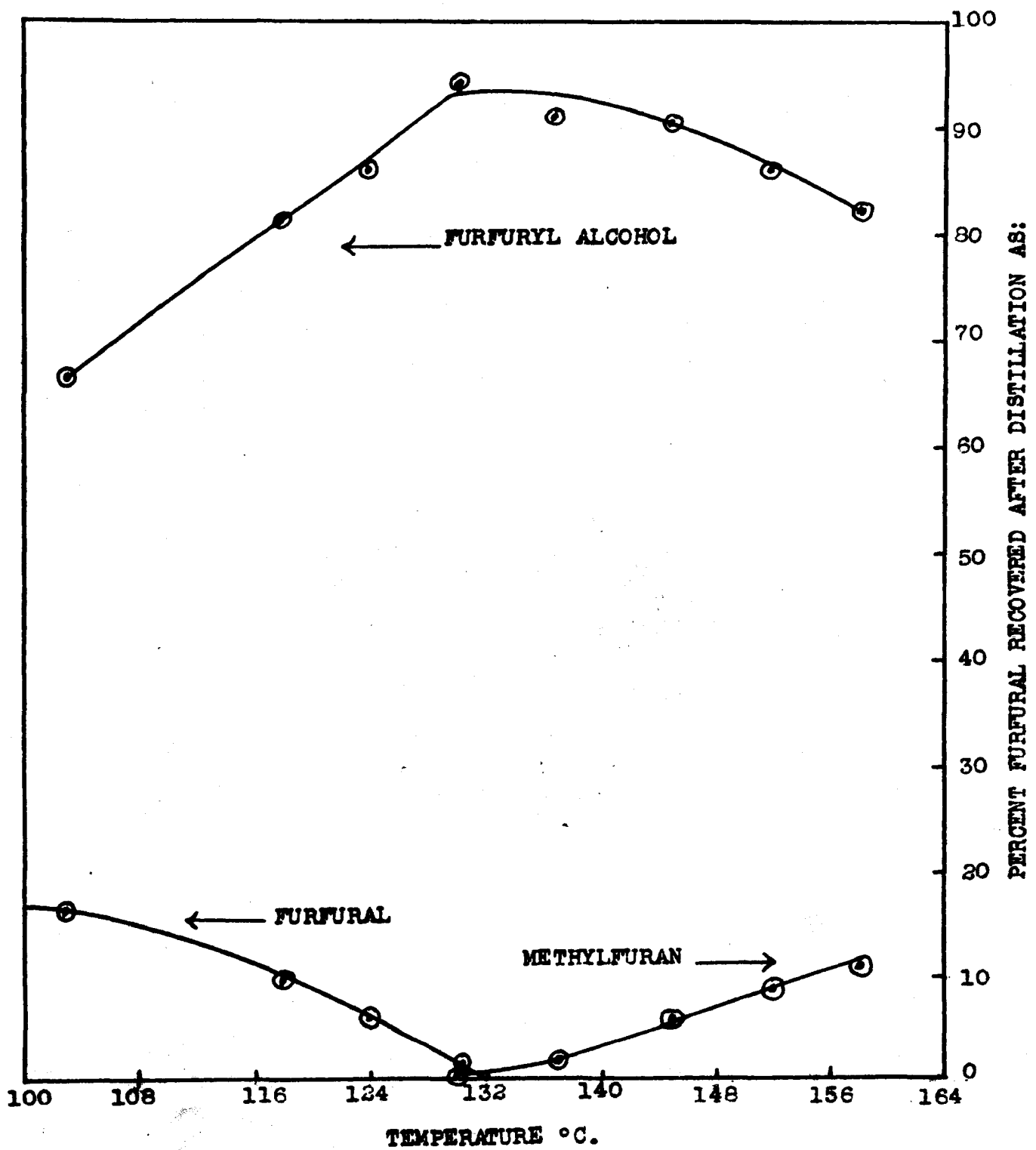


Figure 3.
Relationship Between Temperature and the Products Formed in the Hydrogenation of Furfural.

value would still give 90% recovery of furfuryl alcohol.

It should be noted in passing that by increasing the contact time it would be possible to lower this optimum reaction temperature - note runs 6 and 8 in Series F-109-161. From the standpoint of catalyst life it is certain that the lower temperature would be desirable. A low reaction temperature also cuts down the possibility for methylfuran production but necessitates careful control to insure complete conversion.

Similar detailed studies could be made with the other variables involved - such as bed length, bed diameter, hydrogen to furfural ratio, contact time, etc. However, since such data is of chief value only for the design of a pilot plant and since such a unit would almost certainly be made from metal, the data obtained in glass would be of little value. This is evident when one considers the difference in heating units, heat capacity of the system, tube diameter and depth, feed rate, etc. between a small laboratory apparatus of glass and a metal unit designed to simulate a production design. It has been shown in other experiments in this study that contact time is not too critical, particularly when glass beads are used as a carrier and the vaporizer is employed to introduce the furfural as a vapor. Hydrogen to furfural ratio is important principally as a safety factor in cooling the

catalyst surface and thereby holding down the methylfuran formation. However so long as this is kept > 25 to 1 no serious difficulty is encountered with feed rates up to 23 g/hr. A greater ratio may be desirable with higher feed rates and a greater tube diameter than those employed in this study.

Effect of recycling the product. The experiments described above have shown that one pass through a catalyst bed of ordinary length is sufficient under the proper conditions to give complete hydrogenation of furfural to the desired product. In setting up a production unit of this type it would also be natural to regulate the operating conditions such that one pass would be sufficient. However, there are occasions when mechanical difficulties result in the production of low-grade product. For this reason it was of interest to know what results could be expected from the second pass with a sample of furfuryl alcohol - particularly the yield of methylfuran and the possible resinification of the alcohol in the vaporizer.

Forty-nine grams (0.5 mole) of distilled furfuryl alcohol was passed over the catalyst sample used for Series J. The catalyst temperature was 133-138° C., feed rate 23.1 g/hr. and gas circulation 4100 cc/m. Little or no furfuryl alcohol was lost in the vaporizer and the product collected (50 g.) was water white. Distillation gave

a 2.9% yield of methylfuran.

This data indicates that recycling of the product when necessary would be feasible and that the yield of methylfuran produced on the second pass just about corresponds to what would be expected from doubling of the contact time on the first pass (note that the first pass gave about 1.5% methylfuran at this temperature in Series J).

2. Attempted liquid phase hydrogenation of furfural at atmospheric pressure.

A gas tight apparatus was set up for circulating hydrogen through a suspension of the Cu-Ca-Cr catalyst at 1 to 2 cm. of hydrogen pressure. A three neck flask was fitted with a hydrogen inlet tube which reached to the bottom of the flask. A mercury manometer was fitted to the other side neck and a condenser with a suspended thermometer was placed in the center neck. Hydrogen at the rate of Ca. 2000 cc/min. was then blown through the hot liquid (130-135° C.). The furfural carried out by the H_2 condensed and returned to the flask. The hydrogen was led from the top of the condenser through a dry ice-acetone trap, thence to a flow meter and back to the pump. A "T" tube connected the gas line to a 20 liter bottle.

filled with hydrogen.

A 50 gram sample of freshly distilled furfural and a 20 gram sample of the chromite catalyst were placed in the reaction flask described above. Hydrogen circulation was continued for one hour. No measureable quantity of gas was absorbed.

Repetition of the above experiment using 40 grams of distilled furfural and 10 grams of air dried charcoal supported catalyst gave no gas absorption in a period of 1 hour and 40 minutes.

These experiments indicate that the reaction does not occur in the liquid phase. Hence in those experiments where the liquid furfural is added directly to the top of the catalyst bed the material must first vaporize or at least spread out to a molecular film on the catalyst surface. At the instant of reaction the molecule of furfural is undoubtedly complexed by the catalyst. Hence it makes little difference whether we assume that the molecule goes into this excited state from the vapor phase or from a molecular film.

IV. PRODUCTION OF 2-VALEROLACTONE

A. Review of the Pertinent Literature

In the early part of the war when our supply of natural rubber was cut off a number of possible raw materials for synthetic substitutes was being considered. One process which received considerable attention at Iowa State College involved the following set of reactions:

$$CH_3\ CO\ CH_2\ CH_2\ COOH \xrightarrow[(\text{Raney Ni})]{+H_2} CH_3CHCH_2CH_2 \quad (O\text{—}CO)$$

$$\xrightarrow[CuCr]{+H_2} CH_3\underset{OH}{C}HCH_2\ CH_2\ \underset{OH}{CH_2} \xrightarrow[(Al_2O_3)]{-H_2O}$$

$$CH_3CH : CHCH : CH_2 + CH_2 : CH\ CH_2\ CH : CH_2$$

The reactions were all reported in the literature but the yields were for the most part less than 80% and the procedures described were cumbersome and obviously not suited to commercial production. Preliminary studies were made on each of the reactions in turn and a sample of pentadiene-1,3 was obtained. The hydrocarbon was copolymerized with acrylonitrile by the emulsion technique,

and a sample of rubber-like material was obtained. As a result of the preliminary work it was concluded that production of synthetic rubber by this process would be expensive and impractical. However, the production of 2-valerolactone and pentanediol-1,4 for use as fine chemicals is feasible.

There are a number of methods by which 2-valerolactone has been prepared. In keeping with the general research program dealing with the utilization of agricultural products it was of interest to consider levulinic acid as the starting material. (Levulinic acid is available commercially from the dilute acid hydrolysis of corn starch).

Among the methods described for the reduction of levulinic acid to 2-valerolactone may be mentioned the vapor phase reduction at 250° C. over a nickel catalyst (34). Electrolytic reduction with a mercury or lead cathode (35), treatment with sodium in absolute alcohol (36), or sodium amalgam in 95% alcohol (37) have also been used to hydrogenate levulinic acid to 2-valerolactone. Somewhat more practical procedures include the catalytic reduction with a platinum catalyst in ether solution (38) and reduction of the sodium salt with a nickel catalyst in alkaline solution (39).

Of the methods mentioned above, the catalytic

reductions in liquid phase seem best suited to commercial production. Because of the high initial cost of the platinum catalyst and the hazards involved in handling large quantities of ether this reaction seemed less practical than the reduction of the sodium salt. Allen and his co-workers (39) used a Raney nickel catalyst in alkaline solution. Using an autoclave at a temperature of 75° C. and a hydrogen pressure of 2500 p.s.i. these workers were able to obtain an 84% yield of γ-hydroxy-valeric acid after neutralization and ether extraction of the neutral solution. By adding excess HCl and refluxing for 15-20 minutes before the ether extraction is made the hydroxy acid may be converted to the corresponding lactone.

The proof of structure for 2-valerolactone was given quite early by Messerschmidt (40) and Wolff (41).

Some of the reactions and derivatives of 2-valerolactone have been studied in these laboratories (42, 43).

B. Experimental

1. Reduction of levulinic acid in alkaline solution

The experiment described above (39) was repeated using a technical grade of levulinic acid. One mole of

the sodium salt was prepared from the acid and the required amount of sodium hydroxide in aqueous solution. This preparation with 12 g. of Raney nickel catalyst (44) was hydrogenated in the 500 ml. bomb, with an initial hydrogen pressure of 1825 p.s.i. and a reaction temperature of 112-128° C. About two hours time was required for completion of the reaction. Recovery of the product in the manner described above gave 72 g. of 2-valerolactone $b.p._{13}$ 85-95° C. This represents 72% of theory.

Since the calcium salt of levulinic acid is quite soluble (45) the experiment described above was repeated using this cheaper alkali. Except for the limitation on the amount of material that can be kept in solution no appreciable difference was noted when this salt was substituted for the sodium compound. It was also noted that a Cu-Ba-Cr catalyst (28) could be used to give low yields of 2-valerolactone. For example 0.5 mole of the calcium salt in aqueous solution was hydrogenated at a reaction temperature of 200-26° C. and an initial hydrogen pressure of 1190 p.s.i. to give a 42% yield of 2-valerolactone $b.p._{15}$ 88-95° C. Undoubtedly increasing the initial pressure would boost the yield considerably.

2. Attempted reduction of technical levulinic acid without solvent

The reactions of levulinic acid indicate that it exists chiefly in the lactol form (46). If this is the case then it should be possible to reduce the acid in the presence of a chromite catalyst to pentanediol-1,4. A reduction of this nature was attempted using 0.5 mole of technical levulinic acid and 11 grams of Cu-Ba-Cr catalyst in the 500 ml. bomb. The hydrogen pressure available was quite low (only 850 p.s.i.), and at a reaction temperature of 230-4° C. only a small amount of hydrogen (100 p.s.i. drop in pressure reading) was absorbed during a 3 hour period. At the end of this time the catalyst had been completely reduced to the red cuprous form.

Some vapor phase reductions were also attempted with the technical acid using Raney nickel suspended on glass wool and a reduced nickel catalyst (47). The levulinic acid was carried through a horizontal catalyst tube (heated to 250-265° C.) by bubbling hydrogen through the hot liquid (kept at 130-210° C. depending on the feed rate desired). In these experiments hydrogen was absorbed for a few minutes and then suddenly the reaction would stop. 2-Valerolactone and angelica lactones were

identified as products of the reaction.

With a Raney nickel catalyst and a water solution of technical levulinic acid hydrogenation in the bomb gave a yield of 30% of 2-valerolactone. Eight hours were required for this degree of conversion on a 0.5 mole sample of the acid.

Negative results were obtained when 0.5 mole of the acid was treated with hydrogen in the presence of a catalyst prepared by grinding together 0.7 g. Cu_2O, 0.375 g. V_2O_4 and 0.7 g. CaO. The maximum pressure attained was 2240 p.s.i. at the reaction temperature of 258° C. The reaction time was about 3 hours at the temperature stated.

3. Reduction of pure levulinic acid without solvent

The above experiments indicated that some material present as an impurity in the technical acid might be poisoning the catalysts. Hence a sample of the technical acid was purified by distillation through a Vigreux column at reduced pressure ($b.p._1$ about 134° C.) and subsequent crystallization. One mole of the purified acid with 10 g. of Raney nickel catalyst was hydrogenated in the bomb. The initial pressure of 1720 p.s.i. increased to 2100 at a reaction temperature of 200° C. (Running the reaction at this temperature results in the dehydration of the hydroxy acid in the bomb - thus eliminating the

necessity for further treatment after the reduction is complete. Reaction was quite rapid - the pressure having dropped to 1280 p.s.i. in forty minutes. A 94% yield of 2-valerolactone (b. p. 88-90° C. @ 10 mm.) was obtained by distillation of the filtered product. Pure 2-valerolactone was obtained by another distillation through a Widmer column. The pure material had the following physical constants: $b.p._{1.5}$ 57.5-58° C., $\underline{N}^{20}_{D}$ 1.4318, $\underline{N}^{25}_{D}$ 1.4300, $\underline{d}^{20}_{4}$ 1.0500. Previously reported constants are $b.p._{4}$ 78° C., $\underline{N}^{25}_{D}$ 1.4301, $\underline{d}^{25}$ 1.04608 (37).

In two later experiments the acid was distilled but not crystallized before reduction. Yields of 94% and 97% of theory were obtained with one mole of starting material.

To obtain larger quantities of the lactone for experimental use (42, 43) a 3.85 liter, copper-lined bomb was used to reduce 5 mole portions of the purified acid. Yields were comparable to those given above, i.e. $>$ 94% of theory. In the experiments with the large bomb it was learned that reduction would occur with pressures as low as 170 p.s.i. The reaction of course was much slower and with large quantities of acid the catalyst loses much of its activity during the long reaction period. Good yields were obtained, however, with initial pressures of 500 p.s.i. The percent of catalyst by weight need not be

greater than 2 - 3.

The experimental work on the production of 2-valerolactone in excellent yields was completed in October, 1943. In the course of applying for a patent on the process it was learned that a prior application had been filed embodying essentially the same procedure. This patent was granted January 30, 1945 (48).

4. Production of pentanediol-1,4.

After it was found that good yields of 2-valerolactone could be produced by reduction of the pure levulinic in the presence of Raney nickel it was of interest to repeat the reaction using a chromite catalyst. If such a reaction were successful the production of pentanediol-1,4 would be possible in one step from the levulinic acid.

A 0.5 mole sample of the distilled acid in the presence of 5 g. of Cu-Ca-Cr catalyst was hydrogenated in the small bomb. The initial hydrogen pressure was 1590 p.s.i., and a reaction temperature of 237-72° C. was maintained for 4 hours. Distillation of the filtered product gave a 62% yield of 2-valerolactone ($b.p._{13}$ 95-100° C.) and 21% yield of pentanediol-1,4 ($b.p._{10}$ 120-124° C.).

Later it was shown that increasing the pressure gave a better yield of the glycol (44% yield of pentanediol-1,4 and 11% yield of lactone were obtained). A considerable quantity of 2-methyltetrahydrofuran was also formed by dehydration of the glycol at the reaction temperature of 300° C. (42), indicating that the actual conversion to the glycol was much better than the yield obtained.

Pentanediol-1,4 was identified by conversion to the bis-α-naphthylurethan by heating on a steam bath with the required amount of α-naphthyl isocyonate for 1 hour. After cooling the waxy product was washed with two small portions of petroleum ether. The reaction vessel had to be scratched vigorously with a glass rod to induce crystallization. Recrystallization from a 95% alcohol solution gave a product melting at 127° C. The previously reported value is 128.5-129° C. (49).

5. Preparation and reduction of β-angelicalactone

An earlier investigation has shown that by slow distillation of levulinic acid a partial dehydration may be effected to give a product consisting of water, unchanged levulinic acid and a mixture of α- and β-angelicalactones. Neutralization with K_2CO_3, washing with H_2O

and distillation gives α-angelicalactone b.p.$_{25}$ 51° C. and the β-isomer b.p.$_{25}$ 83° C. (50).

Hydrogenation of these compounds with a platinum catalyst in alcohol solution has been shown to give valeric acid from the α-isomer while the β-isomer is converted to 2-valerolactone (51).

The author was interested in determining whether or not β-angelicalactone might be hydrogenated in the presence of a chromite catalyst to pentanediol-1,4 (the reaction going through 2-valerolactone as an intermediate). Hence a sample of the desired lactone was prepared by the procedure described above. The yield for a 3.45 mole sample of levulinic acid distilled from a Vigreux-modified Claisen flask was 20.7% of β-angelicalactone b.p.$_5$ 65-75° C.

In an attempt to improve the yield of the lactone some preliminary tests were made with dehydration catalysts in a tube heated to 300-360° C. For example one such catalyst was prepared by mixing 1 g. of red phosphorus with enough wet acid-washed kieselguhr to fill the catalyst tube (12 inches long and 30 mm. i.d.). The paste was spread into a thin layer, dried and cut into small cubes. When levulinic acid was passed over this catalyst (50 g/hr.) at 300-360° C. the yield of β-angelicalactone varied from

24 to 50% depending on the temperature (the higher yield being obtained at the higher temperature).

Another catalyst prepared in a similar manner from 1 g. red phosphorus and 5 g. of $Na_2HPO_4 \cdot 10\ H_2O$ gave a 36% yield of the desired lactone at 340-50° C. Marked decomposition occurred with this catalyst above 400° C., and small quantities of a low boiling compound with a very pungent odor were obtained. The compound was a very potent lachrymator and was presumed to be methyl-vinyl ketone or a related compound.

For the reduction of angelicalactone the regular copper chromite catalyst was used without solvent. In one experiment the initial hydrogen pressure was 1600 p.s.i. and the reaction temperature of 175-200° C. was maintained for about 3 hours. For this 65 g. (0.664 m.) sample 15 g. of the catalyst was employed. Distillation of the filtered product gave a 60% yield of 2-valerolactone $b.p._3$ 75-85° C. and 11.5% of pentanediol-1,4 $b.p._6$ 110-122° C.

Somewhat higher proportions of the glycol were obtained by raising the reaction temperature. For example, a 0.684 m. sample when hydrogenated at 220-46° C. in the presence of 15 g. of catalyst gave a 32% yield of 2-valerolactone $b.p._5$ 80-95° C. and a 35% yield of pentanediol-1,4 $b.p._{0.5}$ 95-108° C.

V. SOME FURAN REACTIONS RELATED TO POLYMERIZATION

On the basis of consumption the chief commercial outlet for furan derivatives seems to be in the plastics industry. Furfural has some advantages over formaldehyde in the preparation of the phenol-aldehyde resins. This fact coupled with the shortage of formaldehyde has resulted in an increasing demand for furfural within the past few years. Furfuryl alcohol is also gaining favor in the resin field, and a cheaper method of manufacture will almost certainly cause a sharp increase in the demand for this compound.

Furfural is used in the petroleum industry because of its ability to give preferential extraction. The purification of lubricating oils and the separation of the butene fraction for the preparation of butadiene-1,3 for the rubber industry are two of the main uses here (52).

In a recent address before the French Chemical Society Paul has summarized a large number of potential uses of furfural and its hydrogenation products in organic synthesis. Among the products which can be derived from furfural as a raw material might be mentioned the 1,4- and 1,5-diols, 1,4,5-triols, 1,3- and 1,4-pentadienes, a number of compounds in the pyridine and piperidine series and the several hydrogenation products formed by reduction of the aldehyde

group and/or the furan nucleus. This survey also indicates the present production and the potential quantities of furfural available from various sources. A rather extensive literature survey is included (53).

Recently the Du Pont Company has announced plans to utilize furfural as the starting material in the synthesis of adiponitrile, an intermediate used in the preparation of nylon (54). This represents one of the first major uses of a furan derivative as a chemical raw material for the production of commercially useful intermediates. Continued study should develop other uses which eventually may place furfural in a position comparable to that now held by benzene in the aromatic series.

The study of the chemical properties of the furan nucleus is complicated by the strong tendency to polymerize and produce tars in the presence of a wide variety of reagents. For one who has not worked with these derivatives it is sometimes difficult to appreciate the ease with which this polymerization is initiated, particularly when the nucleus is positively substituted. Of course one must not assume that the problem is beyond solution. Once we are able to understand the mechanism by which the polymerization occurs then it will be much easier to predict what steps should be taken to prevent such reaction. Although

the study of the furan polymers would be complex and time-consuming this in the end might easily be the shortest path to the solution of the problem of preventing tar formation in the synthesis reactions patterned from the benzene analog.

As a part of the long range study on the properties and potential uses of the furan derivatives some preliminary studies were made to determine the course to follow in future study of the problem. These exploratory investigations included (1) the reactions of methylfuran with metal halides (polymerization, mercuration and Friedel-Crafts reaction) and (2) some "cyanoethylation" derivatives of furfuryl and tetrahydrofurfuryl alcohol.

A. Review of the Pertinent Literature

1. Resins from 2-methylfuran

Most of the reactions of 2-methylfuran carried out in the presence of acidic materials have resulted in the formation of some resin - the amount depending on the conditions of the experiment. Atterberg (55) reported that bromine reacts violently with 2-methylfuran. In addition concentrated hydrochloric acid or dry hydrogen chloride in ether caused vigorous polymerization. Bromine water gave a soluble substance which could be ether extracted. Under the conditions of his experiments 2-methylfuran did not react with acetic

anhydride, alkali or sodium.

Harries in 1898 reported that concentrated sodium hydroxide caused polymerization of 2-methylfuran. He found that the yellow color which develops in methylfuran on standing could be destroyed by the addition of small quantities of alcoholic HCl (56).

Gaseous hydrogen iodide reacts violently with 2-methylfuran to give iodine, water and carbon (57).

In a later investigation it has been shown that both bromine and hydrobromic acid produced black polymers at room temperature and at -10° C. (58).

The use of metal halides (e. g. $AlCl_3$ or $FeCl_3$) to polymerize furfural or a furan derivative is covered by a patent (59). No description of the resin or the method of preparation is mentioned in the abstract. Furfuryl alcohol and related furan derivatives are also the subject of a resin patent using hydrochloric acid as the polymerization catalyst (60).

All of the reported attempts to carry out Friedel-Crafts reactions with 2-methylfuran have mentioned the formation of tars and resins as a by-product.

2. Mercuration of 2-methylfuran

Furan and a number of its derivatives have been found

to mercurate normally to give the corresponding chloromercuri compound (61). 2-Methylfuran reacts with one equivalent of mercuric chloride and two equivalents of sodium acetate to give an intermediate of the type postulated by Steinkopf (62) for the product formed from mercuric chloride and 2,5-dimethylthiophene. If this complex is boiled with alcohol 5-methyl-2-chloromercurifuran is obtained. Using four equivalents of sodium acetate gives the mercurial directly in 50% yields.

2-Methylfuran also undergoes metalation reactions. For example ethyl, phenyl and benzyl sodium all react to give on subsequent carbonation poor yields of 5-methylfuroic acid. Lithium, sodium, 4% sodium amalgam, sodamide and sodium hydroxide failed to react at 60-100° C. (63). Later studies showed that 17 and 29% yields of 5-methylfuroic acid could be obtained by using n-butyl lithium and phenyl lithium respectively (64).

3. Friedel-Crafts reaction with 2-methylfuran

Furyl ketones have long been made from unsubstituted furan. The ease of alkylation of negatively substituted furans has been used as a basis for attributing "superaromatic" properties to the furan nucleus (65, 66, 67, 68). In contrast to the similar alkylations of the benzene nucleus molecular equivalents of the catalyst are needed

(due to the formation of an oxonium salt or other type of complex with the furan nucleus). Recently it has been shown that catalytic quantities of hydriodic acid, or fused zinc chloride (69) are effective catalysts for the acetylation of unsubstituted furan. The 76% yield of 2-acetylfuran obtained with the hydriodic acid catalyst represents the best yield reported to date. Two Russian investigators have found that the furyl ketone may be prepared in yields up to 65% by adding $SnCl_4$ in a solvent to a dilute solution of furan and acetic anhydride in benzene (70).

The yields of ketones prepared from 2-methylfuran by the Friedel-Crafts reaction are quite low. Reichstein (71) reported that $SnCl_4$ in benzene and $ZnCl_2$ in ether were the best combinations of catalyst and solvent to use. Russian investigators obtained a 28% yield of the desired ketone by reaction of 2-methylfuran and acetyl chloride in the presence of aluminum chloride as the catalyst (72). Stearoyl chloride and 2-methylfuran in the presence of aluminum chloride catalyst gave methylfuryl heptadecyl ketone in unstated yield (73).

4. "Cyanoethylation" of furfuryl alcohol and related compounds

Christian (42) has previously reviewed the addition of

alcohols to the double bond of acrylonitrile in the presence of a basic catalyst (e. g. 40% aqueous potassium hydroxide solution or 38-40% trimethylbenzylammonium hydroxide).

A rather extensive study has recently been made of the addition of alcohols to the olefinic linkage of alkyl acrylates (74).

Untermohlen (75) has reduced tetrahydrofurfuryl-oxy-propionitrile in liquid ammonia (see review in 42) with Raney nickel as a catalyst to γ-tetrahydrofurfuryloxy-n-propylamine in 55% yield.

B. Experimental

1. Polymerization of 2-methylfuran

Stannic chloride. Stannic chloride forms a solid addition product with 2-methylfuran. If the anhydrous chloride is added to a small sample of 2-methylfuran the solid product settles out of the liquid. Shaking causes the material to redissolve and polymerization of the whole mass begins - the rate depending on the amount of $SnCl_4$ added. If cooling is not applied the highly exothermic reaction proceeds very rapidly and a dark brown to black polymer results. By dissolving the 2-methylfuran in a dry solvent (e.g. $CHCl_3$) the addition product may be filtered from the cold solutions.

The product is not pure as some polymer adheres to the particles. After the product is washed with chloroform and dried it may be redissolved in 2-methylfuran. Polymerization is initiated very slowly by catalytic quantities of this dried complex. Specific examples will be described below.

A 50 cc. sample of freshly distilled 2-methylfuran was cooled in a water bath to 18° C. Then 1 cc. of anhydrous $SnCl_4$ (General Chemical Co.) was added dropwise with shaking while the small flask was cooled in a stream of cold water. An orange colored solid precipitated as the stannic chloride was added. This product slowly redissolved. After 30 min. the flask was removed from the cooling bath, stoppered and allowed to stand overnight at room temperature. The polymerization was not proceeding very rapidly so 1 cc. more of the stannic chloride was added in the manner described above. After four days standing at room temperature the polymer was so viscous that it flowed quite slowly. The material was then removed from the flask and "milled" by pulling with the fingers in a dilute hydrochloric acid solution to remove the catalyst. This "milling" caused the polymer to become quite pliable. It could be melted (about 40° C.) without appreciable darkening. Due to the residual unsaturation and lack of proper milling and plasticizing

the resin aged quite badly - becoming brittle on long standing in air or on solidification after melting. (Probably some catalyst was left in the polymer too.)

Aluminum chloride. When finely powdered anhydrous aluminum chloride is added to a sample of dry methylfuran the polymerization is faster than with stannic chloride. Polymerization of course tends to start around the grains of the catalyst and if the mixture is not stirred considerable darkening of the product will result due to overheating around the catalyst surface. By careful addition of the catalyst and by keeping the material cooled, however, an amber colored resin similar to that described above may be obtained.

Ferric chloride. About 0.5 g. of ferric chloride (not completely anhydrous) was added to 5 cc. of 2-methylfuran. Heat was evolved as the crystals became coated with a brown sticky film. As the mixture was stirred the salt was gradually taken into the organic phase. If cooling is not applied the material sets to a dark brown resin within 15 minutes. By cooling the tube the reaction is slowed down with a resulting decrease in the intensity of the color of the resin.

Iodine. The addition of 0.5 g. of iodine (Merck, reagent grade) to 5 cc. of dry 2-methylfuran results in the immediate formation of a dark tar around the flakes of

iodine. If this tar is broken up and suspended (without cooling) the whole quantity of material sets to a black glass within 15 minutes. Cooling the reaction media delays the reaction, but the resin is still quite dark.

Chloral. To a 5 cc. portion of 2-methylfuran one cc. of chloral (Eastman Kodak Co., stabalized with hydroquinone) was added. At first there was no evidence of reaction. After about 20 min. a greenish yellow color began to form in the solution and the color darkened to amber within a few hours. At the end of 48 hours the material was a viscous oil.

Boron trifluoride. Boron trifluoride gas (Ohio Chemical Co.) was bubbled into a 5 cc. sample of 2-methylfuran which had been dried over Calcium Carbide. A straw color developed within a minute, heat was liberated and the material began to polymerize. The capillary delivery tube plugged up quite readily, indicating rapid polymerization near the higher concentration of the gas. After about 5 minutes the addition of gas was stopped. Within 30 minutes the material was quite viscous and after standing overnight the amber resin was a very brittle solid.

Zinc chloride. A 50 cc. sample of 2-methylfuran was treated with 1 g. of powdered zinc chloride (if the material has been freshly fused cooling should be applied). The

granules soon became coated with a waxy film and after stirring for some time the inorganic salt was associated with sufficient organic matter to give a homogeneous material. After standing for 10 days at room temperature (with occasional shaking until all the zinc chloride has dissolved) the viscosity of the solution is about like that of a heavy varnish. The resin was a very light amber color.

Thirty seven grams (0.45 mole) of the polymer described above was mixed with 49 g. (0.59 mole) of 36% formaldehyde (Merck), 4 cc. of concentrated hydrochloric acid and 100 cc. of dioxane. The material was refluxed for one hour. Then the medium was made alkaline with 10% sodium hydroxide and the resin was pulverized in the alkaline suspension. After drying for two days at 80° C. the resin weighed 46 g. - the increase in weight corresponds to 0.3 mole of formaldehyde. The polymer was insoluble in most of the common organic solvents and was infusible.

Alkali. There seems to be some confusion in the literature regarding the effect of alkali on 2-methylfuran (55, 56, 63, 76). Two of these papers reported no polymerization with alkali while the other two state that a reaction takes place.

A 10 cc. sample of 2-methylfuran (light straw color) was mixed with 10 cc. of concentrated ammonium hydroxide

in a small flask and shaken vigorously. An amber color formed almost immediately and a rather stable emulsion formed which did not break for about 24 hours. When the layers separated the color was practically all in the aqueous phase and the volume of 2-methylfuran was essentially unchanged.

To a 5 cc. sample of 2-methylfuran a 2 cc. portion of 5 N.NaOH was added. (The methylfuran had been allowed to stand until it was dark brown in color.) When the tube was vigorously shaken for a few minutes, most of the color was extracted into the aqueous phase. A second extraction with the alkali removed more color leaving the organic fraction a light orange color.

In another experiment a 200 cc. sample of amber colored 2-methylfuran was shaken with 50 cc. of 40% potassium hydroxide. The layers were separated (most of the color going into the aqueous phase) and a fresh portion of alkali was added. A sample of 2-methylfuran was then distilled from the alkaline suspension in a nitrogen atmosphere. The distilled fraction was mixed with half its volume of 40% KOH and refluxed for four hours in a nitrogen atmosphere. At the end of this time only a very faint straw color was present in the alkaline solution; the methylfuran was still water white.

Unpublished data has also been obtained with alcoholic

alkali which indicates that 2-methylfuran is not polymerized by this reagent (77).

The above data indicate that 2-methylfuran is stable in the presence of alkali, and that the acidic polymeric materials formed as a result of autoxidation are merely extracted into the alkaline solution. These "indicator" acids (78) are undoubtedly the materials which Harries (56) found could be decolorized by the addition of alcoholic HCl to colored 2-methylfuran.

2. Friedel-Crafts reaction with 2-methylfuran

a. Attempted alkylation.

Aluminum chloride catalyst. To 200 cc. of dry carbon disulfide in a three-neck flask there was added 26.6 g. (0.2 mole) of anhydrous aluminum chloride (Merck). The suspension was stirred and cooled to 2° C. Then a solution of 16.4 g. (0.2 mole) of 2-methylfuran and 18.5 g. (0.2 mole) of isobutyl chloride in 20 cc. of carbon disulfide was added dropwise over a period of 1.5 hours. During the addition of the reagents to the catalyst and for 30 minutes afterward the solution was kept at 0 - 2° C. and protected from atmospheric moisture. Then the solution was allowed to warm up to room temperature and stirred for thirty minutes longer. Hydrolysis with cracked ice, extraction with ether and drying according to accepted

practise for this type of experiment completed the reaction. When the solvent and unreacted reagent were removed by distillation 16 g. of a dark brown tar was left. No attempt was made to distill the residue.

Repetition of the above experiment using equimolar quantities of 2-methylfuran, n-butyl bromide and anhydrous aluminum chloride (General Chemical Co.) gave only a tar which did not distill at 270° C. (bath temperature) at 14 mm. pressure.

Chlorosulfonic acid. Chlorosulfonic acid and monohydric alcohols have been used to alkylate benzene and other aromatic hydrocarbons in yields of about 40% for the monoalkyl derivative with varying amounts of the poly-substituted compound being produced as a by-product (79). This procedure was duplicated with 2-methylfuran and isopropyl alcohol. A 30 g. (0.5 mole) sample of isopropyl alcohol, 200 cc. of dry CCl_4 and 45 cc. (0.5 mole) of 2-methylfuran were cooled to -5° C. in a three-neck flask. Then 0.5 mole (65 g.) of distilled chlorosulfonic acid in an equal volume of CCl_4 was added dropwise with stirring and cooling over a period of two hours. During this period it was evident that the furan derivative was rapidly being converted to a tar. After warming to room temperature the resin was already solid and black in color. No attempt was made to recover any product from the brittle sponge-like material.

Boron trifluoride. Boron trifluoride has also been used as a catalyst to initiate alkylation of benzene by monohydric alcohols (80). An attempted alkylation of 2-methylfuran was made with this reagent and n-butylbromide. A 2.3 g. sample of the gas was dissolved in 20 cc. of dry ether and added to 0.2 mole quantitites of 2-methylfuran and the bromide in 150 cc. of dry ether. To keep the medium anhydrous 5 g. of powdered calcium carbide was suspended in the ether. When it was evident that no reaction was occurring BF_3 gas was bubbled into the solution for 0.5 hour. The only product resulting from the treatment was a polymer.

b. Acylation.

Stannic chloride catalyst. Using a standard procedure for Friedel-Crafts reaction 0.2 mole of 2-methylfuran was added to a solution of 0.2 mole each of acetyl chloride and stannic chloride in 200 cc. of dry carbon disulfide at 0-5° C. The mixture was stirred for one hour at room temperature after the temperature had previously been kept at 0-5° C. for 1.5 hours. Hydrolysis with cracked ice and hydrochloric acid, extraction and distillation gave 16% of the expected ketone.

In a second experiment one mole of stannic chloride diluted with 50 cc. of dry benzene was added dropwise over a period of 2.5 hours to a solution of 0.5 mole of benzoyl

chloride (Merck, reagent grade) and 0.5 mole of 2-methylfuran in 150 cc. of benzene. During this time the temperature was kept below 10° C. After standing overnight at room temperature the material was hydrolyzed with ice and steam distilled to attempt to separate the product from the hard tar which formed during the reaction. A good yield of benzoic acid steam distilled but no ketone was recovered. The air dried brittle resin weighed 150 g. (indicating that some stannic chloride might still be present).

Zinc chloride catalyst. One mole of acetic anhydride (b.p. 133-6° C. at 730 mm.),0.5 mole of 2-methylfuran and 2 g. (0.015 mole) of fused zinc chloride (powdered under dry solvent) were mixed at 0-5° C. and stirred for one hour at this temperature. After stirring for another hour at room temperature 200 cc. of water was added. Subsequent to hydrolysis, ether extraction and distillation of the dry solution an 8% yield of the expected ketone was obtained ($b.p._{23}$ 90-6° C.). Five grams of an amber resin was left in the distilling flask.

Repetition of the experiment using 3 g. of $ZnCl_2$ and stirring the reaction mixture for 3.5 hours at room temperature also gave an 8% yield of the ketone ($b.p._3$ 63-6° C.). The resin from this experiment weighed 25 g.

Hydriodic acid catalyst. The catalyst for the experiments described below was prepared by distillation of the preserved material (General Chemical Co., sp. gr. 1.50) in an atmosphere of carbon dioxide. Small ampoules were filled and sealed under CO_2.

One mole of acetic anhydride (b.p. 133-6° C.) and 0.73 mole of 2-methylfuran were cooled to -15° C. Then three 0.5 ml. portions of hydriodic acid were added over a period of 10 minutes. When the temperature was allowed to warm up to 0° C. after the addition of the catalyst there was a rapid jump to 10° C. A dry ice-acetone bath was used to keep the temperature below 15° C. for 0.5 hour. Stirring was continued for 30 minutes at room temperature, and 200 cc. of water was added with stirring. Separation of the organic layer, extraction of the aqueous phase with chloroform, washing the combined organic fractions with 10% $Na_2 CO_3$ to neutrality, and with 10% $Na_2 S_2 O_3$ to destroy the iodine, and distillation of the dried solution gave 9.7% of the 5-methyl-2-furylmethyl ketone b.p.$_{1.5}$ 60-5° C. A viscous brown resin (59 g.) was left in the distilling flask.

In a second experiment 1 cc. of the hydriodic acid catalyst in 10 cc. of acetic anhydride was added dropwise to a solution of 0.5 mole of 2-methylfuran in one mole of

acetic anhydride at 2° C. Stirring was continued for 1.5 hours at a temperature less than 5° C. and then for 6 hours at room temperature. Recovery of the product by the procedure described above gave an 8.9% yield of the ketone ($b.p._{1 \text{ or less}}$ 45-50° C.) and 36 g. of black polymer.

Identification of the 5-methyl-2-furyl methyl ketone obtained in these studies was made by preparation of the semicarbazone from standard procedures. The derivative melted at 185-6° C. The previously reported value is 190-1° C. (71).

2-Furyl methyl ketone. One mole of acetic anhydride (b. p. 134° C.) and 0.5 mole of furan (Eastman Kodak Co., white label) were mixed and cooled to -10° C. Then 1.5 cc. of the hydriodic acid catalyst was added in two portions. The temperature was kept at 0-5° C. for 45 minutes and then allowed to warm to room temperature (with occasional cooling to keep below 30° C.). After the reaction was thought to be complete it was left unattended for a short time. Later the temperature was found to be 50° C. As a result considerable polymerization occurred. The product was steem distilled to separate from the tar. Separation of the organic phase and extraction of the distillate with chloroform was followed by washing the combined fractions with 10% $Na_2 C O_3$ and 10% $Na_2 S_2 O_3$.

Distillation of the dried solution gave 28 g. (51%) of the 2-furyl methyl ketone b.p.$_{16}$ 61-4° C.

2,5 Dimethyl-3-furyl methyl ketone. To a three-neck flask containing 200 cc. of dry carbon disulfide there was added 15.7 g. (0.2 mole) of freshly distilled acetyl chloride and 52 g. (0.2 mole) of anhydrous stannic chloride. The solution was cooled to 2° C. and 19.2 g. (0.2 mole) of 2,5-dimethylfuran in 25 cc. of CS_2 was added dropwise over a period of one hour. Stirring was continued at 2-5° C. for one hour and at room temperature for 0.5 hour. Hydrolysis with cracked ice and hydrochloric acid, separation of the organic material by ether extraction, neutralization with sodium carbonate solution and distillation of the dried extract gave 17 g. of 2,5-dimethyl-3-furyl methyl ketone b. p.$_{11}$ 78-82° C. (61.5% of theory). Yields of 42% (65) and "exceeding 50%" (68) were previously reported. The oxime, prepared by standard procedures, melted at 76-77° C. A previously reported value is 78° C. (65).

3. Mercuration of 2-methylfuran

5-Methyl-2-chloromercurifuran. A sample of 5-methyl-2-chloromercurifuran was prepared for study from a previously described procedure (61). The yield of product obtained from a 0.5 mole sample of 2-methylfuran was 44% (m.p. 130-2° C.).

The above procedure uses mercuric chloride as the mercurating agent. If the acetate is substituted for the chloride the 2-methylfuran is polymerized. For example 21 g. of 2-methylfuran in 50 cc. of alcohol was added with stirring to a solution of 79.5 g. (0.25 mole) of mercuric acetate and 136 g. (1 mole) of $NaC_2H_3O_2.3H_2O$ in 1.5 liters of water. After one minute the solution became cloudy, and a sticky resin began to collect on the stirring rod. Gradually more of the resin formed, and mercurous salts and finally free mercury collected at the bottom of the beaker. This difference is undoubtedly due to the difference in negativity between the acetate radical and the chloride ion (the mercury atom in the 5-methyl-2-acetoxymercurifuran being very close to the mercurous state). Solubility relationships may also enter the picture.

5,5'-Dimethyl-2,2'-difuryl mercury. The procedure previously used to prepare 2,2'-difuryl mercury was followed (61). Fifty-nine grams (0.236 mole) of $Na_2S_2O_3.5H_2O$ was dissolved in 225 cc. of distilled water and 37.5 g. (0.118 mole) of slightly impure 5-methyl-2-chloromercurifuran was added all at once. The mixture was shaken vigorously in an erlenmeyer flask for 10 minutes and then allowed to stand for eight hours with occasional shaking.

The precipitate (dark gray) was filtered and leached with alcohol. Yield of the product was 14.5 g., m.p. 96-98° C. Recrystallization from alcohol-water solution gave a product melting at 101-3° C. (shining plates which tend to clump together). The compound is insoluble in water but soluble in acetone, alcohol, 2-methylfuran and related solvents. On standing in a closed brown bottle the material slowly deposits small amounts of free mercury. The decomposition products are separated with difficulty from the original material (as many as six or seven recrystallizations from diluted alcohol containing suspended norite may be required to raise the melting point from 85-90° C. back to the original value of 101-3° C.). It would be interesting to determine whether 5,5'-dimethyl-2,2'-difuryl might be prepared by reduction of the corresponding R_2Hg compound with a mercury electrode.

Several attempts were made to prepare the R_2 Hg compound directly from 2-methylfuran and a mercuric salt. Some of the experiments gave low yields of the desired compound. In one experiment 64 g. (0.2 mole) of mercuric acetate (Reagent grade, General Chemical Co.) was added in small portions with shaking to a solution of 0.25 mole of 2-methylfuran in 300 cc. of methyl alcohol. At the end of the addition a test with 10% sodium hydroxide showed the absence of any ionic mercury. The solution was filtered,

made alkaline with ammonium hydroxide, diluted with an equal volume of water and chilled in an ice bath. Addition of the ammonia gave first a gray and then a white precipitate. Leaching of the filtered solid, and recrystallization from ethanol-water solution gave 1.5 g. of 5,5'-dimethyl-2,2'-difuryl mercury m.p. 100-1° C. The compound gave a negative test for chloride.

Anal. Calcd. for $C_{10}H_{10}O_2Hg$: Hg, 55.3
Found Hg, 54.5, 54.6 (Hg S from alkaline solution).

In an attempt to follow the course of the mercuration of 2-methylfuran in methanol solution a quantitative titration of the liberated acetic acid was made in the following manner. To 0.25 mole of 2-methylfuran in 300 cc. of methanol there was added 64 g. (0.2 mole) of mercuric acetate in small quantities. The solution was then diluted to 500 cc. with methanol and thoroughly mixed. Five cc. aliquots were removed at various intervals for titration with standard tenth normal sodium hydroxide. A sample removed after one hour gave first mercurous compounds and then free mercury making the end point impossible to determine. After 32 hours and 72 hours 5 cc. aliquots required 30.4 cc. and 30.1 cc. respectively of the standard alkali. No free mercury was formed in either of these reactions. Based on the mercuric acetate taken (0.2 mole)

the data above indicate that 0.38 mole of acid was liberated (calculated as acetic acid).

From 0.1 mole of mercuric chloride, 0.4 mole of sodium acetate and 0.2 mole of 2-methylfuran in 200 cc. of methanol none of the R_2 Hg compound was isolated. Instead a 38% yield of the 5-methyl-2-chloromercurifuran was obtained (m.p. of crude 125-30° C.).

Reaction of 5-methyl-2-chloromercurifuran with H Cl. Thirty grams (0.095 mole) of the compound was suspended in boiling water. Then 75 cc. of hydrochloric acid (1:1) was added dropwise. The 2-methyl furan was distilled from the flask as it formed (along with some water). An 84% yield was recovered.

5-Methyl-2-furyl methyl ketone. It was found that reaction of 5-methyl-2-chloromercurifuran with acetyl chloride gave low yields of the expected ketone. For example 0.1 mole of 5-methyl-2-chloromercurifuran was suspended in 100 cc. of acetone. Then 0.1 mole of freshly distilled acetyl chloride was added dropwise. The mixture was stirred for two hours at 10° C. and then allowed to stand overnight at room temperature. Recovery of the product by the usual procedure for Fiedel-Crafts reaction gave 3 g. of the ketone, $b.p._{18}$ 78-86° C. (24% yield). The semicarbazone melted at 186° C.

4. Some derivatives of β-furfuryloxypropionitrile

β-Furfuryloxypropionitrile. Following the procedure of Bruson and Reiner (81) the compound was prepared in 80-90% yields b.p.$_2$ 105-9° C. The physical constants for the compound have been previously reported (82, 83).

β-Tetrahydrofurfuryloxypropionitrile. This compound has been previously prepared, but the physical constants seem to be listed only in the patent literature (84, 75). From a 2.25 mole reaction using 40% potassium hydroxide as the catalyst an 82.5% yield of product was obtained (99.5% if corrected for the recovered tetrahydrofurfuryl alcohol). The physical constants of the product redistilled through a Widmer column are: b.p.$_2$ 109° C., n_D^{20} 1.4538, d_4^{20} 1.048.

γ-Furfuryloxy-n-propylamine. The procedure previously reviewed by Christian (42) was followed. A 6 g. sample of Raney nickel catalyst (44), and 100 g. (0.663 mole) of γ-furfuryloxypropionitrile were placed in the 500 cc. bomb which was then chilled to -50° C. After 40 cc. of liquid ammonia had been added the bomb was quickly sealed and charged with hydrogen to a pressure of 3700 p.s.i. (25° C.). Hydrogen absorption began at about 100° C. and was complete in 20 min. Slightly more than one mole of hydrogen was absorbed. Filtration of the catalyst and distillation of the filtrate and the methanol washings

gave 82 g. (80%) of the expected amine b. $p._2$ 76-9° C. The material was purified by a second distillation through a Widmer column. Physical constants for the pure amine were b. $p._3$ 83-4° C. n_D^{20} 1.4845, d_4^{20} 1.049.

γ-Furfuryloxy-n-propylamine is miscible with water in all proportions and is quite soluble in all the common organic solvents. It exhibits the characteristic odor of amines only faintly. Concentrated hydrochloric acid, acetyl chloride and similar reagents react violently giving a black tar. Except for this polymerization by the acidic materials the reactions appear to be normal for a primary amine.

Because of its interesting properties this amine was used for the preparation of several other materials to be described below.

γ-Tetrahydrofurfuryloxy-n-propylamine. Using the method described above for the furfuryl derivative this amine was prepared by hydrogenation of 0.5 mole of the corresponding nitrile, 5 g. of Raney nickel catalyst and 35 cc. of liquid ammonia. The yields obtained from two such runs were 88% and 91% (using an initial hydrogen pressure of about 4000 p.s.i.). Untermohlen obtained this compound in 55% yields (75). Purification of the amine was accomplished by a second distillation through a Widmer column: $b.p._{0.5}$ 71-2° C., n_D^{20} 1.4609, d_4^{20} 1.001. The

previously reported values are: b.p.$_{1.5}$ 74-5° C., n_D^{20} 1.4608, d_{20}^{20} 1.0010.

γ-Furfuryloxy-n-propylamine hydrochloride. The hydrochloride was obtained by adding dry HCl gas to the amine in anhydrous ether at -20° C. When the cold solution was poured into the funnel to filter the crystals rapidly turned to a "soup". Addition of cold concentrated hydrochloric acid to the amine in cold anhydrous ether gave an oil. Polymerization began as soon as the materials warmed up to room temperature.

Phenylthiourea from γ-furfuryloxy-n-propylamine. Equal volumes of the amine and phenyl isothiocyanate were mixed in a test tube. Heat was evolved and after the main reaction was complete the tube was warmed gently. Chilling in an ice bath caused the product to crystallize. Recrystallization from an alcohol-water solution gave sparkling needles, m.p. 72.5-73.5° C.

Anal. Calcd. for $C_{15}H_{18}O_2N_2S$: N, 9.65. Found: N, 9.85.

Phenylthiourea from γ-tetrahydrofurfuryloxy-n-propylamine. Attempted preparation of this compound by the procedure described for the furfuryl derivative gave a reaction, but the product was a gum that could be pulled into long threads. All attempts to obtain the urea in a crystalline

form failed.

Salts of γ-furfuryloxy-n-propylamine. Several organic acid salts were prepared from the amine in the following manner: equivalent quantities of the amine and the acid (reagent grade) were mixed in a small beaker with cooling. Sufficient absolute alcohol was added to make a paste and the materials were thoroughly mixed. The solvent was then evaporated in a vacuum desiccator. Purification was accomplished by recrystallization from the solvent indicated for the individual compounds. The salts were all extremely soluble in water. Some were deliquescent and some showed a tendency to associate with the solvent to give gels on cooling. All except the oxalate were quite soluble in alcohol, and all were of course relatively insoluble in ether and the non-polar solvents. Recrystallizations had to be made from anhydrous solvents unless otherwise noted. Note Table 11 for the pertinent data.

Some salts of γ-tetrahydrofurfuryloxy-n-propylamine. The salts were prepared in 3-4 gram quantities in the manner described for the furfuryl derivatives. Crystalline derivatives were obtained only in a few instances because of the tendency of the salts to form gums and gels. The presence of small traces of water was frequently sufficient to produce a gum from a material which was

Table 11

Some Salts of γ-Furfuryloxy-n-propylamine

Salt	Solvent for Recrystallization	m. p. ° C.	% Nitrogen Calcd.	% Nitrogen Found
Malonate	-	gum	-	-
Benzoate	Ether-Ethanol	80-2	5.06	5.22
Oxalate	98% Ethanol	188-91	7.00	7.05
Succinate	Ether-Ethanol	94-5	6.55	6.71
Glutarate	-	gum	-	-
3,5-Dinitrobenzoate	Ether-Ethanol	129-30		
Maleate	Ether-Ethanol	147-9		

being crystallized. Table 12 shows the salts prepared.

Polymerization of γ-furfuryloxy-n-propyl amine. A 0.1 mole sample of the amine in 50 cc. of water was reacted with a slight excess of concentrated hydrochloric acid while the solution was stirred and cooled in an ice bath. Then 0.1 mole of 37% formaldehyde was added (temperature below 25° C.). After stirring for two hours (the solution was covered with a layer of foam during this time) the material was allowed to stand for 48 hours at room

Table 12

Some Salts of γ-Tetrahydrofurfuryl-oxy-n-propylamine

Salt	Solvent for Recrystallization	m. p. ° C.	% Nitrogen Calcd.	Found
Benzoate	-	gum		
Oxalate		waxy solid[a]		
Succinate	Ether-Ethanol	81-6[b]		
3,5-Dinitro-benzoate	Ether-Ethanol	133-4	11.32	11.59
Maleate		waxy solid[c]		

a. The material darkened in a vacuum desiccator and could not be recovered when recrystallization was attempted.

b. Melting point of the crude. The salt was quite deliquescent and was not recovered from solution.

c. Very deliquescent. Readily forms a gel.

temperature. Next the amber solution was stirred and heated to 40° C. A gel formed which included all of the water. Neutralization of the hydrochloride with sodium hydroxide solution gave a white curd quite similar in appearance to latex. The material was spongy and held large quantities of water. It was ground in a mortar with strong alkali to remove all the acid. Then the product was washed with water and soaked in absolute alcohol several times to displace the water. Evaporation of the alcohol in a vacuum desiccator gave a light yellow brittle material which swelled when added to water again. The dry product weighed 15.9 g. Solution of the material could not be effected with the common organic solvents. Since the material could not be purified it was not analyzed.

The above experiment was repeated to obtain a sample of the polymer of lower molecular weight. After 18 hours the reaction was stopped and excess alkali was added. The polymer was a light amber colored oil (sp. gr.> 1). After washing with water it was dissolved in 50 cc. absolute alcohol and with 4 g. Raney nickel was hydrogenated in the bomb (3700 p.s.i., initial, reaction temperature 167° C. max.). About 0.2 mole of hydrogen was absorbed. The hydrogenated polymer was an almost water white viscous oil that flowed with difficulty. It did not distill below 100° C. at one mm. It was soluble in water and reacted with concentrated

HCl without darkening. This material might find application as a plasticizer. Since the reaction proceeds rather slowly at room temperature the degree of polymerization could be controlled to any desired state.

Acid hydrolysis of β-furfuryloxypropionitrile and β-tetrahydrofurfuryloxypropionitrile. A small portion of β-furfuryloxypropionitrile when treated with a few drops of concentrated hydrochloric acid at room temperature darkened immediately, began to char and in a minute or two the reaction was quite violent. Further attempts at acid hydrolysis of this compound seemed futile.

A 46.5 g. (0.3 mole) sample of the β-tetrahydrofurfuryloxypropionitrile was mixed with 60 g. (0.6 mole) of concentrated hydrochloric acid. Heat was evolved and the mixture became homogeneous. After stirring for 10 minutes the solution was heated to 70° C. for 5 hours. Then the temperature was raised to 90° C. for 45 minutes. Forty cc. of water was added to dissolve the ammonium chloride. Extraction with several portions of ether and distillation at reduced pressure gave 27.5 g. of material with a neutralization equivalent of 218. Hence the yield was 42%.

The experiment was repeated using 0.5 mole of the nitrile. Stirring of the reactants was continued for 1.5 hours at 35° C. and 1 hour at 95-105° C. The product was recovered by evaporation to dryness on a water bath in vacuo,

filtering to separate the ammonium chloride and distillation of the filtrate and acetone washings. Distillation gave a fraction of 54 g. b.p.$_2$ 117-55° C. (N. E. 202, hence 53.4% yield).

The two samples of acid described above were combined and distilled three times through a 25 cm. asbestos wrapped Vigreux column, the middle fraction being saved each time. The third distillation gave a product b.p.$_1$ or less 135-135.5° C., N^{20}_D 1.4614, d^{20}_4 1.154, N. E. 180. (The calculated value for the neutralization equivalent is 174). There was some evidence that the compound may have been decomposing slightly during the distillation.

Several attempts were made to prepare a crystalline derivative of the β-tetrahydrofurfuryloxypropionic acid (?). The only solid derivative obtained was the p-bromophenacyl ester. This derivative was low melting (36-40° C. for the crude) and attempted recrystallization by solution in a small quantity of 95% alcohol and cooling to -30° C. gave only gels from which the product was recovered only as an oil. Attempted preparation of the p-bromoanilide and p-toluide gave viscous oils.

Basic hydrolysis of β-furfuryloxy- and β-tetrahydrofurfuryloxypropionitrile. Attempted hydrolysis of the furfuryl derivative with 24% sodium hydroxide under gentle reflux gave a brown viscous oily material which formed as

large quantities of ammonia gas were evolved. Acidification of the cold material gave a solid carbonaceous tar. The experiment was abandoned.

A similar experiment with the tetrahydrofurfuryloxypropionitrile gave after acidification, filtration to remove the salt and distillation 3 g. of material (from 0.5 mole of the nitrile) b.p.$_{0.5}$ 80-110° C., N. E. 207, 208. Ammonia gas was evolved in this experiment also.

The above data indicate that alkaline hydrolysis of these materials is not practical. This is in accord with the previous work by Christian with some related aliphatic derivatives (42).

Attempts to derivatize β-furfuryloxypropionitrile and β-tetrahydrofurfuryloxypropionitrile. Attempts to prepare a solid iminoester hydrochloride (85) of the furfuryl compound gave a black tar at -35° C. Condensation of the tetrahydrofurfuryloxypropionitrile with thioglycollic acid and dry hydrogen chloride (reference 32, page 170) gave a yellow viscous oil which did not crystallize after standing for four days in the refrigerator.

Reaction of the tetrahydrofurfuryl derivative (0.25 mole) with n-butylmagnesium bromide (0.84 mole and 0.25 mole) gave a sticky polymer in both cases. In the second experiment 3.5 g. of the nitrile was recovered unchanged. None of the expected ketone was obtained after hydrolysis.

VI. DISCUSSION

Apparently the production of high yields of furfuryl alcohol by the vapor phase hydrogenation of furfural is dependent on at least three factors: (1) the activity of the catalyst, (2) the reaction temperature - more specifically the temperature on the catalyst surface, and (3) the use of a non-porous carrier. Other factors such as contact time, hydrogen to furfural ratio, feed rate, and bed depth of the catalyst are not to be neglected. However, the use of a very active catalyst, which enables one to work at a relatively low temperature, and a non-porous carrier, which prevents "hold-up" of the reactant and serves to cool the catalyst surface by conduction, seems to make the last group of variables less critical.

It is entirely possible that when larger units are considered for the vapor phase production of furfuryl alcohol the use of the vapor-liquid equilibria (by addition of liquid furfural or the super-saturated vapor) as a coolant for the top section of the catalyst bed may be necessary. This or other cooling devices may be required to hold down the surface temperature of the catalyst when large diameter tubes are employed. These surface temperature surges not only result in the production of higher yields of 2-methylfuran, but shorten the catalyst life as

well.

After long use a given catalyst was found to be coated with a water-insoluble material that appeared to be acidic in nature. Although this apparently had no effect on the catalyst activity up to conversion ratios of 68 grams of furfural to one gram of catalyst longer use might give complete coating of the catalyst surface. In such cases flushing with 2-methylfuran or a similar solvent would be necessary to remove this organic film.

The poisoning of a Raney nickel catalyst by impurities present in the technical levulinic acid is not surprising in view of the method used to prepare the material, i.e. mineral acid hydrolysis of corn starch. The fact that a calcium stabalized copper chromite catalyst was reduced in the presence of the technical acid suggests that traces of the freé mineral acid might have been present.

Friedel-Crafts acylation of 2-methylfuran resulted in much lower yields than were obtained by similar reactions with furan and 2,5-dimethylfuran. In unsubstituted furan not only is the ring resonance undisturbed by the presence of a substituent radical but also two equal positions are available for reaction with the acylating reagent. Although 2,5-dimethylfuran is readily susceptible to ring opening this compound does not seem to polymerize so readily as 2-methylfuran. Since all the catalysts which were tested for

acylation of 2-methylfuran were shown to polymerize the compound at room temperature it seems that the lower yields of ketones may be a result of the difference in the two reaction rates, i.e. polymerization vs. acylation.

The furan mercurials might serve as a good intermediate to use in the study of the furan polymers. Cleavage of the carbon-mercury bond should serve to direct the course of the reaction.

In view of the negative results obtained by Christian (42) with the alkaline hydrolysis of β-alkoxypropionitriles it was not surprising that similar results were obtained with the corresponding furan derivatives discussed above.

Preparation and purification of solid derivatives in the β-tetrahydrofurfuryloxypropionitrile series seem to be complicated by the high solubility of the compounds and also by their association with polar solvents. These same properties are apparently somewhat less pronounced in the corresponding furfuryl derivatives.

VII. SUMMARY

1. Furfuryl alcohol has been produced in overall yields greater than 90% by one pass of the mixed vapors of hydrogen and furfural over a stabalized copper chromite catalyst. The process is simple, economical and capable of adaptation to commercial production.

2. In the unit described 68 grams of furfuryl alcohol were produced for each gram of catalyst used. The catalyst was still active at a temperature below 150° C.

3. For maximum catalyst life and minimum production of 2-methylfuran the reaction temperature is kept below 140° C. Reduction was observed as low as 100° C.

4. A non-porous carrier (e.g. glass beads) has definite advantages over activated charcoal as a catalyst support.

5. When the other variables are held constant the yield of 2-methylfuran was shown to increase with the reaction temperature.

6. 2-Valerolactone has been produced in excellent yields by the low pressure (500 p.s.i.) reduction of levulinic acid over a Raney nickel catalyst without solvent.

7. Levulinic acid has been hydrogenated over a copper chromite catalyst at high pressure without solvent to give an 80% combined yield of 2-valerolactone and 1,4-pentanediol.

8. β-Angelica lactone has been reduced at high pressure over a chromite catalyst to give 2-valerolactone and 1,4-pentanediol.

9. Some of the reactions of 2-methylfuran have been reviewed. These included polymerization by metal halides, Friedel-Crafts reaction and mercuration.

10. γ-Furfuryloxy-n-propylamine has been produced in good yields by the reduction of the corresponding propionitrile in liquid ammonia. The yield of γ-tetrahydrofurfuryloxy-n-propylamine has been improved from 55 to 90%. Several salts of these amines were prepared.

11. An interesting polymer was formed by the reaction between γ-furfuryloxy-n-propylamine and formaldehyde. The reaction is easily controlled to give a product which is of potential value as a plasticizer or an ion-exchange resin.

12. The acid and alkaline hydrolysis of β-furfuryloxypropionitrile and the corresponding tetrahydrofurfuryl derivative have been studied. Alkaline hydrolysis is impractical.

VIII.

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