NOTE TO USERS

SMALL SCALE PRODUCTION AND SOME

REACTIONS OF 2-METHYLFURAN

by

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INTRODUCTION

The loss of our major sources of natural rubber to the Japanese in 1942 made it necessary to develop a satisfactory synthetic substitute. Satisfactory types of synthetic rubber were known at that time, but quantity production was not possible because of the limited availability of raw materials. A study of the following series of reactions was started in this laboratory in an effort to make 1,3-pentadiene available as a raw material for polymerization to rubber:
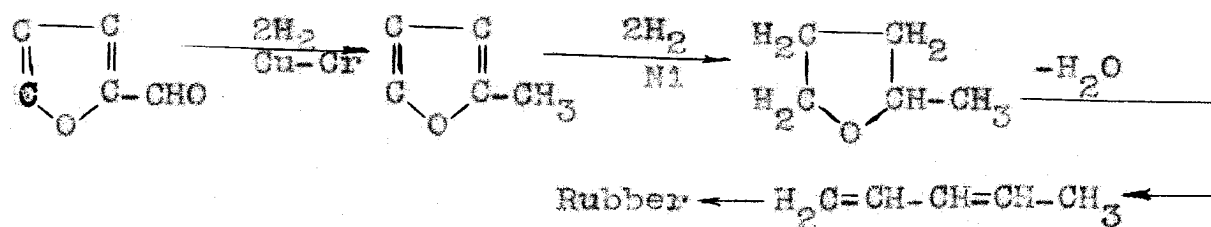
The first two steps were worked out on a laboratory scale during the emergency (1) (2). The project was then discontinued because it had become apparent that the overall process was impractical.

Burnette's work on the first step in the pentadiene synthesis indicated that this reaction might be successfully utilized on a large scale. He was not able to obtain consistently good material recovery in his experiments (1). The losses were presumably due to carbonization or adsorption on

the charcoal carrier since the apparatus was shown to be gas tight. Examination of Burnette's data revealed that in one small run he did obtain a 90 per cent yield of methylfuran, but for runs which involved any but the smallest quantities of material, his yields were 50 to 60 per cent of theory. In every case these low yields were accompanied by a material loss of about 20 per cent. Although he made no specific mention of the point, there is reason to believe that the life of the catalyst was short.

From these facts it seemed that the catalytic method would have to be improved before methylfuran could be produced on a large scale. It was the purpose of this study to devise a laboratory method for making methylfuran by which the yield would be high and the life of the catalyst long. A small pilot unit was constructed in order to obtain preliminary information for full scale pilot plant work.

Some of the reactions of methylfuran which give information on the structure of furan polymers have also been studied.

HISTORICAL

A. Hydrogenation of Furfural to Methylfuran

Since the hydrogenation of furfural in both the liquid and the vapor phase has been adequately reviewed by recent workers in these laboratories (1) (2) (3), only a summary of the more pertinent information on the preparation of 2-methylfuran will be given in this paper.

The primary object of almost all of the previous work on the hydrogenation of furfural has been the production of furfuryl or tetrahydrofurfuryl alcohol. Many of the previous workers reported the simultaneous formation of methylfuran, but in only a few cases has the amount formed been of any consequence (4) (5) (6). In three instances methylfuran has been sought as the sole product of the hydrogenation (1) (5) (7).

In 1929 Richard and Guinot (5) patented a vapor phase process using a copper catalyst for hydrogenating furfural to methylfuran. The product obtained consisted almost entirely of furfuryl alcohol, methylfuran, and unreacted furfural. By recycling the furfuryl alcohol and unreacted furfural, they claimed a yield of methylfuran only slightly less than the theoretical.

In a patent granted to Lazier (6) in 1937 it was claimed

that under the proper conditions, methylfuran is the major product formed in the vapor phase hydrogenation of furfural over copper chromite.

A process devised by Guinot (7) had as its object the synthesis of rubber from furfural. Concerning the first step in his synthesis, he claimed almost quantitative production of methylfuran by the methods revealed in the earlier Richard and Guinot patent.

Burnette studied twenty catalysts for converting furfural to methylfuran but found only two that were satisfactory. The best catalyst tried was copper chromite dispersed on activated charcoal which was observed to give a yield of 90 per cent of methylfuran. The copper catalyst formed by decomposing copper acetate on activated charcoal was found to give 80 per cent yields of methylfuran with one passage of furfural (1).

At the beginning of this study, 50 per cent yields of methylfuran were the best that could be obtained with a copper chromite catalyst. In an effort to increase the yields of methylfuran, a search was made for a more efficient vapor phase catalyst and/or catalyst carrier. Seven catalysts were tried, but none was found to be satisfactory. One was molybdeum trisulfide, used because it had been reported to give methyl-furan and n-amyl alcohol in liquid phase hydrogenations (18) (19).

Paul reported the dehydration of furfuryl alcohol at

390° over alumina to yield methylfuran and furfural as the principal products (8). This reaction was repeated as a simultaneous dehydration-hydrogenation in an effort to obviate the aldehyde formation. However, at 400-450° much polymerization and carbonization occurred and only a very small amount of methylfuran was formed.

Connor and Adkins reported a 36 per cent yield of methylfuran from the liquid phase hydrogenation of furfuryl alcohol over copper chromite at 250° and 175 atmospheres (9). In an effort to increase this yield, a run was made over copper chromite at 140-150° and 275 atmospheres. After five hours no methylfuran could be detected in the product and 70 per cent of unchanged alcohol was recovered.

When these experiments showed little promise of success, attention was directed again to Burnette's work. A review of his data disclosed that he did not state the ratio of dry chromite to dry carrier. In addition, a survey of previous work by Calengaert and Edgar showed that they had discovered the activity of the chromite catalyst to be dependent on its decomposition temperature (10). Burnette did not mention this fact as being important. Subsequent investigation disclosed that a very active copper chromite catalyst could be made if, in the decomposition step of its preparation, the temperature was properly controlled. When this catalyst was distributed on charcoal in a 1:1 ratio, 90-95 per cent yields

of methylfuran were obtained in one passage of furfural through the catalyst. Consequently, copper chromite was adopted as the preferred catalyst for converting furfural to methylfuran.

Copper chromite and related types have been the subject of numerous patents (11) (12) (13) (14) (15).

The investigators' primary aims were to produce a more efficient and a more stable catalyst. Their efforts are particularly significant in view of the results obtained in this investigation. In addition to the decomposition factor pointed out above, it was found that small changes in the method of preparation materially altered the activity of this catalyst.

In 1945 Wilson, while attempting to produce furan from furfural, observed that nickel- or cobalt- containing catalysts gave rises to small amounts of methylfuran. Iron and copper chromite catalysts gave pure methylfuran in 18 and 80 per cent yields, respectively (4).

Natta, Rigamonte, and Beate obtained results that were somewhat different from those of Wilson's. They do not mention copper chromite as being active in producing methyl-furan from furfural but instead state that Ni-Co and Ni-Fe catalysts were active for hydrogenating the lateral chain (16).

A different type of catalyst was employed by Zelinskii, Packendorf, and Leder-Packendorf, who investigated the selective hydrogenation of carbonyl groups that were situated alpha to a phenyl or furyl nucleus (17). With a palladium catalyst, formed in situ from palladium chloride, they obtained a small yield of methylfuran by liquid phase hydrogenation of furfural. Considerable resinification was caused by the hydrochloric acid which formed on reduction of the palladium chloride. Suspension of the catalyst on calcium carbonate would probably obviate this difficulty. However, it is unlikely that a process employing such a palladium catalyst will ever attain industrial significance.

B. Reactions of 2-Methylfuran

Methylfuran was first obtained by Atterberg in 1880 by the distillation of wood tar from spruce (Pinus sylvestris) (20). He recognized it as the next higher homologue of furan and, because of its source, called it sylvan. This compound was later isolated by Harries (21) from beech wood tar and by Fraps (22) from hardwood tar.

Atterberg announced that most reagents polymerized methylfuran. He found that phosphorus pentachloride reacted on methylfuran with considerable charring, giving a volatile liquid which contained chlorine. On the basis of

analysis, he stated it to be a hydrochloride ($C_5H_6O + HCl$)
contaminated with methylfuran. All his efforts to prepare
this chlorine-containing compound in large amounts met with
failure (20).

He also found that concentrated hydrochloric acid or
dry hydrogen chloride in ether caused vigorous polymerization
of methylfuran. He reported that by cooling the reaction well
and by working with small quantities an oil free of chlorine
could be obtained which boiled at 235-245°. On analysis,
this oil was found to have the empirical formula, $C_{15}H_{22}O_2$
(ca. 3 x C_5H_6O), which indicated it to be a trimer. His
attempts to prepare this oil in large quantities also failed.
Bromine was found to react so vigorously that the mixture
ignited. With bromine water Atterburg obtained a soluble sub-
stance which could be extracted with ether from the water
solution. Evaporation of the ether solution left only a resinous
mass. Treatment of the ether solution with silver oxide did
not improve the product. He isolated acetic acid (as the silver
salt) by oxidation of methylfuran with potassium permanganate.
In addition, he found that methylfuran would not react with
alkali, sodium, or acetic anhydride (20).

In 1898 Harries reported that concentrated sodium
hydroxide polymerized methylfuran. He found that the yellow
color which methylfuran developed on standing could be re-
moved by treating it with a very small amount of alcoholic HCl.

Harries also reported that a spruce splinter which had been
moistened with methylfuran turned green when dipped in con-
centrated hydrochloric acid (21).

This investigator hydrolyzed methylfuran to levulinic
aldehyde by heating it in a sealed tube with dilute hydro-
chloric acid at 120° for twelve to twenty-four hours. How-
ever, the yields of aldehyde were not good.

$$\text{(furan ring: HC—CH, HC—O—C-CH}_3\text{)} + H_2O \xrightarrow{\text{HCl}} CH_3COCH_2CH_2CHO$$

Alcoholysis with absolute methanol and dry hydrogen chloride
was accomplished easily at reflux temperatures to give
levulinaldehyde dimethyl acetal in 80 per cent crude yield.

$$\text{(furan ring: HC—CH, HC—O—C-CH}_3\text{)} + 2\ CH_3OH \xrightarrow{\text{HCl}} CH_3COCH_2CH_2CH\big(OCH_3\big)\big(OCH_3\big)$$
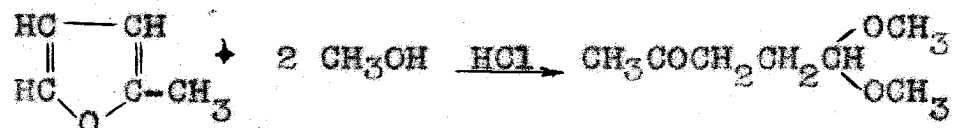
Nellensteyn reported that gaseous hydrogen iodide re-
acted violently with methylfuran to give water, iodine, and
carbon (23). A similar violent reaction with bromine and
hydrogen bromide was observed by Yur'er and Lifanov (34).
They reported that only black tars were formed at room
temperature and at -10°.

Rinkes nitrated methylfuran in acetic anhydride at
-5°. He obtained an open-chain acetoxynitro intermediate
which was cyclized to 5-nitro 2-methylfuran by means of
pyridene (25).

$$\text{CH}_3-\underset{\underset{\text{O}}{|}}{\text{C}}\overset{\overset{\displaystyle \text{HC}---\text{CH}}{}}{\underset{\text{CH}}{}} \quad \xrightarrow[\text{Ac}_2\text{O}]{\text{HNO}_3} \quad \text{CH}_3\underset{\overset{|}{\text{OH}}}{\text{C}}=\text{CH}-\text{CH}=\underset{\overset{|}{\text{NO}_2}}{\text{C}}-\text{OAc} \quad \xrightarrow{\text{C}_5\text{H}_5\text{N}}$$

$$\text{CH}_3\text{C}\overset{\displaystyle \text{HC}---\text{CH}}{\underset{\text{O}}{}}\text{C}-\text{NO}_2$$
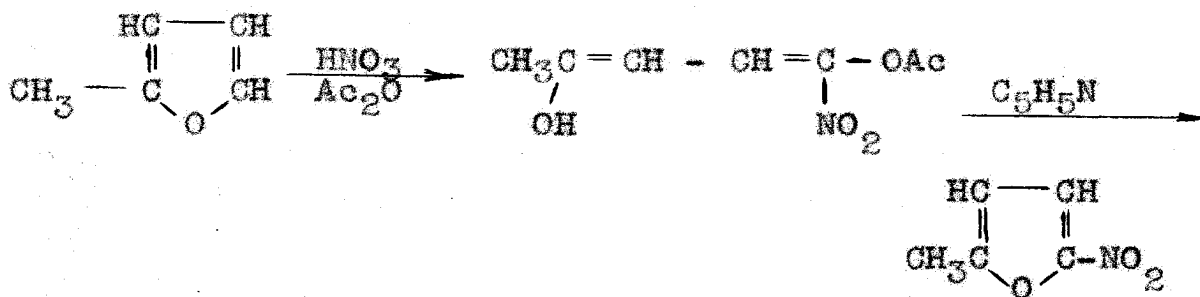
A dinitro derivative was also obtained which could not be cyclized because of the hindering effect of the second nitro group. The proposed structure of this compound is shown below:

$$\text{CH}_3-\underset{\overset{|}{\text{OH}}}{\text{C}}=\underset{\overset{|}{\text{NO}_2}}{\text{C}}-\text{CH}=\underset{\overset{|}{\text{NO}_2}}{\text{C}}-\text{OAc}$$
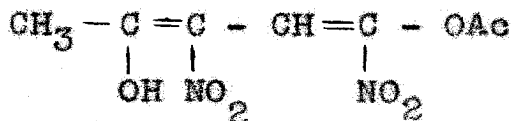
Reichstein (26) prepared 5-methylfurfural in 60 per cent yield from the reaction of methylfuran and dry hydrogen cyanide at -15°. He showed that the ease of the Gatterman reaction in the 5-membered heterocycles was in the order: pyrolle furan thiophene (27).

The Friedel-Crafts reaction has often been employed to make furyl ketones from furan and acid chlorides. However, there are only three recorded instances of methylfuran being used in this reaction. Reichstein synthesized 2-methyl-5-acetylfuran in poor yields from methylfuran and acetyl chloride (28). Zinc chloride was found to be a better catalyst for this reaction than either stannic or aluminum chloride. Shulkin, Shemastina, and Cherkasova (29) synthesized this ketone in approximately the same yields as

Reichstein. Methylfuryl heptadecyl ketone was obtained in
unstated yield by Ralston and Christensen from methylfuran
and stearyl chloride (30). No report appears in the literature
on alkylation of methylfuran by means of the Friedel-Crafts
reaction.

The metalation of methylfuran has been reported by a few
investigators. Gilman and Breuer stated that methylfuran re-
acted with ethyl, phenyl, and benzyl sodium to give on carbon-
ation, poor yields of 5-methylfuroic acid (31). They also
found that sodium potassium alloy gave a trace of the same
acid. Lithium, sodium, 4 per cent sodium amalgam, sodamide,
and sodium hydroxide failed to react in the range from 60°
to 100°. Gilman and Bebb reported that 17 and 29 per cent
yields of 5-methylfuroic acid were obtained from n-butyl lithium
and phenyl lithium, respectively (32). Gilman and Wright pre-
pared 5-methyl 2-chloromercurifuran from methylfuran and
mercuric chloride (33).

The reaction of methylfuran over alumina with aryl
amines (34), ammonia (35) (36), and hydrogen sulfide (37) has
been reported to give low yields of methyl thiophene and the
corresponding methylpyrroles. Yur'ev reported a 24 per cent
yield of 2-methylpyrrole from the reaction of methylfuran
and ammonia at 450° over alumina (34). A yield of 11 per cent
of 2-methyl thiophene was obtained with hydrogen sulfide at

350°. Later this same investigator prepared aryl pyrroles by the action of aromatic amines and methylfuran over alumina at 475°. Thus, 1-phenyl 2-methylpyrrole, 1-o-tolyl 2-methyl-pyrrole, and 1-p-tolyl 2-methylpyrrole were prepared in low yields from the corresponding amines (34). Natta, Mattei, and Bartaletti studied various catalysts for converting methyl-furan to methylpyrrole (36). They found that mixtures of alumina and chromia gave the best results.

Methylfuran forms a diene addition product with maleic anhydride that has been variously reported to melt at 71-2° (37), 80° (38), and 84° (39). The adduct decomposes into its components above its melting point. Methylfuran has also been reported to undergo the Diels-Alder reaction with the dimethyl (40) and diethyl (40) esters of acetylenedicarboxylic acid. It has been found that β-nitrostyrene (41) and quinone (42) will not undergo the diene reaction with methylfuran.

An abnormal reaction has been reported by Alder and Schmidt (43). They have shown that acid catalysts cause methylfuran to undergo, with certain unsaturated compounds, a "substituting addition" instead of the normal diene addition. The reactions are shown below:

$$RH + CH_2 = CHCOCH_3 \xrightarrow{SO_2} RCH_2CH_2COCH_3$$

$$RH + CH_2 = CHCOC_6H_5 \xrightarrow{SO_2} RCH_2CH_2COC_6H_5$$

$$RH + CH_3CH = CHCHO \xrightarrow{SO_2} RCH \quad CH_2CHO$$
$$\underset{CH_3}{|}$$
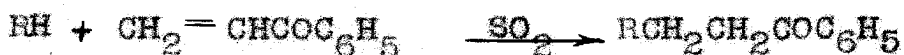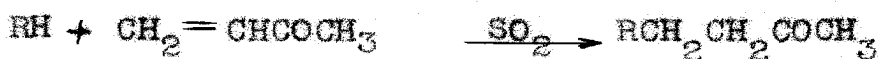
where R represents the

$$\underset{CH_3-C \underset{O}{\diagup} C-}{\overset{HC-CH}{\underset{\parallel \; \parallel}{}}}$$

group.
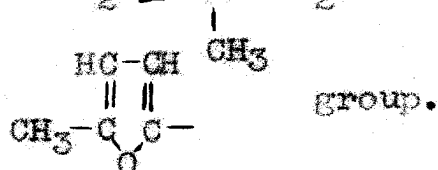
The structure of the crotonaldehyde condensation product was proven by oxidation with potassium permanganate to methyl succinic acid.

Brown has oxidized methylfuran to furoic acid by means of potassium ferricyanide (44). Böeseken, et al reported the oxidation of methylfuran with peracetic acid to give the enol-lactone of β -acetolactic acid (45).

$$ \begin{array}{c} HC - CH \\ \parallel \quad \parallel \\ CH_3 - C \quad \diagdown_O\diagup CH \\ \end{array} + 2CH_3CO_3H \longrightarrow \begin{array}{c} HC - CHOH \\ \parallel \quad \mid \\ CH_3 - C \quad \diagdown_O\diagup C=O \\ \end{array} + 2CH_3CO_2H $$
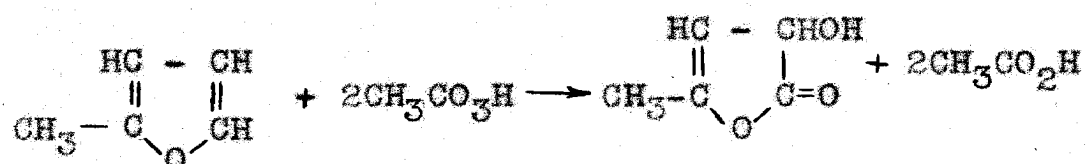
The liquid and vapor phase hydrogenation of methylfuran has been reviewed by Heumann (2). Topchiev has stated that the double bond between the unsubstituted carbon atoms is first to be saturated (46). He drew this conclusion from the fact that the simultaneous hydrogenation and hydration of methylfuran gave 3-acetopropyl alcohol. This compound could only be formed by hydrogenation to 4,5-dihydromethylfuran and subsequent hydrolysis to the keto alcohol as shown below:

$$ \begin{array}{c} HC - CH \\ \parallel \quad \parallel \\ CH_3 - C \quad \diagdown_O\diagup CH \\ \end{array} + H_2 \longrightarrow \begin{array}{c} HC - CH_2 \\ \parallel \quad \mid \\ CH_3 - C \quad \diagdown_O\diagup CH_2 \\ \end{array} \xrightarrow{H_2O} CH_3COCH_2CH_2CH_2OH $$
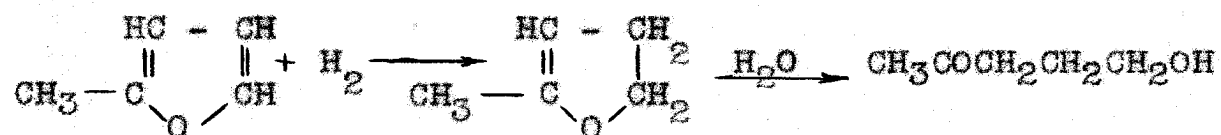
An English patent suggests the use of methylfuran as a selective solvent for the purification of crude anthracene (47). In view of the wide use of furfural as a selective solvent, it would not be surprising if methylfuran also found application in this field.

C. Furan Resins

Although it has long been known that furan compounds could be readily polymerized, little progress has been made toward proving the structure of the polymers. The polymerization of furan, furfural, and furfuryl alcohol takes place so readily that only intractable materials have been isolated from the reactions.

Before conducting experiments on methylfuran, it seemed advisable to review previous work on the structure of related resins. The relation of the monomers cyclopentadiene, indene and coumarone to methylfuran is evident from the structural formulae below:
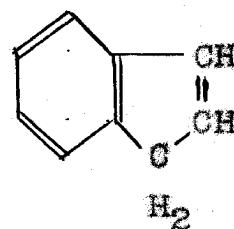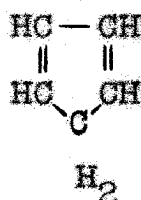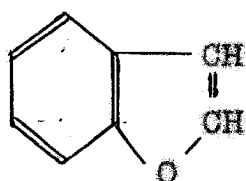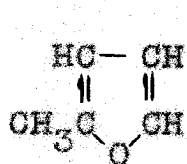
Methylfuran   Coumarone   Cyclopentadiene   Indene

Staudinger, et al report that cyclopentadiene forms two types of polymers. Heat caused the formation of a polymer whose structure was formulated as (48):
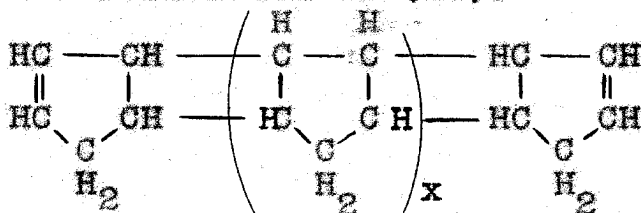
This substance was an amorphous, insoluble and infusible material. Metallic chlorides gave polymers that apparently had the structure (49):

$$HC = CH \quad \left(HC = CH \right) \quad HC = CH$$
$$H_2C \quad CH - HC \quad CH - HC \quad CH_2$$
$$C \quad C \quad C$$
$$H_2 \quad H_2 \quad_x \quad H_2$$
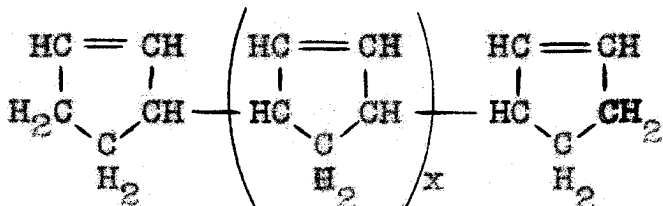
These polymers were crystalline substances that could be separated into fractions of high and of low molecular weight. They exhibited varying degrees of solubility and showed some rubber like properties.

The resins produced from indene and coumarone by acid catalysts were postulated as having the structure (50):

$$H_2C - CH \quad \left(\begin{array}{cc} H & H \\ C - C \\ CH_2 \end{array} \right) \quad C = CH$$
$$CH_2 \qquad \qquad \qquad \qquad CH_2$$
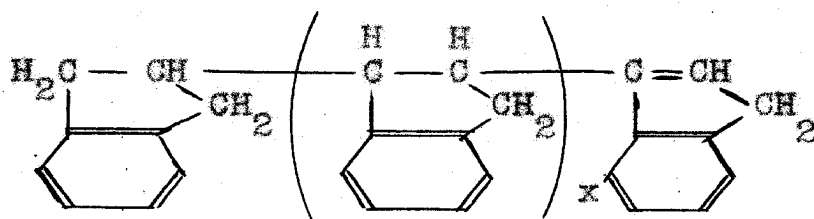
The poor aging characteristics of these resins have been attributed by Carmody to the residual double bond in the cyclopentadiene nucleus (51). Removal of this double bond by hydrogenation greatly stabilized the resins (52) (53).

The foregoing authors presented no conclusive evidence that the assigned structures are correct. In contrast, the dimer and trimer of cyclopentadiene have been reported to have the structures (54):
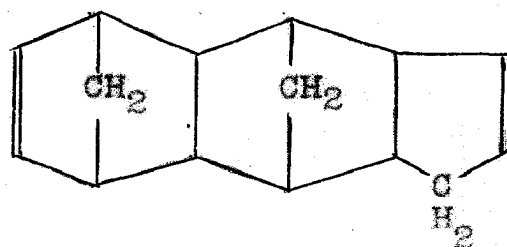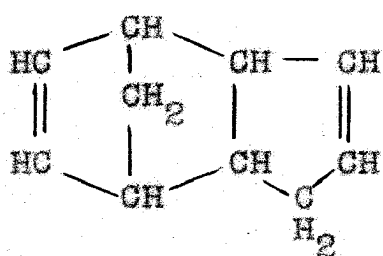
The polymerization in this case would be essentially that of a Diels-Alder reaction.

EXPERIMENTAL

A. Hydrogenation of Furfural to Methylfuran

1. Source of materials

The furfural used in the laboratory experiments was a middle fraction obtained by vacuum distillation of the technical product. Furfuryl alcohol was obtained in a similar manner from the Eastman practical material. Unless otherwise stated, commercial furfural was used without purification in the semi-pilot unit.

Norite A (American Norite Company, Inc.) and Nuchar (West Virginia Pulp and Paper Company) were the trade names of the two types of 4-10 mesh activated charcoal used in the investigation.

The following materials were the reagent grades supplied by the General Chemical Company: copper nitrate trihydrate, ammonium dichromate, barium nitrate, calcium nitrate tetrahydrate, cupric acetate monohydrate, nickelous acetate tetrahydrate, ferous oxalate dihydrate, and ammonium molybdate.

The $Cu_2-V_2O_4-CaO$ catalyst was made from materials kindly supplied by Dr. Lefrancois (55).

2. Description of laboratory apparatus

(a) Hydrogenation unit. The apparatus shown in figures 1 and 2 is essentially that of Burnette (1) with the exception that a drying tower has been omitted from the system. The catalyst chamber 2 was a 28 mm x 55 cm pyrex tube filled to a depth of 44 cm with catalyst, with six to eight centimeters of glass beads on top to act as an evaporator. The electric furnace 3 was constructed by winding nichrome wire on a 35 mm pyrex tube.

After the catalyst had been dried at $190-200^{\circ}$ in a slow stream of hydrogen, gas recirculation was started by means of the diaphrgm pump 9. Furfural was then added dropwise from 1 onto the hot beads where it was vaporized and swept into the catalyst. The water and unchanged furfural condensing from the gas stream in 4 were collected in 7, which was kept immersed in an ice bath. The gas stream then passed into the dry ice-acetone condenser where the methylfuran and the last traces of water were removed. The unreacted hydrogen was recirculated over the catalyst.

The water and furfural were removed from 7 whenever desired by opening the clamp on the drainage tube. The ice crystals which occasionally plugged the entering tube of 8 were removed by raising the trap and warming the tube until the ice fell into the small flask.
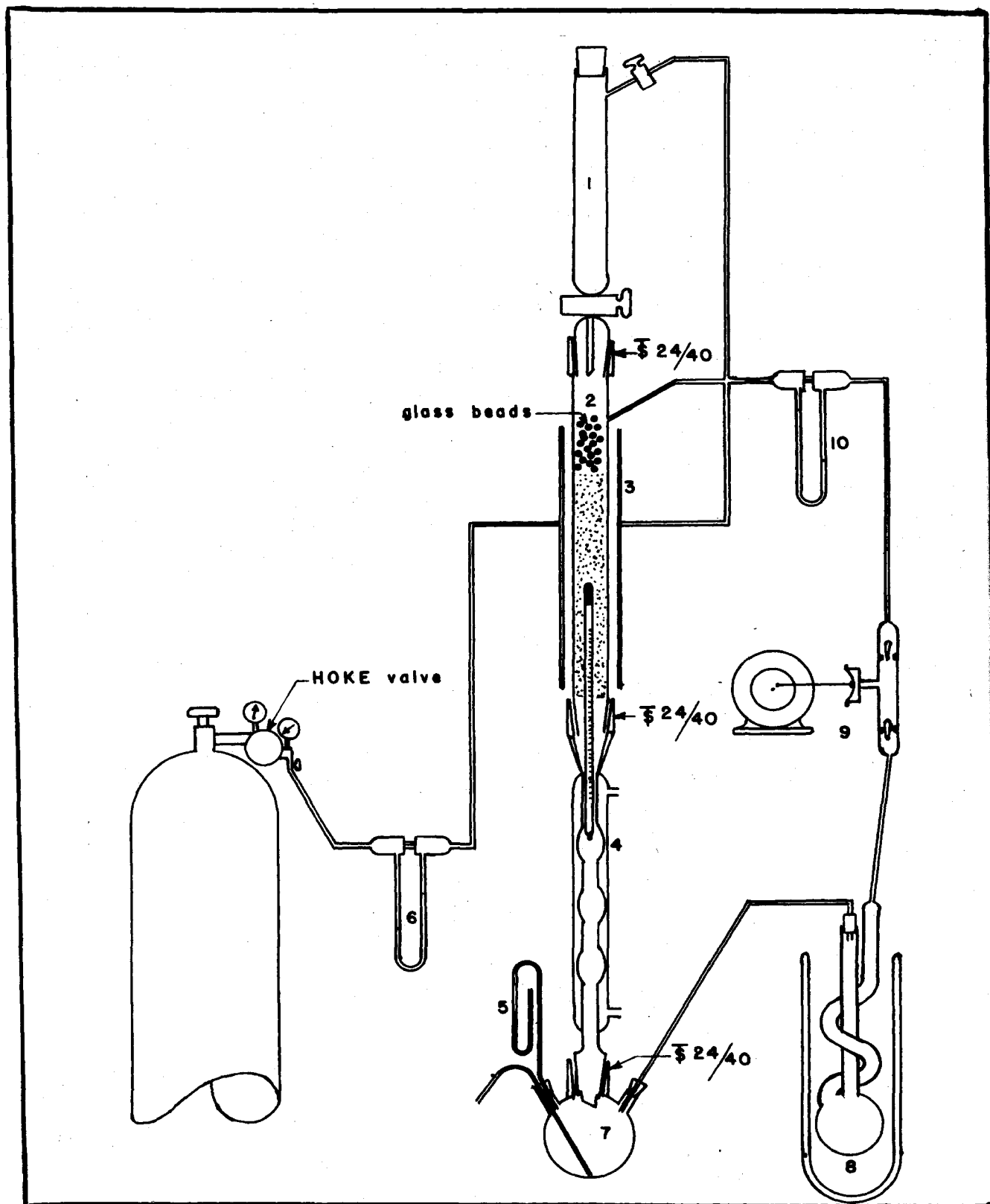
Figure 1.   Laboratory Hydrogenation Apparatus
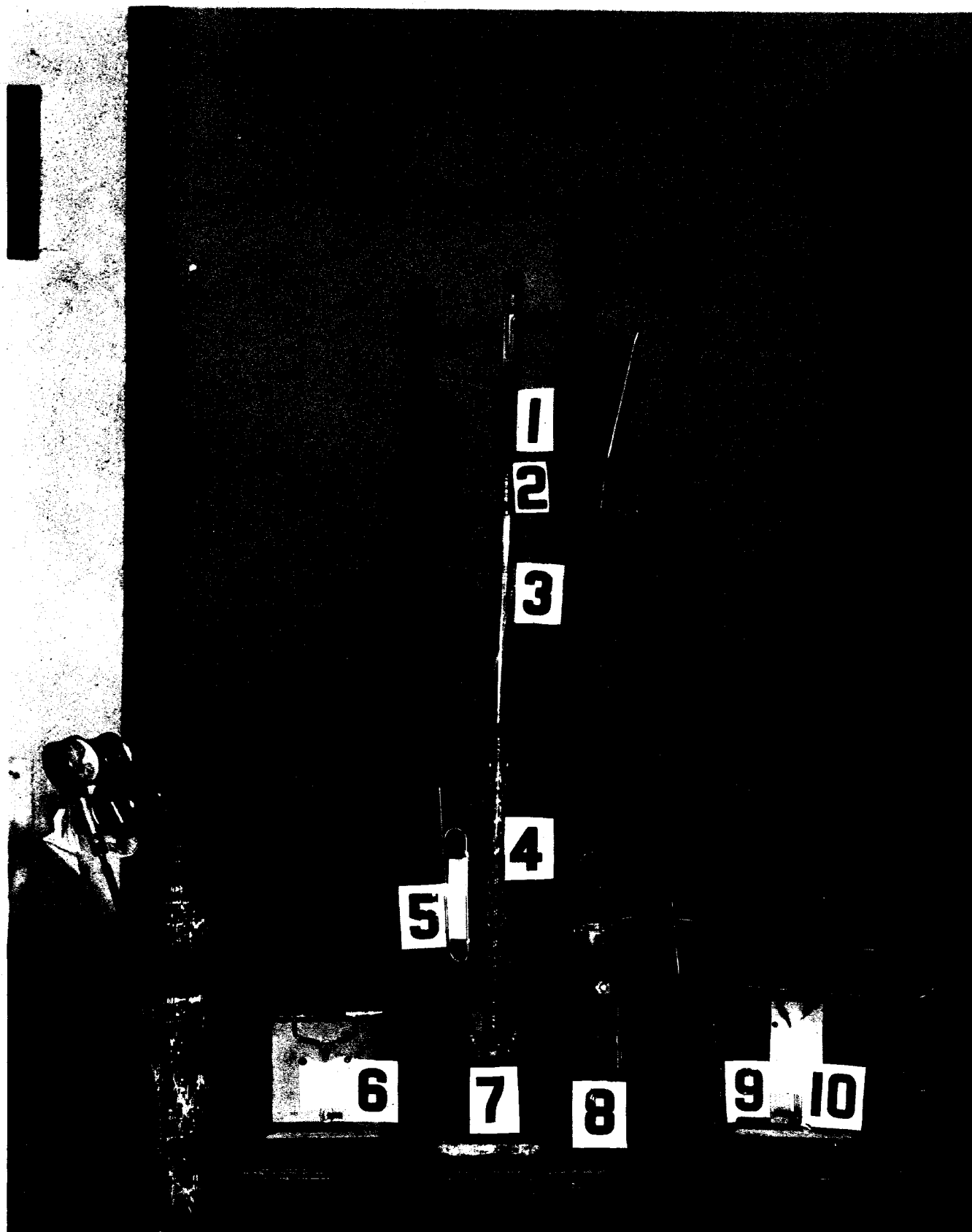
Figure 2.   Laboratory Hydrogenation Apparatus

Flowmeter 6 indicated the rate at which hydrogen was being consumed, while 10 indicated the rate of hydrogen recirculation. The hydrogenation pressure, as measured by manometer 5, was controlled within $\pm$ 1 cm of atmospheric pressure by the Hoke valve on the hydrogen tank.

(b) <u>Kiln for decomposing copper chromite</u>. A small kiln was constructed in the following manner: A 28 mm x 60 cm pyrex tube was placed on wooden bearings spaced 50 cm apart and inclined at an angle of 3°. A 3" wooden pulley, clamped around the upper end of the tube, was connected by a 3/8" V-belt to a drive that rotated the tube at 30 rpm. The kiln was heated over a 40 cm length with a small electric furnace. Temperatures in the kiln were measured by a 360° thermometer inserted in the high end so the bulb rested on the glass about one-third the way down the tube.

After the apparatus was heated to $300-305^o$, the complex chromates were fed to the kiln at such a rate that the heat of decomposition caused a temperature rise of approximately 40° C. During operation, the bulb of the thermometer was rested at the point where the decomposition proceeded vigorously in order to record the highest temperature attained in the kiln.

It was necessary to keep a slow stream of air blowing down the kiln during the decomposition in order to remove evolved gases.

3. Description of laboratory experiments

    (a) Liquid phase hydrogenation.

Experiment No. 1

Four and six-tenths grams of ammonium molybdate were dissolved in 10 cc of concentrated ammonium hydroxide diluted with 25 cc of distilled water. A rapid stream of hydrogen sulfide was passed in for 15 minutes and the MoS_3 then precipitated from the dark red solution by addition of 6N sulfuric acid. After the trisulfide was washed thoroughly with water, it was allowed to stand overnight at 90° in 1% barium chloride to remove the last traces of occluded sulfuric acid. The product was then washed with two 200 cc portions of boiling water, one 100 cc portion of anhydrous alcohol, and finally with 100 cc of Skelly D.

Twenty-five grams of furfural were hydrogenated over 4 g of this catalyst in a Parr bomb for two hours at 240° and 2000 psi. The product, which smelled strongly of sulfides, was distilled directly to give 5 g of material boiling below 70°. Although this fraction gave a pine splinter test for methylfuran, it could not be polymerized to any great extent by concentrated sulfuric acid, thus indicating that the methylfuran content was small.

A MoS_3 catalyst, prepared by precipitation with acetic acid instead of sulfuric acid, caused decomposition of the furfural on attempted hydrogenation.

Experiment No. 2

Ten grams of copper chromite (p. 24) and 98 g of furfuryl alcohol were heated at 140-150° for five hours under a hydrogen pressure of 275 atmospheres. Distillation of the reaction mixture gave 5 g of n-amyl alcohol, 15 g of a mixture of pentanediol-1,2 and -1,5, and 70 g of unchanged furfuryl alcohol. No methylfuran could be detected.

(b) _Vapor phase hydrogenation_. The hydrogenation units described by Burnette were used for the first 11 experiments.

Experiment No. 1

A double quantity of complex chromate, prepared according to Adkins (56), was decomposed in a casserole in such a manner that only a small amount of incadescence was observed during the ignition. The yield of leached chromite was 300 g.

The 300 g. of chromite were distributed on 600 g of wet Norite A and placed in Burnette's large hydrogenation apparatus. With the catalyst at 200-215°, 1500 g. of furfural were hydrogenated in 12 hours. The run was discontinued after 12 hours because hydrogen was no longer being absorbed. Distillation of the product gave 500 g (39%) of methylfuran.

Experiment No. 2

A double quantity of complex chromate, prepared as before, was allowed to become incandescent during the decomposition

to the chromite. The yield of chromite after extraction with 10% acetic acid was 280 g.

No hydrogenation occurred at 200-250° when this catalyst was tested in Burnette's large apparatus.

Experiment No. 3

The complex chromate prepared using the quantities described by Adkins, loc. cit., was not allowed to become incandescent during the decomposition to the chromite. The yield of leached catalyst was 155 g.

Twenty-five grams of this chromite were sprinkled on 125 g of 14-30 mesh activated alumina (Aluminum Ore Co., Grade A) wet with ether. The catalyst was dried for two hours at 200° in a slow stream of hydrogen in the laboratory unit described by Burnette.

The chromite was deactivated when furfural was admitted to the catalyst because of a 100° temperature rise resulting from the heat of hydrogenation. Only 5 g (11.6%) of methylfuran were obtained from 50 g of furfural.

A duplicate hydrogenation was made in which care was taken to avoid the temperature surge of the earlier run. In 12 hours, 220 g of furfural were hydrogenated at 200-250° to give 61.9 g (32.9%) of methylfuran. In addition, 27.7 g of furfural, 27.0 g of furfuryl alcohol and 22.0 g of high boiling material were obtained. The total material recovery was 68% of theory.

Experiment No. 4

Twenty-five grams of the copper chromite prepared in experiment 3 were sprinkled on 105 g of ether-wet silica gel and the catalyst dried for two hours at 200° in a slow stream of hydrogen.

While the catalyst was held at $200-240^o$, 280 g of furfural were passed through the unit in 8 hours to give 220 g of product, of which 69 g (28.8%) were methylfuran. The methylfuran obtained in this run did not turn yellow after three weeks exposure to light and air. This is in direct contrast to all other preparations which turned yellow within 24 hours.

Experiment No. 5

A $Cu_2O-V_2O_4-CaO$ catalyst was prepared as follows: Sixteen grams of Cu_2O and 8 g of V_2O_4 were ground together in a mortar. Sixteen grams of freshly prepared calcium oxide and 30 g of medium-fine asbestos fiber were then intimately mixed with the oxides. The catalyst was packed into the hydrogenation chamber and heated to 200° in a stream of hydrogen. No hydrogenation occurred when 115 g of furfural were passed through the catalyst.

Experiment No. 6

Sixty grams of ferrous oxalate dihydrate were reduced in a stream of hydrogen at 500° for 3 hours and the resulting pyrophoric iron allowed to stand overnight at 250° in an atmosphere of hydrogen. No hydrogenation occurred in the

temperature range of 210-325° when 50 g of furfural were
passed over the catalyst.

Experiment No. 7

A catalyst, made by mixing 25 g of copper chromite
(Exp. 3, p. 24) with 15 g of freshly prepared calcium oxide,
was placed in the hydrogenation chamber with no carrier. When
50 g of furfural were passed over the catalyst at 200°, only
2-3 g of methylfuran were obtained.

Experiment No. 8

Twenty-five grams of MoS$_3$ were prepared from 27.6 g of
ammonium molybdate in the manner described on page 20. The
trisulfide was distributed on 60 g of porous plate and dried
for two hours at 200° while the unit was flushed with hydrogen.
No hydrogenation occurred when 50 g of furfural were passed
through the catalyst.

Experiment No. 9

Seventy-eight and five-tenths grams of monohydrated
cupric acetate and 1.06 g of nickelous acetate tetrahydrate
were dissolved in 800 cc of hot 10% acetic acid. Seventy-
eight and a half grams of lump Norite A were added to this
solution, the mixture boiled for two minutes, filtered and
the charcoal lumps dried in an oven for thirty minutes. This
alternate saturation and drying of the carbon was repeated
until all of the cupric and nickel acetates had been deposited
on the charcoal. Fifty milliliters of hydrochloric acid were

added to the last 200 cc of solution to prevent hydrolysis of the acetates.

This catalyst, after overnight reduction in a stream of hydrogen at 225-250°, contained 25 g of copper and 0.25 g of nickel on 78.5 g of charcoal. No hydrogenation occurred when 50 g of furfural were passed over the catalyst.

Experiment No. 10

A saturated solution of nickelous acetate containing the equivalent of 5 g of metallic nickel was poured over 220 g of 4-6 mesh activated alumina (Aluminum Ore Co.). This material was reduced with hydrogen at 400-425° for five hours.

Ninety-eight grams of furfuryl alcohol were passed over the catalyst at 400-450° during the course of 4 hours. Twenty-one grams of water and 5 cc of a light blue oil, which was not further investigated, were recovered from the water condenser. The dry ice trap yielded 13 g of a liquid which gave, on distillation, 8 g of material boiling at 40-60° and 3 g of material boiling at 60-70°. No pure methylfuran could be isolated from the higher-boiling fraction.

Experiment No. 11

The complex copper-ammonium chromate was prepared according to Adkins, loc. cit., with the exception that 31 g of $Ca(NO_3)_2 \cdot 4H_2O$ were used instead of 31 g of $Ba(NO_3)_2$. The decomposition, carried out in a casserole in 10 small batches to avoid a violent reaction was observed to be

self-sustaining for only a very brief period. The chromite
obtained after extraction with 10% acetic acid had a definite
brownish cast. The yield of catalyst was 160 g.

Ten grams of the chromite were sprinkled on 30 g of wet
Norite A and the mass dried in hydrogen at 220-250°. Fifty
grams of furfural were passed through the catalyst while the
temperature was held at 210°. Five grams of methylfuran were
recovered from the dry ice trap.

Experiment No. 12

This experiment was conducted over an extended period of
time and varying many conditions. Subheads a, b, c, will be
used to separate the component parts.

12a. Burnette's laboratory apparatus was modified as
follows: The reaction chamber was set in a vertical position
and jacketed with a glass heater in order that the catalyst
might be observed at all times. The furfural was added drop-
wise to a hot flask (190°) and the vapors passed up through
the catalyst bed. Activated alumina was used as a drying
agent instead of calcium chloride.

12b. Thirty-five grams of copper chromite (p. 27) were
deposited on thirty grams of Nuchar in the following manner:
The charcoal was immersed in distilled water for a minute or
two, the excess water poured off, and a 5 g portion of copper
chromite then sprinkled over the surface of the wet charcoal.
After the chromite and charcoal had been thoroughly mixed

together, another 5 g portion of chromite was spread over the surface of the carbon. This deposition process was repeated until all of the chromite had been deposited on the charcoal. The catalyst was placed in the hydrogenation chamber and dried overnight at 200° in a stream of hydrogen.

The catalyst, which filled the tube to a depth of 46 cm when wet, settled on drying so that the catalyst bed was approximately 44 cm in length.

12c. Hydrogen recirculation was set at 1100 cc/min to give a contact time of approximately 10 seconds (see Calculations, p. 57). Furfural was added dropwise to the hot vaporization flask at such a rate that the heat of hydrogenation caused the catalyst bed temperature to rise from 215° to 218°. Extended operation showed that the furfural was being hydrogenated at a rate of 20 g/hr.

When all of the furfural had been passed through the catalyst, 10 cc of water having a strong odor of amyl alcohol was recovered from the water condenser. Saturation of the water with potassium carbonate caused separation of 1/2 cc of an oil, assumed to be amyl alcohol. The dry ice trap contained 28.5 g (66.8%) of crude methylfuran. The total material recovery was 74% of theory.

12d. Hydrogenation of 50 g of furfural was started at a rate of 20 g/hr with the drying tower removed from the system. However, after a half an hour of operation the tower

was inserted again because the methylfuran condenser plugged with ice crystals.

The formation of ice in the methylfuran trap during the last half hour of the hydrogenation indicated that the drying tower was exhausted. Fresh activated alumina was placed in the tower at the end of the run.

The products of hydrogenation consisted of 38 g (89%) of crude methylfuran and 10 cc of water containing 1/2 cc of amyl alcohol. The material recovery was 48 g, or 92% of the calculated amount.

12e. The catalyst was then allowed to stand overnight at 200° with a slow stream of hydrogen passing through it. The next day 50 g of furfural were hydrogenated at 228° and a rate of 25-30 g/hr. The total weight of product was 32 g, representing an 81% material recovery. In addition to 30.5 g (71.5%), of methylfuran, there was obtained 9 g of water and 1.5 g of unreacted furfural. No amyl alcohol could be detected in the water layer.

The appearance of the unreacted furfural indicated that the furfural-hydrogen ratio had become too low for complete conversion of the furfural to methylfuran. (see Calculations, p. 57).

12f. The next 50 g of furfural was hydrogenated at 220° at a rate of 15-20 g/hr to give 35.5 g (83%) of methyl-furan. The total material recovery was 87%.

At the end of this run it was evident from the ice formation in the methylfuran condenser that the drying tower was exhausted.

12g. A comparison of the results of the previous experiments showed that: (1) when fresh alumina was used both the material recovery and methylfuran yields were low and (2) as the drying agent became exhausted both the recovery and methylfuran yields increased. This indicated that the losses were due to absorption on the alumina. Consequently, the drying tower was omitted for the duration of the next run.

Fifty grams of furfural, when passed through the catalyst at 225° and 20 g/hr, yielded 42.5 g (100%) of crude methyl-furan. The total material recovery was 100% of that calculated.

The results of this run substantiated the contention that methylfuran was being lost by absorption on the alumina. In all future runs a drying tower was omitted.

12h. At this point the combined products from the 250 g of furfural were distilled after drying over sodium. The total yield of methylfuran boiling at 61-65°/735 mm was 174 g which represented an 81.5% overall yield. That the crude product was practically pure methylfuran was shown by the fact that no forerun appeared and only one gram of distilla-tion residue remained.

12i. The catalyst was then allowed to stand at 200° for two days with a slow stream of hydrogen passing through it.

When operations were resumed, the contact time was

reduced from 10 to 5 seconds by increasing the hydrogen recirculation rate to 2160 cc/min. Fifty grams of furfural were hydrogenated at 230° at a rate of 25 g/hr to give 40.0 g (93.7%) of methylfuran. The total material recovery was 96%. Since the decreased contact time apparently had no ill effects, a 5-second contact was used in subsequent runs.

The next 50 g of furfural was hydrogenated at 36-38 g/hr and a temperature of 235° to give 40.1 g (94%) of methylfuran.

12j. The next 100 g of furfural were hydrogenated at 240° and 40-45 g/hr to yield 73 g (85.5%) of methylfuran. Ten grams of unchanged furfural were also recovered from the water condenser. The unchanged furfural obtained here and in 12e indicate that a hydrogen to furfural mol ratio greater than 10 to 1 is required for good conversion in one pass over the catalyst. (See calculations, p. 57)

Arbitrary operating conditions of 20-30 g/hr of furfural and a hydrogen recirculation rate of 2160 cc/min were imposed at this point to insure the presence of a 15-fold excess of hydrogen, and to prevent excessive operating temperatures in the catalyst bed. Under these conditions the heat of hydrogenation caused the temperature of the catlyst to rise from 200° to about 230°. Higher temperatures were avoided in order to prevent inactivation of the catalyst.

12k. The apparatus was cooled to room temperature and allowed to stand for four days in an atmosphere of hydrogen.

When operations were resumed on the fifth day, the hydrogenation of 142 g of furfural, yielded 117 g (96%) of methylfuran.

The unit was kept hot for the next two days during which time 87 g of furfural were hydrogenated at 230° and 20 g/hr to give 71 g (95.5%) of methylfuran.

12l. The unit was cooled to room temperature and allowed to stand for a week in an atmosphere of hydrogen. When operations were resumed, the first 100 g of furfural gave 78 g (91%) of methylfuran.

The apparatus remained hot for the next three days during which time 166 g of furfural were hydrogenated under the usual conditions to give 129 g (91%) of methylfuran.

12m. The unit was again cooled to room temperature and allowed to stand in an atmosphere of hydrogen for a week. It was then dismantled and the catalyst allowed to stand open to the air for two weeks. The apparatus was modified on reassembly so it was essentially that shown in figures 1 and 2. When operations were resumed, 100 g of commercial undistilled furfural were hydrogenated at the usual rate and temperature to give 77 g (90%) of methylfuran. The catalyst was discarded after this run in order that a different batch of chromite could be tested in the unit.

The overall yield of methylfuran from 1035 g of furfural was 806 g (91.2%).

Experiment No. 13

In the previously described preparations of the complex copper-ammonium chromate, it was observed that an alkaline mother liquor was obtained if the ammonium hydroxide used came from a full bottle, while a slightly acid mother liquor resulted on use of ammonium hydroxide from a bottle 1/4 - 1/3 full. The observed difference was due to loss of NH_3 from the partially used bottle.

Previous workers indicated that a superior catalyst resulted from neutral precipitation (57) (58). In the preparation to be described in this and all subsequent experiments, a small test run was made to determine the amount of concentrated NH_4OH necessary to give a neutral mother liquor. Generally, it was found that 150-200 cc of concentrated NH_4OH were required instead of the 225 cc given by Adkins.

A quantity of complex chromates six times that described by Adkins was prepared in three double-size batches. It was decomposed in the laboratory kiln in the temperature range of 300-350°. The yield of leached catalyst was 950 g.

Thirty grams of this chromite were distributed on 30 g of Nuchar in the manner described on p. 33. When 50 g of furfural were hydrogenated under the usual conditions, 37.0 g (88%) of methylfuran were obtained. The water formed in the reaction smelled strongly of amyl alcohol.

Experiment No. 14

The catalyst prepared above was found to be incompletely decomposed. The decomposition was completed on 200 g of the material by heating 20 g batches with constant stirring in an air bath at 320-350° for two minutes. The material was then extracted with 10% acetic acid as usual.

Thirty-five grams of this chromite were distributed on 30 g of carbon and heated to 200°. One hundred grams of commercial, undistilled furfural were hydrogenated to give 77.0 g (90.0%) of methylfuran. The recovered water smelled strongly of amyl alcohol. The next 100 g of technical furfural were hydrogenated to give 82 g (96%) of methylfuran. No amyl alcohol was formed in this hydrogenation.

In experiments 12, 13, and 14 it was observed that amyl alcohol formed only when a fresh chromite catalyst was used. A similar observation was made during runs in the small pilot plant.

Experiment No. 15

A sample of copper chromite used by the Hooker Company for the liquid-phase hydrogenation of furfural to furfuryl alcohol was tested in the vapor phase unit.

Thirty-five grams of the chromite were distributed on Nuchar and dried as usual. On hydrogenation of 100 g of technical furfural, 75 g (88%) of methylfuran were obtained. At the end of the hydrogenation the catalyst had acquired a

reddish tinge which indicated that deactivation was taking place. The hydrogenation abruptly ceased during the passage of the next 100 g of technical furfural through the catalyst.

Experiment No. 16

An effort was made to stabilize the Hooker catalyst by treating separate 50 g portions of the chromite as follows: (1) mixing with 7% CaO; (2) extracting with 250 cc of 10% acetic acid; and (3) extracting with 250 cc of acetic acid and then mixing with 7% of CaO.

When distributed on Nuchar, these catalysts showed no increased stability over the untreated chromite.

Experiment No. 17

A series of runs was made to determine the effect of methylfuran on the course of the hydrogenation. The runs were standardized at a hydrogenation rate of 15 g of furfural per hour. Twenty-five and seven-tenths grams of copper chromite (p. 35, exp. 14) were distributed on 22 g of Nuchar. When placed in the hydrogenation chamber this amount of catalyst gave a contact time of 3-4 seconds at a recirculation rate of 2160 cc/min. In the percentage yields of methylfuran shown below, allowance has been made for the added methylfuran. It is evident that a large excess of methylfuran did not affect the hydrogenation.

Table 1. Effect of Methylfuran on the Vapor
Phase Hydrogenation of Furfural

Grams of Furfural	Grams of Methylfuran added to the Furfural	Mol Ratio of Furfural to Methyl- furen	Yield of Methyl- furan grams	Percentage Yield of Methylfuran
15	6.4	2:1	17.9	90
15	12.8	1:1	24.3	90
15	19.2	1:1.5	30.9	92
15	25.6	1:2	37.1	90

Experiment No. 18

This experiment was made to determine the effect of removing the dry-ice trap from the system. The catalyst was the same as that used in experiment 17.

One hundred and twenty grams of furfural were hydrogenated in 8 batches of 15 g each. Only 64.0 g of crude methylfuran was obtained.

When all of the furfural had been hydrogenated the dry-ice trap was placed in the system and the catalyst swept for an hour with hydrogen. At the end of this time 6 g of methylfuran was recovered from the trap.

Distillation of the combined organic fractions gave 62 g (60.5%) of methylfuran. The total organic recovery was 68% of the calculated amount.

A subsequent test with pure methylfuran, in which the catalyst was removed from the chamber, showed that the loss was due to leaks and not to absorption of the methylfuran on the catalyst.

Experiment No. 19

Twenty-five grams of copper chromite (exp. 14, p. 35) was distributed on 22 g of Nuchar and dried as usual. Eighteen and seven-tenths grams of furfuryl alcohol was hydrogenated to give 12.8 g (82%) of methylfuran. Fifteen grams of furfural was then hydrogenated to yield 11.0 g (86%) of methylfuran.

Thirty-two grams of the catalyst was removed from the tube to reduce the contact time to approximately one second. Fifteen grams more of furfural gave 11.2 g (87.5%) of methylfuran.

Experiment No. 20

Copper chromite was prepared directly on the charcoal in the following manner: Fifty-two grams of trihydrated copper nitrate and 6.2 g of calcium nitrate tetrahydrate were dissolved in 50 cc of water. This was just enough solution to thoroughly wet 30 g of Nuchar.

Enough water was added to 45 cc of 28% ammonium hydroxide and 30.2 g of ammonium dichromate to just dissolve the salt (about 130 cc). This solution was poured over the charcoal and the mixture allowed to stand for an hour. It

was filtered, washed twice with 50 cc portions of water, and dried for four hours at 90°.

Ignition of the chromate-charcoal mixture was accomplished by stirring 20 g batches in a large casserole heated on one side with a small flame until the decomposition was well started. The flame was then removed and the reaction allowed to proceed to completion with no further heating. The ignited catalyst was extracted for 30 minutes with 10% acetic acid, washed with water until the washings were colorless and dried overnight in the catalyst chamber at 200° in a stream of hydrogen.

Thirty grams of furfural was hydrogenated under the usual conditions with this catalyst to give 16.9 g (65.6%) of methylfuran.

Experiment No. 21

This experiment was made in order to observe the effect mercury would exert if a thermometer broke while a hydrogenation was in progress.

Mercury (0.025 g) was mixed with 25 g of copper chromite (exp. 14, p. 35) and the catalyst treated as usual. No hydrogenation occurred when 50 g of furfural was passed through the catalyst.

4. Description of the small pilot unit

The small pilot unit as shown in figures 3 and 4 was

designed directly from the laboratory apparatus. (see Calculations, p. 57).

The vaporizer 1 was an electrically-heated section of two-inch pipe about 8 inches in length. Two vaporizers were connected in parallel so periodic cleaning could be accomplished without interrupting unit operation. Vapor temperatures were read by a thermometer inserted in a well at the center of the vaporizer.

The catalyst chamber 2 was a section of standard three-inch pipe four feet long, jacketed with a four-inch pipe to permit heating by Dowtherm. The Dowtherm, which was heated in the side arm 3, was circulated in the direction shown by means of a three-blade impellor. The temperature of the Dowtherm, which was maintained at 195-205°, was read by thermometers inserted in wells at the points where the liquid entered and left the jacket.

Temperatures of the catalyst were measured by means of iron-constantan thermocouples located in the top, middle and bottom sections of the bed. Two thermocouples were placed in each section, one in the center of the bed the other at the wall. The temperatures were recorded by a Brown recording potentiometer 9.

The furfural was pumped from the reservoir 10 into the vaporizer 1 by a Wilson pulsafeeder 8. After passing through the catalyst chamber 2, the vapors were condensed in the cold-water condenser 5. The hydrogen and remaining methylfuran
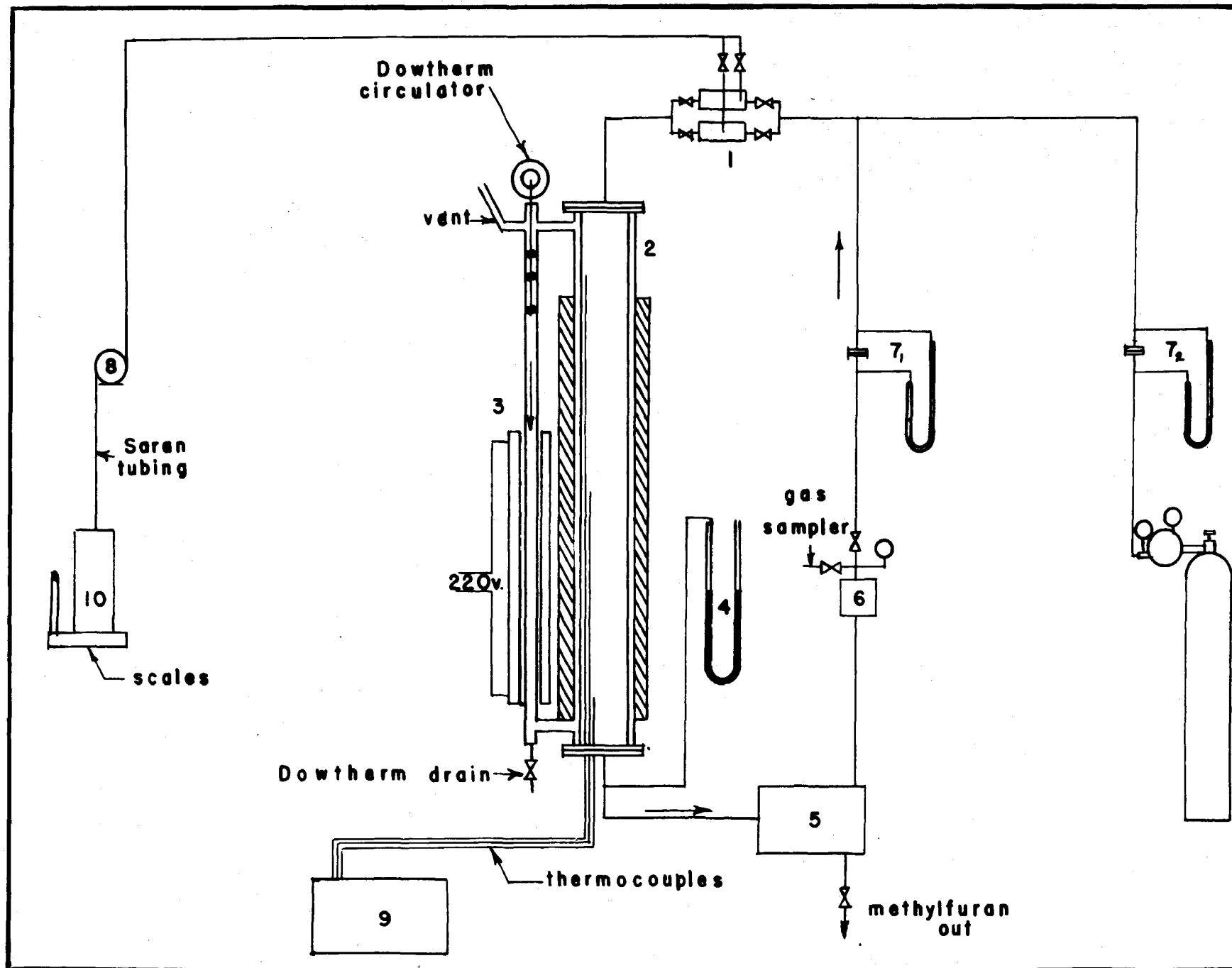
Figure 3. Flow Diagram of Small Pilot Plant
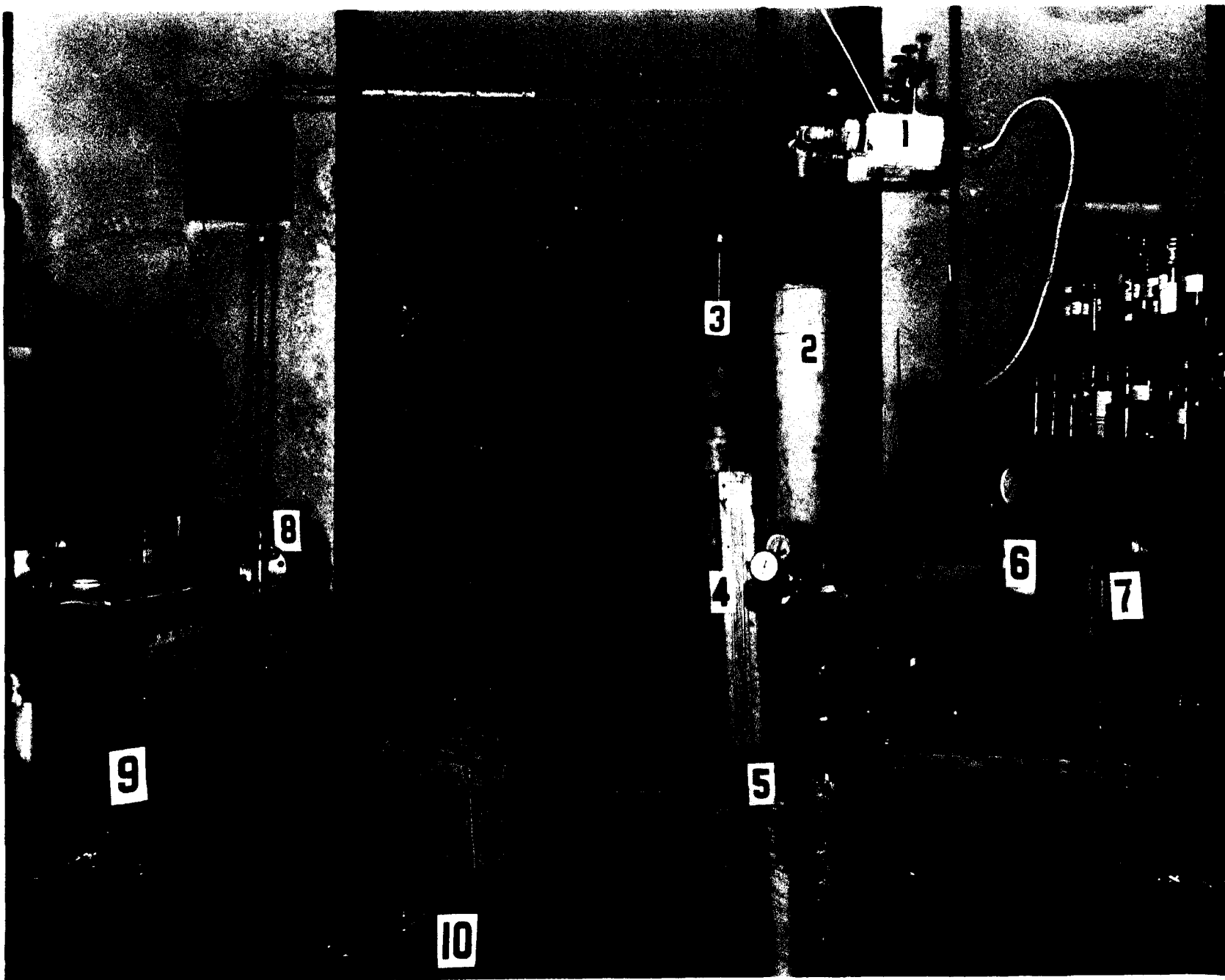
Figure 4. Small Pilot Plant

vapors were recycled over the catalyst by the Kelvinator compressor 6. The flow meter 7_1 showed the rate of hydrogen recirculation, while 7_2 showed the rate of hydrogen consumption.

The furfural reservoir shown was used only at high furfural-feed rates. At reduced feed rates, the furfural was weighed into a small tank from which it was gravity fed to the pump.

Operation of the unit was very smooth. After a steady operation state had been reached, all that was required of the operator was removal of the product from the condenser about once an hour.

5. Description of the runs in the small pilot unit

Run No. 1

Seven hundred grams of copper chromite (exp. 13, p. 34) was distributed on 600 g of Nuchar in a manner similar to that described on page 28 (12b) except that threefold quantities were used.

This was an intermittent run made over the period of a month. The catalyst was heated to 200°, the given amount of furfural hydrogenated, then the unit cooled to room temperature and allowed to stand until the next batch of furfural was hydrogenated, when the cycle was repeated. No thermocouples were used in this run because it was assumed that if the jacket temperature was held at 200° the heat of hydrogenation would

give a temperature of approximately 230° in the catalyst bed. This assumption was later shown to be erroneous. The data in Table 2 were obtained during the run.

Run No. 2

Seven hundred grams of copper chromite was prepared in the manner described on page 34, exp. 13. In spite of the precautions taken, the mother liquor resulting from precipitation of the complex chromate was alkaline.

The chromite was distributed on 600 g of Nuchar, placed in the unit and dried in a stream of hydrogen up to 200°. On starting the hydrogenation it was evident from the water formation and hydrogen absorption that this catalyst was not fully active. The run was discontinued after 3000 g of furfural had been hydrogenated to give 1640 g (64%) of methylfuran.

Run No. 3

Seven hundred grams of copper chromite was prepared in the manner previously described. The catalyst was a slightly underroasted product similar to that obtained in exp. 13, page 34.

With the jacket and catalyst at 190°, a 65° temperature rise was recorded by the potentiometer when furfural was introduced to the catalyst. A continuous run of 50 hours was made at a catalyst temperature of 240°.

Table 2. Operation Data from Semi-pilot Run No. 1

No.	Grams of Fur- fural	Feed Rate g/hr	Product		Methylfuran		Water		Furfuryl Alcohol		Furfural		Residue Grams
			Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent	
1	1160	175	1010	87.9	600	60.0	210	97.2					200
2	1172	705	1198	98.0	825	82.5	230	105					143
3	1130	565	1176	100	810	85.0	216	102					149
4	1350	375	1394	99.0	955	83.0	253	100					186
5	1150	1470	1173	98.0	609	62.0	161	65.0					403
6	1150	1060	1158	96.5	534	54.5	142	65.7					482
7	1150	627	1196	101	635	65.0	165	118	287	24.4	50	4.3	59
8	1150	634	1200	100	415	42.2	105	110	509	43.2	135	11.7	40
9	1610	624	1673	100	700	50.9	158	103	715	43.5	54	3.4	43

During the run it was observed that the heat of hydrogenation was sufficient to raise the temperature of the Dowtherm about 10°. This made it necessary to decrease the

Table 3. Data from Semi-pilot Run No. 3

Furfural Used #	Furfural Feed Rate: #/hr	Yields						
		Product		Methylfuran		Water		
		#	Per-cent	#	Per-cent	#	Per-cent	# Residue
52	1.04	51.3	96.6	35.5	80.2	9.6	98	6

heat on the jacket so that an operating temperature of 240° could be maintained.

Only a slight deactivation of the catalyst was noticed after 50 hours of operation. The results of this run compare favorably with those obtained in experiment 12 in the laboratory.

Fifteen grams (0.06%) of residue was removed from the vaporizer at the end of the run.

Run No. 4

Seven hundred and fifty-five grams of completely decomposed copper chromite was prepared in the manner described previously. This amount of chromite was distributed on 625 g of Nuchar.

A temperature surge of 125° occurred when furfural was introduced to the catalyst, after which the temperature rapidly fell off to an operating level about 50° above the jacket temperature. This is approximately the same temperature differential as was observed in run 3.

A continuous run of seven and one-half days was made during which time the data in table 4 were obtained. The results of the experiment are plotted in figure 5. The residue removed from the vaporizer weighed 0.187 lb.

Run No. 5

Seven hundred and twenty-two grams of completely decomposed chromite was distributed on 615 g of Nuchar. In its preparation the catalyst was extracted with 25% acetic acid instead of the usual 10% acid, because Adkins, et al (57), reported enhanced activity of the catalyst by washing with 20% acetic acid. However, as seen from the data of table 5, treatment with 25% acid lowered the activity of the catalyst.

A temperature surge similar to that observed in run 4, occurred when furfural was admitted to the catalyst.

Run No. 6

A quantity of complex chromate five times that described by Adkins, loc. cit., was decomposed in the laboratory kiln. The resulting underroasted chromite was completely decomposed by heating in a muffle at $350-400^{\circ}$ for two hours. The yield of

Table 4.   Operation Data on Semi-pilot Run No. 4

Date	Hours	Furfural Used #	Feed Rate #/hr	Yields									
				Total Product		Methylfuran		Water		Furfuryl Alcohol		Furfural		Residue
				Lbs.	Percent	Lbs.	Percent	Lbs.	Percent	Lbs.	Percent	Lbs.	Percent	Lbs.
8/14/45	9	10.47	1.17	9.94	91.0	6.46	72.3	1.72	87.9					1.76
8/15/45	15	17.82	1.19	18.25	100	13.66	89.7	3.55	106					1.04
8/16/45	24	29.50	1.23	27.75	93.5	17.32	71.0	4.69	87.6					5.74
8/17/45	24	26.92	1.12	27.40	97.0	15.13	65.9	3.15	62.5	5.25	19.8	3.01	11.6	0.90
8/18/45	24	25.39	1.02	24.55	93.0	10.67	49.1	2.00	42.0	7.45	28.8	3.12	12.3	1.38
8/19/45	24	23.80	0.99	24.06	99.0	6.69	32.9	1.24	27.8	12.10	49.6	2.85	12.0	1.19
8/20/45[1]	22.5	22.72	1.01	22.66	97.7	3.86	19.9	0.93	21.8	12.90	55.4	4.03	17.8	0.90
8/21/45	24	27.03	1.13	27.02	97.8	1.10	4			13.50	48.9	10.30	38.0	2.40
8/22/45	13	17.20	1.32	17.05	95.0					6.70	37.5	8.85	51.5	1.45
Totals		200.85		198.68		74.89	43.8			57.90	28.3			

[1] Trouble was encountered on 8/20/45 because of a vapor lock in the furfural feed pump.
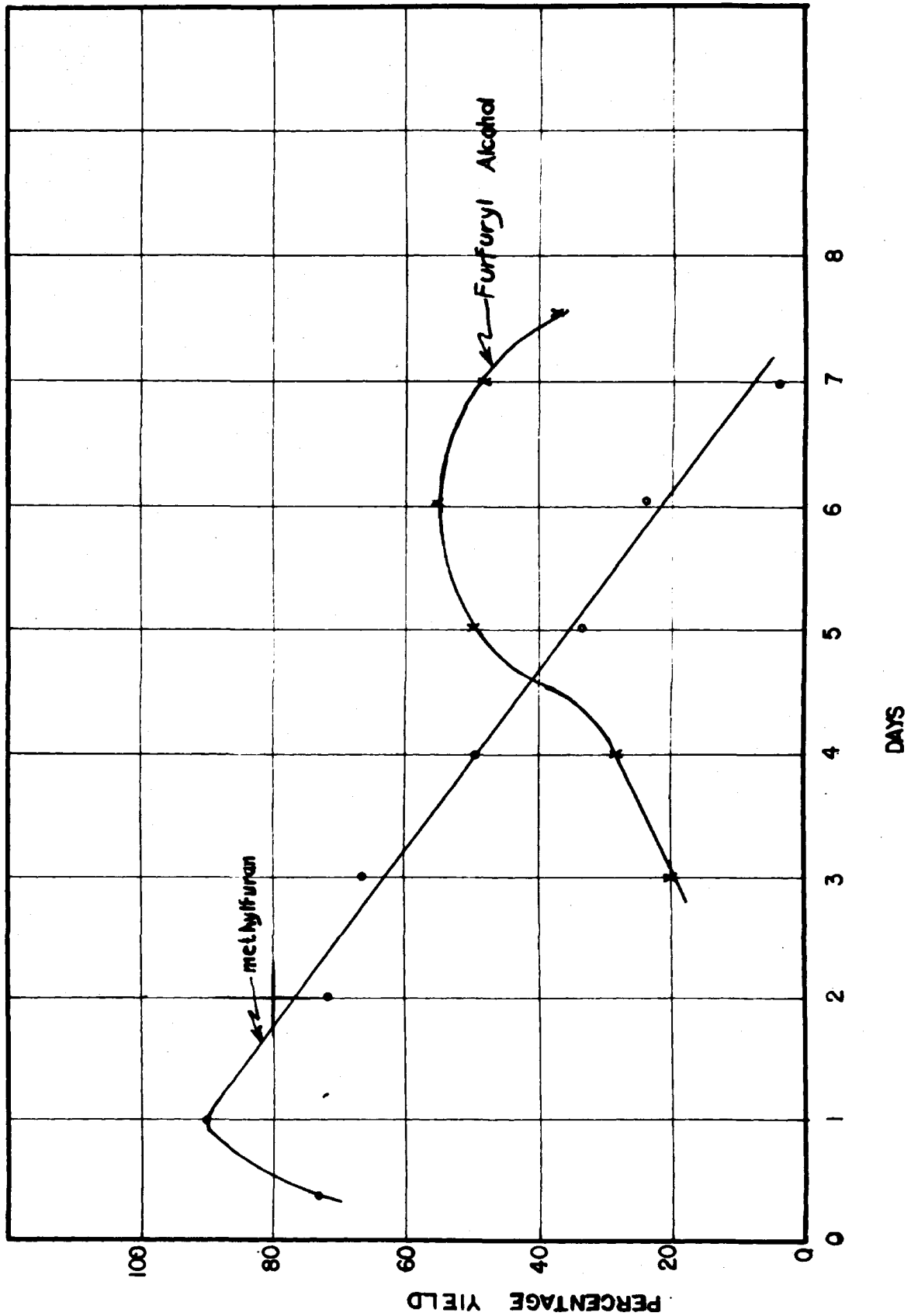
Figure 5. Results of Pilot Run No. 4

Table 5. Operation Data on Semi-pilot Run No. 5

| Date | Hours | Furfural Used # | Feed Rate #/hr | Yields | | | | | | Residue |
| | | | | Total Product | | Methylfuran | | Water | | |
				Lbs.	Per-cent	Lbs.	Per-cent	Lbs.	Per-cent	Lbs.
9/19/45	12	13.00	1.060	13.40	99.4	7.35	66.9	2.35	97.5	3.70
9/20/45	24	23.63	0.985	24.75	100.0	14.72	73.0	3.92	88.4	6.11
9/21/45	24	23.63	0.985	23.94	97.0	13.13	65.1	3.38	76.3	7.43
9/22/45	21	23.69	1.128	24.85	100.0	13.70	67.9	3.48	78.5	7.67
Totals		83.95		86.94	99.5	48.90	68.1			

Table 6.   Operation Data on Semi-pilot Run No. 7

| Date | Hours | Furfural Used Grams | Feed Rate g/hr | Yields | | | | | | Residue |
| | | | | Total Product | | Methylfuran | | Water | | |
				Grams	Percent	Grams	Percent	Grams	Percent	Grams
2/1/46	13	1390	106	1324	91.3	826	69.4	280	92.9	218
2/2/46	24	4432	185	4505	97.6	3089	81.7	804	96.9	612
2/3/46	24	4292	179	4404	98.6	2766	75.9	672	83.8	966
Totals		10,114		10,233	97	6701	77.5			

catalyst after extraction with 10% acetic acid was 720 g.

This catalyst was discarded after a three-hour run in the unit because it showed only 50% of the usual activity. The hydrogenated product obtained during this time contained enough dissolved and precipitated water to give an estimated methyl-furan yield of 20%.

Run No. 7

This run was made in an effort to increase the catalyst life by reducing the furfural mass-rate of flow to that employed in the laboratory. Redistilled furfural was hydrogenated at a rate of 180 g/hr instead of the 500 g/hr of previous runs.

Two hundred and seventy grams of completely decomposed copper chromite was distributed on 225 g of Nuchar. With the jacket and catalyst bed at 200°, a temperature surge less drastic than that observed in runs 4 and 5 occurred when furfural was introduced to the catalyst. However, the operating temperature of the catalyst rose to a level about 40° above the jacket temperature.

Five hours after operations were commenced, a 75° temperature surge resulted from the sudden injection of excess furfural into the vaporizer. The sudden injection was due to a lowered pressure in the hydrogenation apparatus. When normal operations were resumed it was observed that the catalyst was not as active as it had been previous to the temperature surge.

The data obtained during the run are given in table 6.

6. Vapor pressures and vapor-liquid data

The indication obtained in the laboratory (exp. 18, p. 37) that methylfuran was adsorbed on the catalyst made it seem probable that absorption equipment would be needed to prevent deactivation of the catalyst. Therefore, vapor pressure at 20°, 25°, and 30°, and vapor-liquid data at 738 mm were determined in order that the absorption and distillation equipment might be installed if necessary.

The furfural used for the determinations was a middle fraction obtained by distillation of the technical product under reduced pressure. The methylfuran prepared in the catalytic studies was dried over sodium and then distilled through a short column. The materials had the following constants:

	Furfural	Methylfuran
B.P., $^\circ$C	63-54/25 mm	61-63/738 mm
Density - $D_{20/4}$	1.160	0.915
Refractive Index, nd^{20}	1.5268	1.4338

(a) <u>Vapor pressure measurements</u>. A modified form of the apparatus of Smith and Menzies (59) was used to determine vapor pressures (Figure 6) because it gave reasonably accurate results with a minimum expenditure of time. The vapor pressure of water, determined at 25°C as a check on the apparatus, was found to be within 1% of the accepted value. The data on the total vapor pressures of furfural-methylfuran solutions are

given in Table 7. Since furfural is relatively non-volatile its partial pressure over these solutions can be calculated by means of Raoult's law with sufficient accuracy for engineering purposes. The vapor pressures of pure methylfuran are recorded in Table 8.

The capacities of A and B (Figure 6) were 50 cc and 25 cc, respectively. For determination of vapor pressures, bulb A was three-fourths filled with glycol, after which a 10 cc sample of a furfural-methylfuran solution was introduced into B. After closing the side arm on B with a rubber tube and clamp, the apparatus was immersed in a constant temperature bath. A pump and manometer were connected to tube C and the pressure lowered to a point just below the vapor pressure of the solution in B. After allowing about a minute for complete expulsion of air from B, the pressure in A was slowly raised to the point where bubbles just stopped issuing from the capillary. After reading the manometer the pressure was lowered about 10 mm and the vapor pressure determined again. Successive determinations were made until measurements checked within a millimeter, the last determined value being taken as the vapor pressure. Air was then admitted to A and the clamp on the side arm of B quickly opened to prevent the liquid from surging through the bulb between A and B. A sample was taken from B by means of a capillary pipet and the composition determined by refractive index. A small amount of methylfuran, or furfural as the case may be, was added to B and another

determination made in the described manner. A correction for
the immersion of the capillary was made as described by Smith
and Menzies (59).

(b) <u>Vapor-liquid data</u>. The apparatus (Figure 7) used to
determine vapor-liquid equilibria was essentially that of Othmer
(60). The liquid (250 cc) was boiled in flask A (500 cc capa-
city) until vapors emerged at stopcock B. After the stopcock
was closed, the vapors passed up the inner tube into condenser
C from which the liquid collected in receiver D (10 cc capacity).
The boiling was continued until a steady temperature state was
maintained for 20 to 30 minutes. In this way four or more
complete changes of the liquid in D were assured. It was assumed
that this was sufficient to establish equilibrum between the
liquid and vapor. A small sample of the liquid was drawn off
at E into a flask immersed in a dry ice-acetone bath. Simul-
taneously the receiver D was drained into a test tube. The
liquid compositions were then determined from the refractive
index curve. The data obtained in this manner are recorded in
Table 4.

No change in refractive index of the furfural-methylfuran
solutions was observed on boiling at atmospheric pressure for
one hour. This check was made because of the change in the
furfural-furfuryl alcohol system noted by Dunlop and Trimble
(61).

T 4" Thermometer
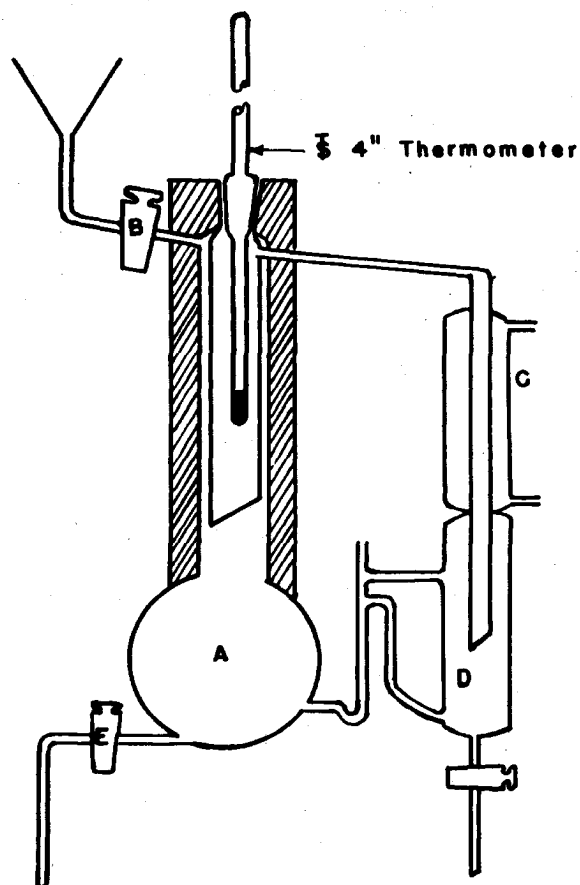
Figure 7. Vapor-liquid Equilibria
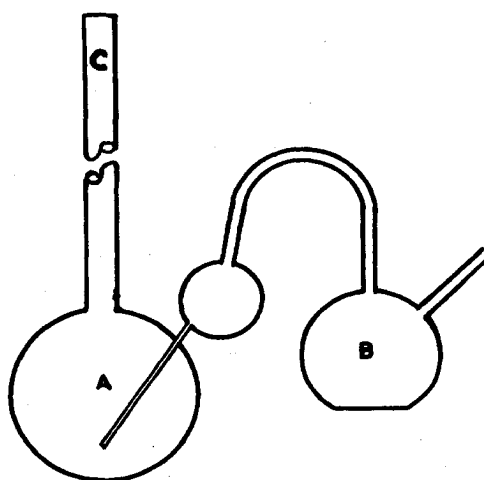
Figure 6. Vapor Pressure

7. Calculations

    (a) <u>Laboratory data</u>.

        Catalyst Bed = 2.8 cm x 44 cm

        Empty volume = 271 cm^3

The tube was filled with damp catalyst, water added until level with the top of the bed, then the water drained into a small flask, after which the catalyst was dried in a stream of hydrogen to 200°. The total amount of water recovered (drainage + drying) amounted to 175 cc.

    Hence,

        If the free space in filled tube = 175 cc or 65% voids

        and the hydrogen recirculation = 1100 cc/min,

        the contact time = 175 x $\frac{1}{1100}$ x 60 = 10 seconds at 1100 cc/min

At a hydrogen rate of 2160 cc/min, the contact time by similar calculations can be shown to be 5 seconds.

    At a furfural rate of 25 g/hr and 1100 cc H_2/min:

1100 cc x 60 x $\frac{273}{300}$ x $\frac{740}{760}$ x $\frac{1}{22,400}$ = 2.60 mols of H_2/hr at 27° and 740 min

and

    25 g/h x $\frac{1}{96}$ = 0.26 mols furfural/h, or the

mol ratio of furfural to H_2 is 10:1

    At a furfural rate of 45 g/hr and 2160 cc H_2/min:

2160 x 60 x $\frac{273}{300}$ x $\frac{740}{760}$ x $\frac{1}{22,400}$ = 5.35 mols H_2/hr at 27° and 740 min.

Table 7. Refractive Index of Furfural-Methylfuran System

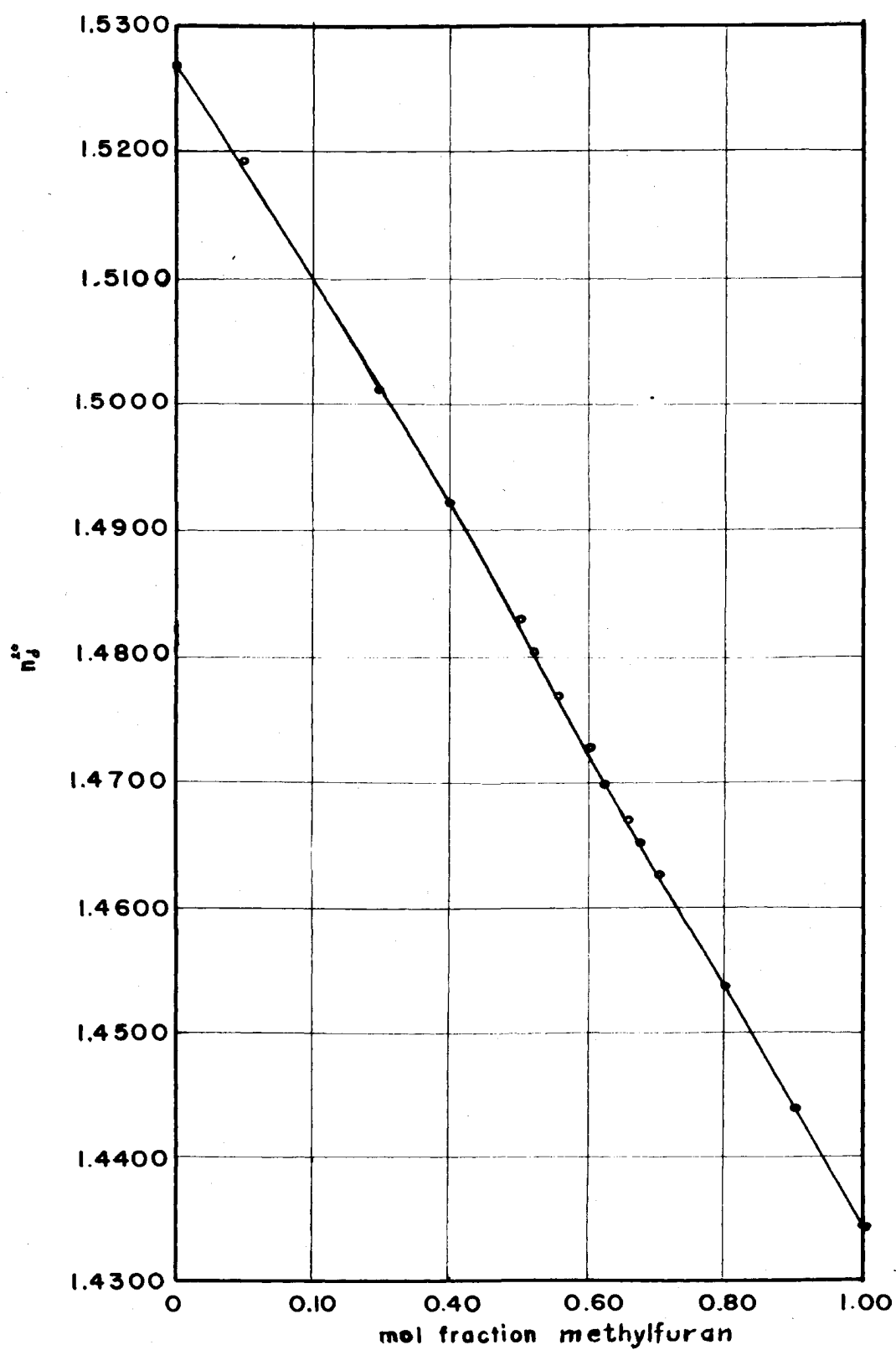| Furfural		Methylfuran		n_D^{20}
gms	mol frac	gms	mol frac	
	1.00			1.5268
108.0	0.900	9.16	0.100	1.5190
62.40	0.700	22.90	0.300	1.5009
80.50	0.600	45.75	0.400	1.4921
54.60	0.500	45.75	0.500	1.4825
5.80	0.475	5.47	0.525	1.4800
5.80	0.450	6.06	0.550	1.4772
35.70	0.400	45.75	0.600	1.4728
5.80	0.375	8.26	0.625	1.4698
5.80	0.345	9.43	0.655	1.4670
5.80	0.325	10.30	0.675	1.4650
22.85	0.300	45.75	0.700	1.4628
13.25	0.200	45.75	0.800	1.4535
5.95	0.100	45.75	0.900	1.4440
			1.000	1.4340

Figure 8.   Refractive Index Curve of
            Furfural-Methylfuran System.

Table 8. Total Vapor Pressures of Furfural-Methylfuran System

At 68.0°F (20.0°C)			At 78.0°F (25.6°C)			At 86.0°F (30.0°C)		
nd^{20}	Mol Fraction of Methylfuran	Vapor Pressure mm Hg	nd^{20}	Mol Fraction of Methylfuran	Vapor Pressure mm Hg	nd^{20}	Mol Fraction of Methylfuran	Vapor Pressure mm Hg
-	0	3	-	0	4	-	0	5
1.5195	0.092	26	1.5212	0.070	23	1.5208	0.076	35
1.5140	0.156	39	1.5190	0.098	34	1.5165	0.128	50.5
1.5069	0.236	56	1.5155	0.140	46	1.5113	0.187	70
1.5018	0.293	65	1.5100	0.202	61	1.5055	0.251	86
1.4945	0.372	76	1.5028	0.280	86	1.5008	0.303	101
1.4921	0.398	80	1.4890	0.431	109	1.4955	0.361	113
1.4885	0.436	86	1.4764	0.562	128	1.4950	0.367	119
1.4829	0.492	91	1.4665	0.663	141	1.4910	0.409	125
1.4774	0.550	98	1.4518	0.815	157	1.4880	0.441	130
1.4685	0.640	106	1.4440	0.896	166	1.4852	0.469	157
1.4569	0.752	117	1.4400	0.938	174	1.4794	0.531	148
1.4458	0.878	126				1.4719	0.605	159
1.4395	0.944	133				1.4700	0.625	160
						1.4675	0.651	165.5
						1.4640	0.688	172.5
						1.4630	0.698	172
						1.4550	0.782	183
						1.4450	0.886	197
						1.4395	0.943	210
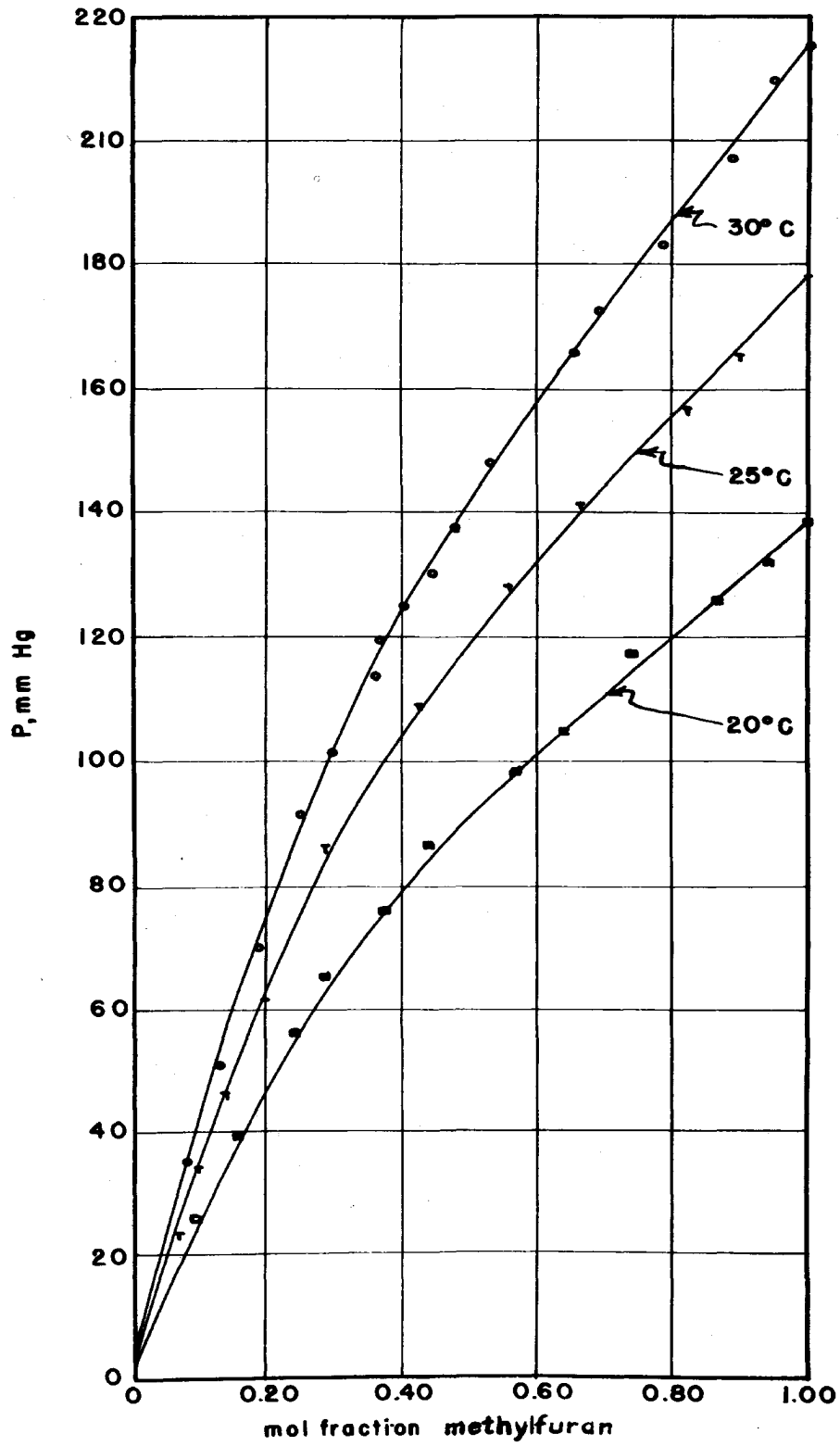
Figure 3.   Total Vapor Pressures of
Furfural-Methylfuran System.

Table 9. Vapor Pressure of Pure 2-Methylfuran

| Temperature | | Pressure |
$^\circ$F	$^\circ$C	mm Hg
86.0	30.0	216
78.0	25.6	179
77.0	25.0	174
68.0	20.0	139
59.0	15.0	110.5

Table 10. Liquid-Vapor Composition

| Temp. $^\circ$C | Liquid | | Vapor | |
	n_D^{20}	mol fraction methylfuran	n_D^{20}	mol fraction methylfuran
65	1.4650	0.662	1.4355	0.988
71	1.4780	0.542	1.4360	0.980
76	1.4900	0.420	1.4370	0.970
80	1.4965	0.350	1.4381	0.958
92	1.5071	0.234	1.4418	0.919
110	1.5160	0.134	1.4491	0.844
121	1.5191	0.097	1.4579	0.752
130	1.5210	0.074	1.4680	0.648

Figure 10. Vapor Pressure of Pure Methylfuran

Figure 11. Boiling Point Diagram of Furfural-Methylfuran System.

45 g/hr x 1/96 = 0.47 mols furfural/hr

Hence the ratio of furfural to H_2 is 11:1 under these conditions.

Assume an average furfural feed rate of 25 g/hr at a hydrogen recirculation rate of 2160 cc/min:
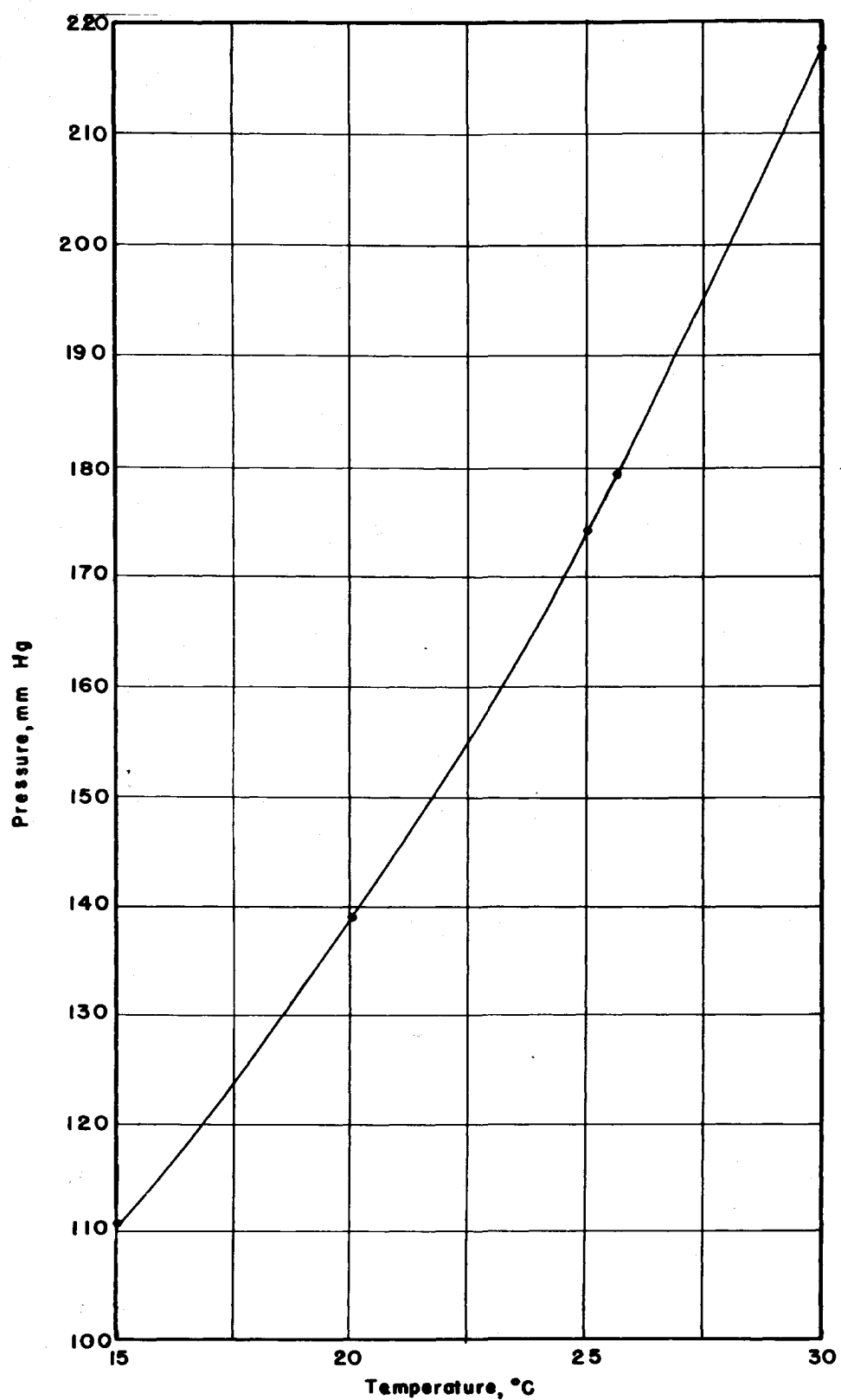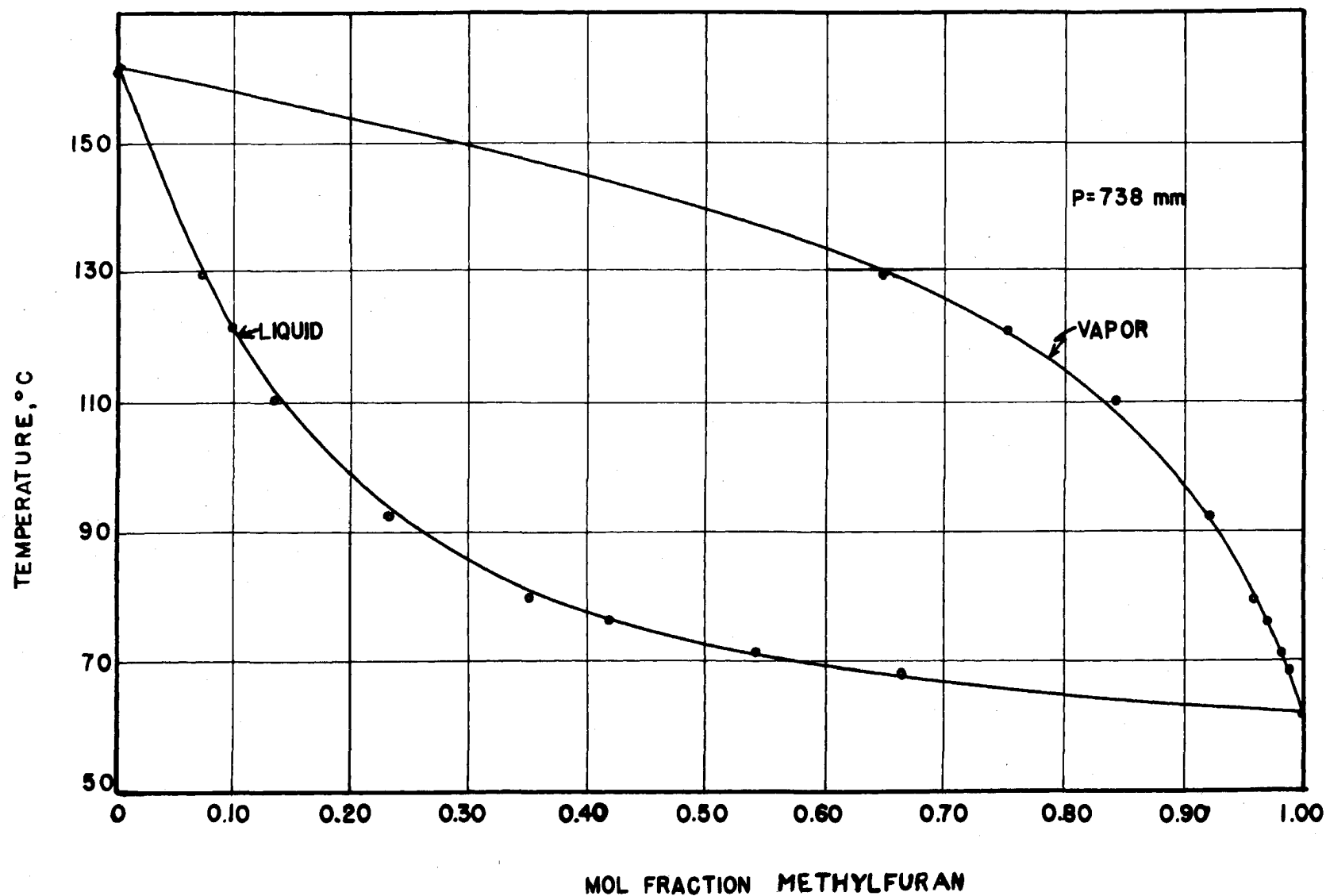
$$\frac{25}{434} \times \frac{4 \times 144}{} \frac{(2.54)^2}{(2.80)} = 8.3 \text{\# furfural/hr/ft}^2 \text{ is the average mass rate of flow}$$

Under the same conditions the concentration of furfural in the gas phase is

$$\frac{25}{454} \times \frac{2.83 \times 10^4}{2160 \times 60} \times \frac{760}{740} \times \frac{300}{273} = 0.0135 \frac{\text{\# furfural}}{\text{ft}^3 \text{ free } H^2} \text{ at STP}$$

$1 \text{ ft}^3 = 2.83 \times 10^4$ cc

(b) <u>Semi-pilot unit data</u>. The unit was designed for a capacity approximately 20 times that of the laboratory unit. The following specifications were selected:

Furfural = 500 g/hr

H_2 recirculation = 56500 cc/min or 2cfm

Catalyst chamber = 5550 cm^3 or 0.196 ft^3

The hydrogen recirculation selected gave a greater excess of hydrogen than that employed in the laboratory unit. In the absence of any knowledge concerning the heat effects, it was decided to construct the catalyst chamber after the laboratory unit.

If a 3" pipe is selected a convenient tube length is obtained by maintaining dimension ratios similar to those in the glass unit as shown by the following calculation:

$$\frac{\pi}{4} \times \frac{(3)^2}{144} \times L = 0.196$$

L = 4 ft = length of catalyst chamber.

If the same free space is assumed in the catalyst bed as in the laboratory unit

0.196 x 0.65 = 0.1275 ft^3 void

the contact time = 0.1275 x $\frac{1}{2}$ x 60 = 4 seconds for the flow rate of 2 cubic feet of H_2 per minute.

The catalyst required for the unit can be calculated as follows:

35 x 20 = 700 g copper chromite

30 x 20 = 600 g activated charcoal

The mass rate of flow then calculates:

$$\frac{500}{454} \times \frac{4 \times 144}{\pi \times (3)^2} = 22.4 \text{ #furfural/hr} \times ft^2$$

To reduce the mass rate in the pilot unit to that employed in the laboratory, the furfural feed rate would have to be reduced by a factor of

22.4/8.3 = 2.7

The amount of catalyst and the hydrogen recirculation should be reduced by a like factor.

(c) <u>Calculations for scrubbing hydrogen gas with furfural to remove methylfuran vapors.</u> The vapor pressures of the furfural-methylfuran system determined by experiment are somewhat greater than those calculated by Raoult's law: Because of the indicated greater escaping tendency in solution, the partial pressure of furfural was assumed constant at 3 mm over

the range concerned. Using this assumption, the data of figure 9 at 25° (78°F) were recalculated and are tabulated in table 11 and plotted in figure 12.

Table 11. Recalculated Vapor Pressures of the Furfural-Methyl-furan System at 25° (78°F)

Mol Fraction Methylfuran	Total Vapor Pressure	Vapor Pressure of Methylfuran	$\dfrac{\text{Mol Methylfuran}}{\text{Mol Furfural}}$	$\dfrac{\text{Mol Methylfuran}}{\text{Mol inert gas}}$
0.03	10.5	7.5	0.0310	0.0102
0.05	18	15.0	0.0526	0.0207
0.08	27.2	24.2	0.0870	0.0338
0.10	33.0	30.0	0.111	0.0423
0.15	48.6	45.6	0.177	0.0666
0.20	62.0	59.0	0.250	0.0866
0.25	74.5	71.5	0.333	0.107
0.30	86.5	83.5	0.428	0.127

Methylfuran could be removed from the hydrogen gas stream by countercurrent adsorption in furfural. The rich gas could enter the bottom of a packed tower, and, after being stripped of methylfuran, the lean gas would leave the top of the tower, to be recirculated over the catalyst.

For calculations it is assumed that the absorption tower would operate isothermally at 740 mm and 78°F with 80 mm partial pressure of methylfuran in the entering vapors. At this partial
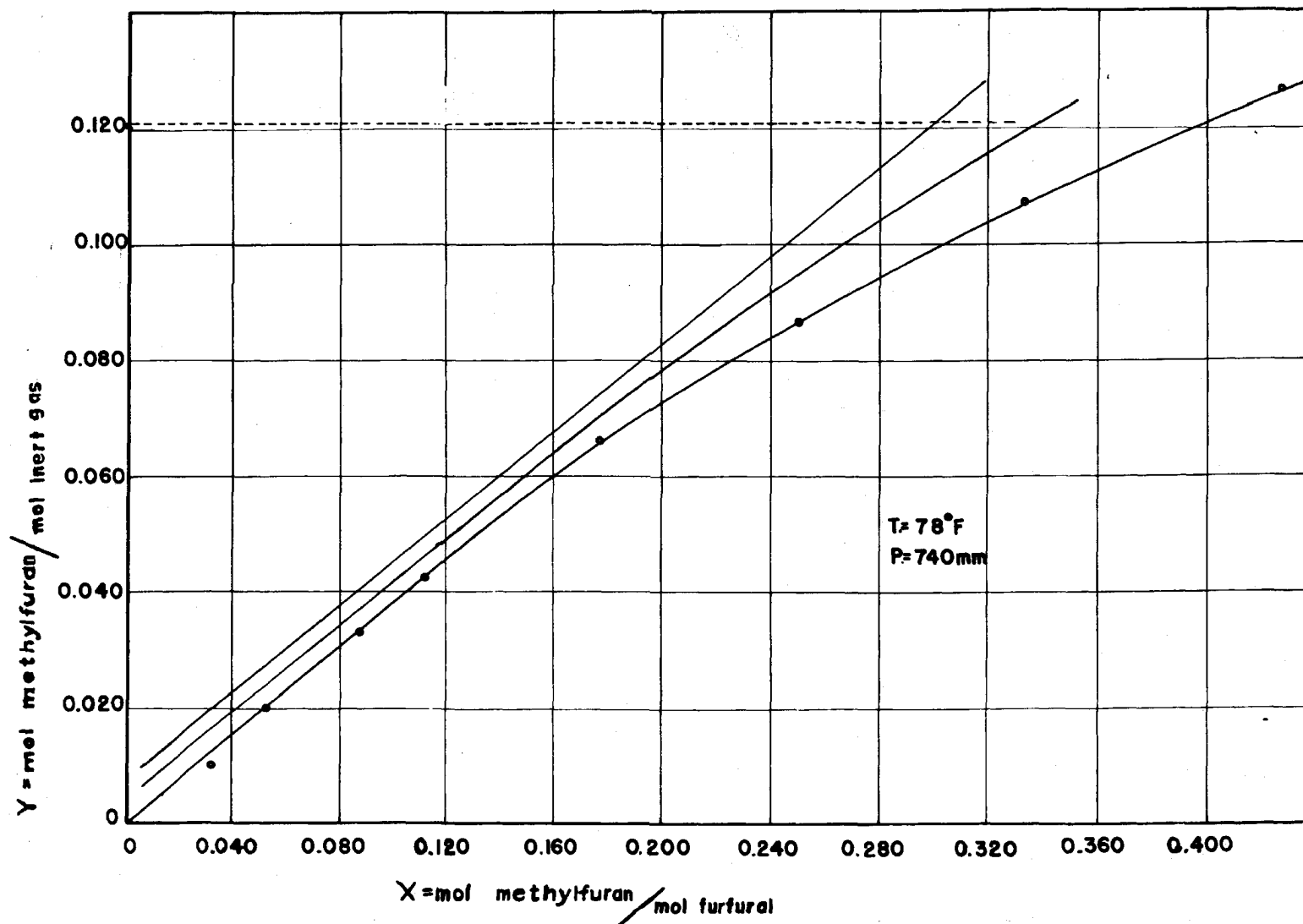
Figure 12. Absorption Column Diagram for System Furfural-Methylfuran

pressure, the concentration of methylfuran in the gas enter-
ing the tower would be 0.121 mol/mol of inert gas. It was
further assumed that the methylfuran content of the gas leav-
ing the tower would be reduced to 0.010 mol/mol of inert gas
by the furfural which would contain 0.009 mol of methylfuran/mol
of furfural on entering the tower.

Under these conditions, the theoretical maximum concen-
tration of methylfuran obtainable in the furfural is 0.340
mol/mol. Using an operating figure of 0.300 mol/mol for the
exit furfural, the straight operating line was drawn in figure
12. The number of transfer units required to remove the methyl-
furan from the gas stream is found to be 12.2 by the method
of Baker (62). These lines were not drawn in the figure be-
cause they would tend to obscure the diagram.

(d) <u>Calculations for distillation of methylfuran from the
furfural absorbing system</u>. The solution from the adsorption
tower may be assumed to run directly into the distilling
column. The feed will enter at 78°F and contain 0.231 mol
fraction of methylfuran. It was assumed that the distillate
from the tower will contain 0.5 mole per cent furfural and the
bottoms 0.5 mol per cent methylfuran. The bottoms will be re-
turned to the top of the adsorption tower.

In the absence of heat data, the heat of vaporization of
methylfuran was calculated from the Clapeyron equation and the
vapor pressures. The heat capacity of the liquid was taken as
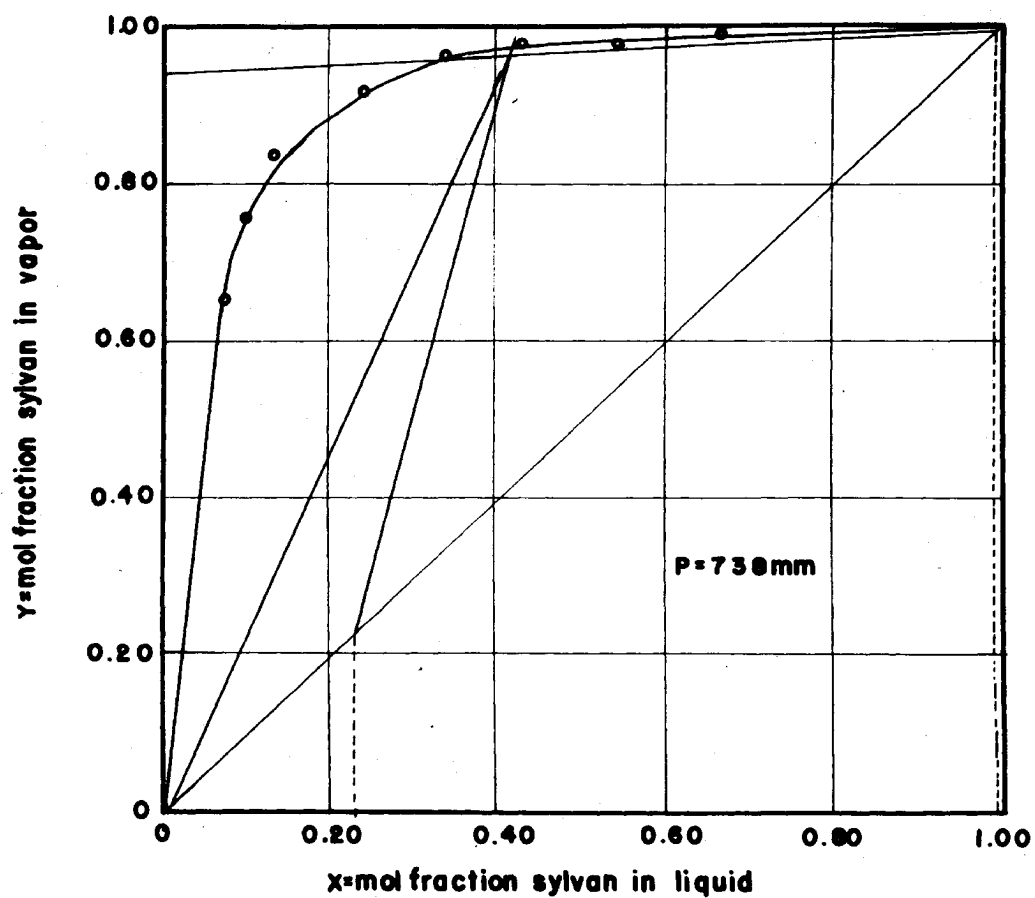
Figure 13.   Equilibrium Diagram for System
             Furfural-Methylfuran

equal to that of furfural or 0.42 cal/gm/deg. This was also assumed to be the heat capacity of pure methylfuran.

If B.P. of feed = 92°C (from B.P. diagram) then $92-25 = 67^{\circ}$C = temp interval.

The heat capacity of sylvan in liquid is $0.42 \times 82 = 34.4$ cal/mol/deg

The heat capacity of 1 mol of the vapor minus the heat capacity of 1 mol of the liquid is:

$$\frac{d(\Delta H)}{dT} = \Delta Cp$$

The heat capacity of the vapor can be estimated at 15 cal/mol/deg.

Then $\Delta H = \Delta H_O - \Delta CpT$

$\Delta Cp = \Delta H_v - \Delta H_\ell = 15-34 = -19$

or

$\Delta H = \Delta H_O - 19T$

From the Clapeyron equation

$$\frac{d\ln p}{dt} = \frac{\Delta H}{RT^2}$$

$$\frac{d\ln p}{dt} = \frac{\Delta Ho-19T}{RT^2}$$

Integrating

$$R\ln P = -\frac{\Delta H}{T} - 19 \ln T - I$$

$$R\ln P + 19 \ln T = I - \frac{\Delta Ho}{T}$$

Substituting the vapor pressure data:

15°C - (a) $1.98 \ln 110.5 + 19 \ln (288) = I - \frac{\Delta Ho}{288}$

$20^{\circ}C$ - (b) $1.98 \ln 139 + 19 \ln (293) = I - \dfrac{\Delta Ho}{293}$

$25^{\circ}C$ - (c) $1.98 \ln 174 + 19 \ln 298 = I - \dfrac{\Delta Ho}{298}$

$30^{\circ}C$ - (d) $1.98 \ln 216 + 19 \ln 303 = I - \dfrac{\Delta Ho}{303}$

Solving for an average value of I and ΔHo we obtain: $I = 168$ and $\Delta Ho = 14,750$.

Hence

$\Delta H = 14,750 - 19T$

at $63^{\circ}C$ at $92^{\circ}C$

$\Delta H = 14,750 - 19 (339)$ $\Delta H = 14,750 - 19 (365)$

$= 8,370$ cal/mol $= 7800$ cal

The value at $63^{\circ}C$ gives a Troutons constant of 22.1.

The foregoing ΔH is only approximate because (1) the vapor pressures used were for 0.02 atm. of sylvan instead of 1 atm., (2) the Kirchoff equation is only approximate, and (3) the assumption of the perfect gas laws for sylvan vapor is probably quite bad.

For 100 mols of solution of mol fraction 0.231 sylvan

$23.1 \times 82 = 1900$

$76.9 \times 96 = \underline{7380}$
                9280 or a mol weight of 92.8

Sp Ht/mol = $0.42 \times 92.8 = 39$ cal/mol/$^{\circ}C$

Sensible heat = $39 \times (92-25) = 2520$ cal
Latent heat (at 92°) $= \underline{7800}$ cal
                       $10,320$ cal

by definition

$$q = \frac{10,320}{7800} = 1.32$$

slope of line $= \frac{1.32}{1.32-1} = 4.12$

The reflux ration was assumed to be 0.05 mol/mol of overhead distillate which is 25% greater than the theoretical minimum. Using a sheet of paper 18 in. or an edge and drawing the q line at its proper slope, the number of plates is found to be three in the rectification section and 5 in the stripping section. Assuming a plate efficiency of 75%, four plates are required in the rectification section and 7 plates in the exhausting section of the column.

(e) <u>Cost estimate for small scale production of methyl-furan</u>. This estimate is only an approximation of the cost of making methylfuran. More pilot plant data are needed before an accurate estimate can be made.

Assume: a production rate of 500# methylfuran/day, 300 working days/year and a plant cost of $20,000 to be depreciated by straight line method in five years. Since the semi-pilot unit operated so smoothly, it was assumed that only one operator/shift would be needed. The best pilot conditions obtained, 80% yield and 0.04# catalyst/# methylfuran, will serve as a basis for calculations.

1 x 96/82 x 1/0.8 = 1.45# furfural will be required on this basis for each pound of methylfuran produced.

Cost calculation on basis of 1# methylfuran:

Raw Materials

Furfural @ 10¢/lb $0.145

Hydrogen @ 50¢/1000ft^3 . . . . . 0.005

Catalyst @ $1.00/lb 0.040

Purification Costs 0.040

Heat and Power 0.050

Labor @ $1.45/hr 0.070

Depreciation, taxes, etc. 0.050

Total cost/lb $0.400

B. Reactions of Methylfuran

1. Source of materials

The methylamine and dimethylamine hydrochlorides were
the Eastman white label products and were used without further
purification.

The hydrochlorides of n-butyl amine, allyl amine, ethano-
lamine, cyclohexyl amine and benzyl amine were prepared by
treating the Eastman white label amine with the calculated
quantity of concentrated HCl and evaporating to dryness. The
hydrochlorides were recrystallized from ether-ethanol mixtures.
The hydrochlorides of morpholine and piperidine were prepared
in the same manner from the Eastman practical material.

The octyl, dodecyl and octadecyl amines were supplied
through the courtesy of the Chemical Division of Armour and

Company. The amine hydrochlorides were prepared as indicated above and recrystallized from absolute EtOH.

Iso-propyl amine was prepared by catalytic hydrogenation of Eastman practical 2-nitropropane. The hydrochloride was prepared as described above.

2. Analysis

The nitrogen analyses reported were made by the Dumas method if followed by the letter "D". The results not so marked were obtained by the Kjehdahl method.

The chlorine analyses were made for soluble chlorine. The solutions were kept cold throughout the determination to prevent reduction of AgCl by the organic material present.

All melting points reported are uncorrected. They were taken on a Fischer-Johns micro block.

3. Hydrochloride salts

The hydrochlorides of the amines were prepared by dissolving 3 - 5 cc of the amine in 20 cc of anhydrous ether and cooling to $0°$. The calculated quantity of cold, concentrated HCl was then added. The hydrochlorides were recrystallized from acetone-alcohol mixtures.

If the hydrochloride separated as an oil crystallization was induced by dissolving the salt in 100 cc of acetone and evaporating to a volume of 25 cc. The solution was then poured slowly into 100 cc of boiling ether.

4. N-(5-methylfurfuryl)-alkylamines

N-(5-methylfurfuryl)-ethylamine. (A) To a 500 cc rb 3-necked flask equipped with a dropping funnel, stirrer, and reflux condenser, were added 162 g (2.0m) of 37% formaldehyde and 163 g (2.0m) of ethylamine hydrochloride. The flask and contents were warmed to 30° with stirring to dissolve the hydrochloride, after which 82 g (1.0m) of 2-methylfuran were added dropwise over the period of an hour. Stirring was continued until the reaction no longer evolved heat.

The reaction was cooled to room temperature, neutralized with 80 g of NaOH dissolved in 160 cc of water, and extracted with 100 cc of ether. The ether layer was washed with two 50 cc portions of water and dried over sodium sulfate. The ether was removed on a water bath and the residue distilled under reduced pressure to give 36.0 g (25.9%) of a colorless oil boiling at 71-6°/17 mm.

D25/4 - 0.944　　　　　　nd^{25} - 1.4689

Calcd. for $C_8H_{13}NO$: N,10.1　　Found: N,10.2

Hydrochloride - The salt was prepared from 4 grams of the amine and 2.22 cc of concentrated hydrochloric acid. It crystallized as white plates which melted at 138-9°.

Calcd. for $C_8H_{14}NOCl$: N,8.0 Found: N,8.0

Cl, 20.2　　Found: Cl,20.0

(B) To a 500 cc rb 3-necked flask equipped with a dropping funnel, stirrer and thermometer that reached into the liquid, were added 90 g (1.1m) of ethylamine hydrochloride and

95 g (1.17m) of 37% formaldehyde. After the flask was heated to 30° to dissolve the hydrochloride, 82 g (1.0m) of methylfuran was added over the period of an hour while the temperature of the reaction was controlled at 30-35°.

When the evolution of heat ceased the reaction was worked up in the manner previously described to give 62 g (44.6%) of material boiling at 76-80°/21 mm.

N-(5-methylfurfuryl)-n-butylamine. Sixty-five and two-tenths grams (0.60m) of n-butylamine hydrochloride and 48.6 g (0.60m) of 37% formaldehyde were added to a 500 cc flask equipped with a stirrer and reflex condenser and a thermometer reaching into the liquid. The flask was heated to 50° and then 49.2 g (0.60m) of methylfuran was added through the condenser as fast as it reacted. The reaction was stirred for ten minutes after the addition of the methylfuran was complete.

The reaction was neutralized with 25 g of NaOH in 50 cc of water and worked up in the described manner to give 21 g (21%) of colorless oil boiling at 110-15°/22 mm.

D25/4 - 0.921 nd^{25} - 1.4659

Calcd. for $C_{10}H_{17}NO$; N,8.4   Found: N,8.3

Hydrochloride – Five grams of the amine was neutralized with 2.5 cc of concentrated HCl to give glistening white plates, which melted at 169-70°.

Calcd. for $C_{10}H_{18}NOCl$: N,6.9 Found: N, 6.8

Cl,17.4 Found: Cl,17.2

<u>N-(5-methylfurfuryl)-n-octylamine</u>.   To 125 g (0.760m) of
n-octylamine hydrochloride and 90 g (1.11m) of 37% form aldehyde
contained in a 500 cc flask equipped with a dropping funnel,
stirrer and reflux condenser, 63.5 g (0.775m) of methylfuran
was added dropwise over the period of one-half hour.

The reaction mixture was then worked up in the previously
described fashion to give 53.5 g (31.0%) of the secondary
amine which boiled at 115-8°/2 mm.

   D25/4 - 0.904 nd^{25} - 1.4671

   Calcd. for $C_{14}H_{25}NO$: N,6.3 Found: N,6.1

<u>Hydrochloride</u> - The salt from 5.0 g of the amine and
2.0 cc concentrated HCl crystallized as white plates which
melted at 145-6°.

   Calcd. for $C_{14}H_{26}NOCl$: N,5.4 Found: N,5.0

   Cl,13.7   Found: Cl,13.6

<u>N-(5-methylfurfuryl)-n-dodecylamine</u>. To 115 g (0.522m) of
n-dodecylamine hydrochloride and 90 g (1.11m) of 37% formal-
dehyde contained in a 500 cc flask equipped with a dropping
funnel, stirrer and thermometer reaching into the liquid,
41.0 g (0.500m) of methylfuran was added over 1½ hours while
the reaction was kept at 30°. The hydrochloride of the
secondary amine crystallized when the reaction was complete.
The salt decomposed an attempted purification, so it was
treated with excess base and the free amine worked up in the
previously described manner to give 21 g (15%) of a colorless

liquid which boiled at $135^{\circ}/2$ mm..

$D_{25/4}$ - 0.888 nd^{25} - 1.4678

Calcd. for $C_{18}H_{33}NO$: N, 5.0   Found: N, 4.9

Hydrochloride - The salt was prepared from 5.0 g of the amine and 1.5 cc of concentrated hydrochloric acid. It crystallized as white leaflets melting at $147-8^{\circ}$.

Calcd. for $C_{18}H_{34}NOCl$: N, 4.4 Found: N, 4.5

A chlorine analysis was not made because the hydrochloride was too insoluble.

N-(5-methylfurfuryl)-n-octadecylamine. Twenty-one grams (0.25m) of methylfuran was added over 45 minutes to 75.6 g (0.25m) of n-octadecylamine hydrochloride and 32 g (0.40m) of 37% formaldehyde in a 500 cc flask equipped with a reflux condenser, stirrer and dropping funnel. The reaction product, isolated as previously described, weighed 30.5 g (33.6%) and boiled at $195-7^{\circ}/2$ mm..

The compound solidified to a waxy solid at room temperature. Recrystallization from absolute alcohol gave white plates melting at $27-8^{\circ}$.

Calcd. for $C_{24}H_{45}NO$: N, 3.9   Found: N, 4.0

Careful distillation was required to separate the dodecylamine and octadecylamine reaction products in a pure state.

Hydrochloride - The salt, which was prepared from 5 g of the amine and 1.15 cc of concentrated hydrochloric acid, crystallized as white leaflets melting at $105-7^{\circ}$.

Calcd. for $C_{24}H_{46}NOCl$: N,3.5 Found: N,3.7

A chlorine analysis was not made because the salt was too insoluble.

N-(5-methylfurfuryl)-dimethylamine. Eighty-one grams (1.0m) of 37% formaldehyde, 81.5 g (1.0m) of dimethylamine hydrochloride and 82 g 91.0m) of methylfuran were heated at reflux with vigorous stirring for 24 hours. At the end of this time only a small amount of methylfuran was unreacted.

The reaction mixture was cooled, extracted with two 100 cc portions of ether, then neutralized with 100 cc of concentrated NH_4OH. The oil layer was separated, the water extracted with two 50 cc portions of ether, and the combined ether and amine layer dried overnight over Na_2SO_4.

The ether was removed and the residue distilled in vacue to yield 90 g (64.7%) of colorless oil boiling at 68-70°/25 mm.

$D_{25}/4$ - 0.921 nd^{25} - 1.4620

Calcd. for $C_8H_{13}NO$: N,10.1 Found: N,10.2

Hydrochloride - The salt, which was prepared from 2 cc of the amine and 1.5 cc of concentrated hydrochloric acid, crystallized as colorless needles melting at 158-158.5°.

Calcd. for $C_8H_{14}NOCl$: N,8.0 Found: N,8.0

Cl,20.2   Found: Cl,20.0

N-(5-methylfurfuryl)-1-propylamine. Forty-two grams (0.44m) of 1-propylamine hydrochloride and 50.0 g (0.62m) of 37% formaldehyde were heated to 60° with stirring, and then 34.5 g (0.42m) of methylfuran added dropwise over 1½ hours.

After three-fourths of the methylfuran had been added, the mixture was heated to reflux and refluxing continued until the reaction was complete.

The reaction was worked up in the usual fashion to yield 14.3 g (22.2%) of secondary amine that boiled at $82-3°/$ 20mm.

$D_{25/4}$ - 0.923 nd^{25} - 1.4630

Calcd. for $C_9H_{15}NO$: N,9.1 Found: N,9.2

<u>Hydrochloride</u> - Two grams of the secondary amine and 1.1 cc of concentrated hydrochloric acid gave the salt which crystallized as white needles melting at $138-9°$.

Calcd. for $C_9H_{16}NOCl$: N,7.4   Found: N,7.3

Cl,18.8   Found: Cl,18.5

<u>N-(5-methylfurfuryl)-allylamine</u>. To 93.5 g (1.0m) of allylamine hydrochloride and 81 g (1.0m) of 37% formaldehyde in a flask equipped with a dropping funnel, stirrer and thermometer reaching into the liquid, 82 g (1.0m) of methylfuran was added over $1\frac{1}{2}$ hours while the temperature was held at $20-25°$.

The secondary amine, which was isolated as usual, weighed 19 g (12.6%) and boiled at $93°/21$ mm..

$D_{25/4}$ - 0.959 nd^{25} - 1.4832

Calcd. for $C_9H_{13}NO$: N,9.3 Found: N,9.1

<u>Hydrochloride</u> - The salt formed as an oil on treating 5.0 g of the amine with 2.8 cc of concentrated hydrochloric

acid and had to be crystallized in the manner described on page 73. It was obtained as white leaflets melting at 90-91°.

Calcd. for $C_9H_{14}NOCl$: N,7.5 Found: N,7.3

Cl,19.0   Found: Cl,18.8

N-(5-methylfurfuryl)-morpholine. Eighty-two grams (1.0m) of methylfuran was added during two hours to a stirred solution of 130 g (1.05m) of morpholine hydrochloride in 95 g (1.17m) of 37% formaldehyde. Soon after the addition of the methylfuran was complete, the hydrochloride of the tertiary amine began to separate.

After the reaction had stood at room temperature for two hours, one liter of acetone was added followed by 500 cc of absolute ethanol. The faintly yellow crystals were filtered, washed with 100 cc of absolute alcohol, and dried. The yield of crude salt melting at 201-3° 21th decomposition was 161 g (78.5%).

One recrystallization from absolute alcohol gave colorless needles that melted at 202-4°d.

Calcd. for $C_{10}H_{16}NO_2Cl$: N,6.4   Found: N,6.5

Cl,16.3   Found: Cl,15.9

The free base was prepared from 80 g of the hydrochloride by neutralization with NaOH.

BP_{20}: 123° $D_{25/4}$ - 1.057 nd^{25} - 1.4961

Calcd. for $C_{10}H_{15}NO_2$: N,7.7   Found: N,7.7

N-(5-methylfurfuryl)-ethanolamine. The compound was prepared by adding 41 g (0.5m) of methylfuran during one

hour to a stirred mixture of 88 g (0.91m) of ethanolamine hydrochloride and 81 g (1.0m) of 37% formaldehyde.

The reaction mixture was treated as usual to yield 33.0 g (42.6%) of colorless oil boiling at $100\text{-}102^\circ/3$ mm. This compound was completely soluble in water.

$D_{25/4}$ - 1.082 nd^{25} - 1.5020

Calcd. for $C_8H_{13}NO_2$: N, 9.0   Found: N, 8.9

Hydrochloride - The salt precipitated as an oil when 5.0 g of the amine were treated with 1.7 cc of concentrated hydrochloric acid. Crystallization was induced as described previously to give white leaflets melting at $79\text{-}79.5^\circ$.

Calcd. for $C_8H_{14}NO_2Cl$: N, 7.3   Found: N, 7.3

Cl, 18.6   Found: Cl, 18.2

N-(5-methylfurfuryl)-piperidine. Forty-four grams (0.54m) of methylfuran was added to a stirred mixture of 65 g (0.54m) of piperidine hydrochloride and 50 g (0.62m) of 27% formaldehyde while the temperature was maintained at $70\text{-}80^\circ$.

The reaction product, which was isolated as previously described, weighed 74.5 g (77.6%).

BP_6: $88\text{-}89^\circ$ BP_7: $92\text{-}3^\circ$

$D_{25/4}$ - 0.981 nd^{25} - 1.4950

Calcd. for $C_{11}H_{17}NO$: N, 7.8 Found: N, 7.9[D]

Hydrochloride - The salt formed as an oil when 5.0 g of the base were treated with 2.3 cc of concentrated hydrochloric

acid. After crystallization from boiling ether, the compound was obtained as white plates melting at 147-8°.

Calcd. for $C_{11}H_{18}NOCl$: N,6.5   Found: N,6.5[D]

Cl, 16.5   Found: Cl,16.3

N-(5-methylfurfuryl)-benzylamine. Seventy-four grams (0.90m) of methylfuran was added as rapidly as possible to a stirred solution of 143.5 g (1.0m) of benzylamine hydrochloride in 85 g (1.05m) of 37% formaldehyde while the temperature was maintained at 30-35°.

The reaction was stirred for 1½ hours at room temperature after all the methylfuran had been added, then neutralized and the base purified as usual.

The secondary amine, which was obtained as a colorless oil, boiled at 104-8°/1 mm and weighed 62.5 g, or 34.6% of the theoretical amount.

$D_{25/4}$ - 1.042 nd^{25} - 1.5411

Calcd. for $C_{13}H_{15}NO$: N,7.0   Found: N,7.1

Hydrochloride - The salt, obtained as a white powder from 5.0 g of the amine and 2.1 cc of concentrated hydrochloric acid, melted at 178-180 with decomposition.

Calcd. for $C_{13}H_{16}NOCl$: N,5.9 Found: N,5.9

Cl,15.0   Found: Cl,15.3

N-(5-methylfurfuryl)-cyclohexylamine. One hundred and fifty grams (1.10m) of cyclohexylamine hydrochloride and 90 g (1.11m) of 37% formaldehyde were rapidly stirred in a 500

cc flask while 82 g (1.0m) of methylfuran was added as rapidly as possible. The reaction was kept at 30-35° by means of external cooling.

The reaction product, which was purified as usual, weighed 102 g (52.8%) and boiled at 75-7°/7 mm.

$D_{25/4}$ - 0.984 nd^{20} - 1.4960

Calcd. for $C_{12}H_{19}NO$: N,7.2   Found: N,7.4

Hydrochloride - The salt, prepared from 5 g of the base and 2.15 cc of concentrated hydrochloric acid, was obtained as small glistening white plates melting at 167-8°.

Calcd. for $C_{12}H_{20}NOCl$: N,6.1   Found: N,6.1

Cl,15.5   Found: Cl,15.3

N-(5-methyltetrahydrofurfuryl)-ethylamine. (A) Fifty-one and eight tenths grams (0.47m) of 5-methylfurfural (63) and 64.3 g (0.47m) of 33% ethylamine were mixed with cooling in a 200 cc Erlenmeyer flask. After the strong heating had subsided the reaction was allowed to stand at room temperature for one hour with occasional shaking. At the end of this time the upper organic layer was separated and washed once with 100 cc of water.

The crude imine was hydrogenated directly, using 4 g of Raney nickel catalyst and an initial hydrogen pressure of 1700 lbs. Distillation of the product gave 43.8 gm of colorless oil, BP_{50} 92-5°. This represents a 56% overall yield from 5-methylfurfural.

Calcd. for $C_8H_{17}NO$: N,9.8   Found: N,9.6

(B) Twenty-five grams of N-(5-methylfurfuryl)-ethylamine (page 74), was hydrogenated using 2 g of Raney nickel catalyst and an initial hydrogen pressure of 1800 lbs. Distillation of the product yielded 23 g (90%) of colorless oil, B.P. $67-70/_{20mm}$.

Calcd. for $C_8H_{27}NO$: N, 9.8   Found: N, 9.8

A purified sample of the tetrahydro amine had the following physical constants:

nd^{25} - 1.4387 $D_{25/4}$ - 0.887

Hydrochloride - The salt was prepared as described previously. It crystallized as buff plates from acetone. M.P., 98-99.

Calcd. for $C_8H_{18}NOCl$: N, 7.8   Found: N, 7.7

Cl, 19.8   Found: Cl, 19.6

N-ethyl-N-(5-methyltetrahydrofurfuryl)-3,5-dinitrobenzamide. The 3,5-dinitrobenzoate of the amine from (A) was prepared according to Shriner and Fuson (64).

Colorless needles from alcohol. MP, 89-89.5°

Calcd. for $C_{25}H_{39}N_3O_6$: N, 12.5   Found: N, 12.6

The derivative of the amine from (B) was prepared in the same manner.

Colorless needles from alcohol. MP, 87-88.5°

Calcd. for $C_{25}H_{19}N_3O_6$: N, 12.5   Found: N, 12.2

A mixed melting point of the two derivatives was 87-88.

N,N-di(5-methylfurfuryl)-ethylamine. Eighty-two grams (1.0m) of methylfuran was added during 1½ hours to a stirred

solution of 40.8 g (0.5m) of ethylamine hydrochloride in 81 g (1.0m) of 37% formaldehyde. After stirring at room temperature for two hours, the mixture was heated at reflux for three hours to complete the reaction.

The product, separated and purified as usual, was a yellow-tinted oil weighing 50.5 g (49.4%).

BP_6 - 127-30° $D_{25/4}$ - 1.018 nd^{25} - 1.5000

Calcd. for $C_{14}H_{19}NO_2$: N, 6.0 Found: N, 6.2

<u>Hydrochloride</u> - Five grams of the amine and 1.8 cc of concentrated hydrochloric acid gave a salt which crystallized as white prisms that melted at 151-2°.

Calcd. for $C_{14}H_{20}NO_2Cl$: N, 5.2 Found: N, 5.3^D

Cl, 13.1 Found: Cl, 13.1

A run with 14.2 g (0.173m) of ethylamine hydrochloride, 28.5 g (0.348m) of 37% formaldehyde and 28.4 g (0.346m) of methylfuran, in which the temperature was held at 30-40°, gave 29.7 g (73.5%) of the tertiary amine that boiled at 97-8°/1mm.

<u>N,N-di(5-methylfurfuryl)-n-octylamine</u>. The amine was obtained by distillation after the secondary amine was isolated (page 77). The yield of yellowish oil boiling at 150-153/1mm was 43.0 g (35%).

$D_{25/4}$ - 0.947 nd^{25} - 1.4840

Calcd. for $C_{20}H_{32}NO_2$: N, 4.4 Found: N, 4.5

Acid Oxalate - The hydrochloride and picrate were un-crystallizable oils. The acid oxalate was prepared by mixing equivalent quantities of the amine and oxalic acid in ether. It crystallized as white leaflets melting at 201-2° with decomposition.

Calcd. for $C_{22}H_{33}NO_6$: N,3.4   Found: N,3.5^D

N,N-di(5-methylfurfuryl)-benzylamine. The tertiary amine was isolated by distillation after the secondary amine had been removed from the reaction mixture (page 81). Forty-four and a half grams (33.4%) of yellowish oil was obtained that boiled at 138-141°/1mm.

$D^{25/4}$ - 1.063 nd^{25} - 1.5435

Calcd. for $C_{19}H_{21}NO_2$: N,4.7   Found: N,4.8^D

Hydrochloride - The salt was obtained from 5.0 g of the amine and 1.4 cc of concentrated hydrochloric acid as a white powder melting at 154-6° with decomposition.

Calcd. for $C_{19}H_{22}NO_2Cl$: N,4.2   Found: n,4.5^D

Cl,10.7   Found: Cl,10.2

Reaction of 2,5-dimethylfuran, formaldehyde, and ethyl-amine hydrochloride. Nineteen and two-tenths grams (0.2m) of 2,5 dimethylfuran, 16.2 g (0.2m) of 37% formaldehyde and 16.3 g (0.2m) of ethylamine hydrochloride were refluxed together for 24 hours. At the end of this time, 17 g of 2,5 dimethyl furan was recovered unchanged.

C. Furan Resins

Polymerization of methylfuran with 95% sulfuric acid

Preliminary experiments showed that methylfuran alone, or in benzene solution, was polymerized violenty to a black, hard infusible resin by concentrated sulfuric acid. A light colored resin could be obtained by polymerization in chloroform solution.

(a) One and nine-tenths grams of 95% sulfuric acid was added to 8.2 g (0.1m) of methylfuran and 75 cc of chloroform in a 200 cc Erlenmeyer while the flask was shaken vigorously. A strong reaction set in which caused the solvent to boil. After the reaction had subsided, the flask was sheken for 2-3 minutes, then 4 g of sodium hydroxide was added to neutralize the acid. The organic layer was separated and washed with 50 cc of water.

Evaporation of the solvent yielded 5 g of a yellow-brown, glassy resin. The polymer was brittle and could not be extruded into fibers. The resin darkened to cherry red after standing for a month in contact with the air.

Hydrogenation of a portion of the polymer over Raney nickel gave a very light yellow resin that did not darken on exposure to light and air. However, this material resembled the unhydrogenated resin in that it was brittle and could not be extruded into fibers.

(b) Eight and two-tenths grams (0.1m) of methylfuran in 25 cc of Skelly B was treated with 0.04 g of 60° Be' sulfuric acid. After the initial reaction had subsided, 0.3 g of 95% sulfuric acid was added, the flask shaken for three minutes and the acid then destroyed with excess base. The organic layer was separated, washed with 25 cc of water and the solvent evaporated to give 4 g of a light brown glassy resin similar to that obtained previously.

Destructive distillation of the polymer caused the separation of water and the formation of an unstable oil which boiled over the range 100-260°/740. Since no pure material could be isolated, the substance was not further investigated.

Polymerization of methylfuran with 70% nitric acid

When 8.2 g (0.1m) of methylfuran were added dropwise to 10 cc of 70% nitric acid, a vigorous reaction ensued which formed 3 g of a light yellow, infusible resin.

A similar polymer was obtained by treating the sulfuric acid resin with 70% nitric acid.

Polymerization of methylfuran with 36% hydrochloric acid

Ten grams of concentrated hydrochloric acid was added to 8.2 g (0.1m) of methylfuran and 25 cc of chloroform in a 125 cc Erlenmeyer. A strongly exothermic reaction occurred which turned the solution dark red.

The polymer obtained was similar to that formed by sulfuric acid polymerization.

Polymerization of methylfuran with anhydrous aluminum chloride

Two grams of methylfuran were dissolved in 3 cc of chloroform in a 25 cc Erlenmeyer. When 0.2 g of aluminum chloride were added, a vigorous reaction set in that caused the solution to boil. Addition of 10 cc of water precipitated a white, amorphous solid which weighed 1.5 g when dry. The resin was soluble in ether, chloroform, alcohol and acetone.

Polymerization of methylfuran with 6N hydrochloric acid

Twenty-one grams of methylfuran was added to a solution of 25 cc of concentrated hydrochloric in 25 cc of absolute ethanol, the reaction stirred at 20° for half an hour, then the acid neutralized with excess sodium hydroxide. The oil was taken up in 50 cc of ether, the ether layer washed with 25 cc of water, and dried over sodium sulfate.

The polymer was stabilized by hydrogenation of the ether solution over 4 g of Raney nickel. After removal of the ether, distillation of the hydrogenated product gave 7 g of material boiling at $50-165^{\circ}/740$ mm, and 5 g of very viscous oil boiling at $157-163^{\circ}/1$mm. These fractions were not further investigated.

Polymerization of furfuryl alcohol with 3N hydrochloric acid

Ten grams of furfuryl alcohol was dissolved in 100 cc of 3N HCl in a separatory funnel. The liquid soon clouded, turned purple, then green and finally light brown in color.

The heavy oil which began to precipitate rapidly was separated as fast as it formed. The funnel was cooled under the tap occasionally to keep the reaction at 20-30°. The polymer formed in this fashion always contained some furfuryl alcohol.

Distillation of a hydrogenated sample of the polymer gave material boiling over the range 100-200°/25 mm. No pure fraction could be isolated.

Treatment of the hydrogenated polymer with dry hydrogen bromide gave a black tar that was not further investigated.

Polymerization of methylfuran, ammonium chloride and formaldehyde

Equimolar quantities of methylfuran, ammonium chloride and formaldehyde were allowed to stand for twelve hours with occasional shaking, at the end of which time the methylfuran layer had practically disappeared. Neutralization of the red solution with sodium hydroxide precipitated a light brown amorphous solid. The product was alternately washed with water and acetone until the washings were colorless, then dried overnight at 100°. The weight of the product was about 50% of the weight of the reactants. Forcing the reaction gives a gummy resin.

Analysis of two different preparations of the polymer showed a nitrogen content of 8.8%. On the basis of the nitrogen analysis, the resin is theoretically capable of absorbing 0.57 equivalents of acid per 100 g of resin, or 23 g of HCl per 100 g of resin.

One gram of the resin, 20 cc of o.1181N hydrochloric acid and 50 cc of water were shaken together for an hour. Titration of the sample showed that the acid had been completely absorbed. A blank, in which the acid was omitted, was run simultaneously with the unknown.

Three-tenths gram of the resin was shaken with 20 cc of 0.1181N HCl and 50 cc of water for an hour. Back titration, after allowing for the blank, required 14.00 cc of 0.1040N NaOH. This represents approximately 50% of the theoretical uptake of acid, or about 11 g of HCl per 100 g of resin.

These experiments indicate that the material could be used as an ion-exchange. However, evaporation of the supernatent liquid showed that the resin was soluble to the extent of 5% in the acid solutions. This solubility would have to be reduced before the material would find practical application.

Polymerization of furfuryl alcohol, ammonium chloride, and formaldehyde

Ten grams (0.102m) of furfuryl alcohol, 8.1 g (0.1m) of 37% formaldehyde and 5.4 g (0.1m) of ammonium chloride were heated to 50°. A violent reaction set in causing the liquid to boil and turn dark. Neutralization of the reaction mixture with KOH precipitated a gummy, red-brown resin.

A similar gummy material was obtained when ethylamine hydrochloride was substituted for ammonium chloride.

Polymerization of methylfuran, ethylamine hydrochloride, and furfural

One-tenth mol of the reactants was mixed and refluxed for 12 hours. At the end of this time the reaction had set to a black solid.

The same sort of resinous material was obtained if furfural and ethylamine hydrochloride were refluxed 12 hours. Evidently the hydrochloride is sufficiently acidic to cause polymerization of the furfural.

Reaction of methylfuran and formaldehyde in the presence of ammonia

This reaction was run in an attempt to prepare a Bakelite type of resin. However, no reaction occurred when 8.2 g (0.1m) of methylfuran and 16.0 g (0.2m) of paraformaldehyde were heated together in the presence of a drop of concentrated ammonium hydroxide.

Reaction of methylfuran and trichloroacetic acid

A few drops of water were added to a solution of 1 g of trichloroacetic acid in 8.2 g of methylfuran. A small amount of black residue had precipitated from the dark green reaction mixture after four days at room temperature, otherwise there was no indication of polymerization.

Reaction of methylfuran and potassium hydroxide

Fourteen and seven-tenths grams of methylfuran was recovered unchanged after refluxing 16.4 g (0.2m) of methylfuran and 30 g of 30% KOH for thirty hours.

Acidification of the base layer precipitated a dark brown solid which was not further investigated.

Reaction of furfural and dry sulfur dioxide

Six and right-tenths grams (0.1m) of sulfur dioxide and 9.6 g (0.1m) of furfural, which were sealed in a tube with no added catalyst, gave a very small amount of black polymer after standing for three weeks.

Reaction of methylfuran and acrylonitrile

An attempt was made at emulsion polymerization of methyl-furan. Fifteen grams of methylfuran, 5 g of acrylonitrile, 4 g of ammonium oleate, 2 g of sodium perborate and 2 g of secondary sodium phosphate were sealed in a tube and shaken. The tube was allowed to stand for ten days at room temperature with occasional shaking. At the end of this time no evidence of reaction was observed.

Reaction of furfuryl alcohol and acrylonitrile (KOH catalyst)

Nine and eight-tenths grams (0.1m) of furfuryl alcohol, 1.5 cc of 40% potassium hydroxide and 15 cc of dioxane were

placed in a 200 cc flask equipped with a dropping funnel, stirrer, and thermometer that reached into the liquid. While the temperature was maintained at 35°, 5.3 g (0.1m) of acrylonitrile was added dropwise to the stirred solution over the period of an hour. Stirring was continued for thirty minutes after all of the nitrile had been added.

Seventy-five grams of water containing 5 cc of concentrated hydrochloric acid was added to the reaction. The organic layer was separated, washed with two 15 cc portions of 10% sodium bicarbonate, twice with 20 cc portions of water, dried over sodium sulfate and distilled in vacue. The yield of the cyanoethyl ether boiling at $152^{\circ}/25$ mm was 11.0 g (73%).

No reaction was obtained when benzyltrimethylammonium hydroxide was used as a catalyst instead of potassium hydroxide.

Fifty per cent sulfuric acid polymerized the cyanoethyl ether to a black resin so insoluble that no attempts were made to hydrogenate it. The cyano group in the resin was slowly hydrolyzed by boiling 30% potassium hydroxide.

Reaction of furfuryl alcohol and acrylonitrile (SO_2 catalyst)

One milliliter of concentrated aqueous sulfur dioxide, 9.8 g (0.1m) of furfuryl alcohol and 5.3 g (0.1m) of acrylonitrile were stirred at reflux for 45 minutes.

The organic layer was dissolved in 25 cc of ether, washed with 25 cc of 5% sodium carbonate, 20 cc of water and dried over sodium sulfate. Distillation yielded 5 g of

acrylonitrile, 5 g of furfuryl alcohol, and 3 g of material boiling at 120-145°/40 mm. In its odor and appearance the high-boiling material resembled that obtained by the action of 3N hydrochloric acid on furfuryl alcohol (page 89).

Reaction of acetyl chloride and tetrahydrofurfuryl acetate

Three hundred and forty-one grams (2.37m) of tetrahydrofurfuryl acetate, 314 g (4.00m) of acetyl chloride and 25 mg of fused zinc chloride were refluxed together for 1½ hours.

At the end of this time the unreacted acetyl chloride and tetrahydrofurfuryl acetate were removed at the water pump. Distillation of the residue yielded 295 g (56%) of mixed chloroacetates (65) boiling at 127-8°/4 mm.

nd^{15} - 1.4492 D_{15} - 1.148

M. R. (calcd) - 51.9   M. R. (Obsd) - 51.9

Constants given by Paul (66):

nd^{15} - 1.4482 D_{15} - 1.151

No polymer was formed when the mixed chloroacetates were heated with diethyl malonate in the presence of aluminum ethoxide catalyst.

1,4-Dibromopentane

Dry hydrogen bromide, generated by dropping bromine on boiling tetralin, was passed into 43 g (0.5m) of methyltetrahydrofuran in the presence of 20 mg of fused zinc chloride

as a catalyst. The reaction was maintained at 80-90° until the adsorption of hydrogen bromide ceased. Noticeable amounts of black tarry material were present at the end of the reaction.

The dibromide was washed with water, 50 cc of 5% sodium bicarbonate, dried and distilled under reduced pressure. The yield of colorless oil boiling at 100-103/14mm was 85 g (74%).

1,4-Dichloropentane

The dichloride could not be prepared by passing dry hydrogen chloride into methyltetrahydrofuran.

One hundred seventy-two and eight-tenths grams (2.0m) of concentrated hydrochloric acid, 136.3 g (0.0m) of fused zinc chloride and 43.0 g (0.5m) of methyltetrahydrofuran were heated 12 hours with stirring at 60-70° while dry hydrogen chloride was passed into the reaction mixture.

The dark organic layer was separated and washed successively with 100 cc of water, 10 cc of cold (0°) 95% sulfuric acid, 50 cc of water and 25 cc of 5% potassium carbonate. After drying over sodium sulfate, the reaction product was distilled in vacuo to yield 53.6 g (76%) of the dichloride boiling at 55-6°/14mm.

DISCUSSION

A.   Hydrogenation of Furfural to Methylfuran

The experimental results show that the activity of copper chromite for vapor phase hydrogenation is quite dependent on its method of preparation, while its life is a function both of the method of preparation and the experimental conditions under which it is used.

The results of laboratory experiments 1, 2, 3, and 12, as well as semi-pilot run No. 6, clearly show that the activity of the chromite is an inverse function of the decomposition temperature, i.e., within limits, the lower the ignition temperature the higher the activity of the catalyst.

That other preparation details are important is indicated by the fact that the complex chromate prepared from an alkaline mother liquor gave, on ignition, a chromite of low activity (run No. 2, p. 44). In addition, extraction with strong acetic acid apparently lowers the catalyst activity (run No. 5, p. 47).

Considering only the three variables mentioned, it is evident that rigid control of experimental conditions is necessary to prepare a consistently active catalyst.

Optimum conditions for precipitation, ignition, and extraction were not determined. Other factors which could be

expected to influence the activity and stability of the catalyst, but which were not investigated, are: (1) the kinds and amount of stabilizer used, (2) the nature of the salts from which the catalyst is made, (3) the concentration of reagents employed, and (4) the amounts of chemicals used.

The variations observed in catalyst activity in the semi-pilot unit were due, in part, to difficulties encountered in duplicating conditions on the large scale preparations of the catalyst. This difficulty was also experienced by Adkins, et al (57).

That the life of the catalyst depends on its method of preparation, as well as the experimental conditions under which it is used, is indicated by the results of experiment 15 (p. 35). The deactivation of the Hooker catalyst is presumed to occur because stabilizing metals such as calcium or barium were not included in its preparation.

Burnette showed the catalyst to be deactivated at temperatures above $280°$ (1). The results of experiment 3 (p. 24) and run No. 7 (p. 52) confirm these earlier observations. This deactivation would be expected in view of the fact that ignition temperature is so important in catalyst preparation. At the present time, the most satisfactory operating temperature appears to be in the range of $200-230°$.

The thought that a high furfural mass rate of flow would cause deactivation because of temperature effects on

the surface of the catalyst, is not borne out by the results
of runs 3 (p. 44) and 7 (p. 52). However, a closer investiga-
tion of this point must be made before it can be stated with
certainty that no harmful effects result from a high mass
flow.

No rigorous interpretation of the semi-pilot data can
be made because of the variations that occurred in the pre-
paration of the catalyst from run to run. However, there are
indications that acidic materials in the technical furfural
and absorption of methylfuran on the catalyst both adversely
affect the catalyst.

The results of runs 3 (p. 44), 4 (p. 46), 5 (p. 47),
and 7 (p. 52) indicate that small amounts of acid impurities
contribute to deactivation of the catalyst. The furfural
used in runs 3 and 4 was technical, undistilled, while that
used in 5 and 7 was purified by distillation. The catalyst
employed in run 3 was an under-roasted product that was basic
in nature. Only a slight deactivation was shown throughout
run 3 because the remaining basic components of the catalyst
neutralized the acids. In run 4, where a completely decomposed,
neutral chromite was used, the steady decline of the catalyst
was presumably caused by the action of the acids on the
catalyst. However, in runs 5 and 7 yields remained practically
constant throughout because purified furfural was being used.

With the same catalyst, the yields obtained in the pilot
unit were never consistently as good as those observed in the

in the laboratory. No explanation can be offered for this behavior. In experiment 18 (p. 37) it was shown that methylfuran was adsorbed on the catalyst when a dry ice trap was not used in the system. If this absorbed methylfuran reacted to form a coating over the catalyst it would explain in part the observed difference in the laboratory and pilot results. That a coating is formed over the semi-pilot catalyst is revealed by the fact that used catalyst from the unit cannot be wet with water.

Materials of construction may have influenced the reaction to the extent of the observed difference in laboratory and pilot results. This point should be investigated.

A critical study of the weight ratio of chromite to charcoal carrier was not made. However, the results of experiments 11 and 12 (pgs. 27 and 28) indicated that a ratio of approximately 1:1 is necessary for complete conversion of furfural to methylfuran with one pass over the catalyst.

Contact times were reduced to approximately one second with only a slight evidence that the yields were adversely affected. Determination of the proper contact time should be made in subsequent investigations.

A comparison of laboratory and semi-pilot results is shown in Table 12.

During the work it was observed that the activity of a copper chromite catalyst could be judged from the products of hydrogenation. The most active catalysts gave some amyl

alcohol as well as methylfuran. As deactivation took place, no amyl alcohol could be detected. With greater deactivation furfuryl alcohol was produced. The fact that this gradation of products occurs suggests the possibility that with proper control of conditions either methylfuran or furfuryl alcohol could be produced by vapor phase hydrogenation.

X-ray studies of the copper chromite showed that the catalyst was amorphous. Only faint evidence for crystallinity could be detected. An analysis of the copper chromite from run 3 is given below:

$$
\begin{array}{lr}
\text{Ignition loss} - - - - - & 9.2\% \\
Cu_2O - - - - - - - - - & 39.3\% \\
Cr_2O_3 - - - - - - - - - & 51.1\% \\
CaO - - - - - - - - - & 0.1\%
\end{array}
$$

These results do not indicate whether copper is mono- or divalent in copper chromite. Hence no conclusion can be drawn as to the true structure of the catalyst.

B. Reaction of Methylfuran

Little attempt was made to find optimum conditions for the Mannich reactions involving methylfuran. Some of the amine derivatives, notably the ethyl, benzyl, and cyclohexyl compounds, formed readily at 30-35°, whereas others such as the iso-propyl, and dimethylamino compounds formed readily only at reflux temperatures. The stated yields could undoubtedly be improved by further study.

That the reaction took place at the free alpha position in the methylfuran nucleus was indicated by the fact that 2,5-dimethylfuran did not condense under similar conditions.

Table 12. Comparison of Laboratory and Semi-pilot Data

Unit	Run No.	Weight of Copper Chromite Used	Weight of Furfural Used	Furfural Mass Rate of Flow $\#/hr/ft^2$	Methyl furan Produced	Percent Yield of Methyl-furan	$\dfrac{\text{Wt. catalyst}}{\text{Wt. Methylfuran}} \times 100$
Laboratory	12	35g	1035g	8.33	806g	91.2	4.35
Semi-pilot	1	700g	11,022g	31.2	6083g	64.6	11.5
	3	1.54 lb	52.0 lb	21.2	35.5 lb	80.2	4.35
	4*	1.66 lb	110.1 lb	23.4	63.2 lb	67.2	2.63
	5	1.59 lb	83.95 lb	22.4	48.9 lb	68.2	3.25
	7	270g	10.114g	8.3	6701g	77.5	4.03

* For the sake of comparison, it was arbitrarily assumed that the catalyst would be discarded at the end of four days for economical reasons. Hence, only data from the first four days of this run are included here.

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Proof for the structure of N-(5-methylfurfuryl)-ethylamine, as given in the experimental section, is outlined below.
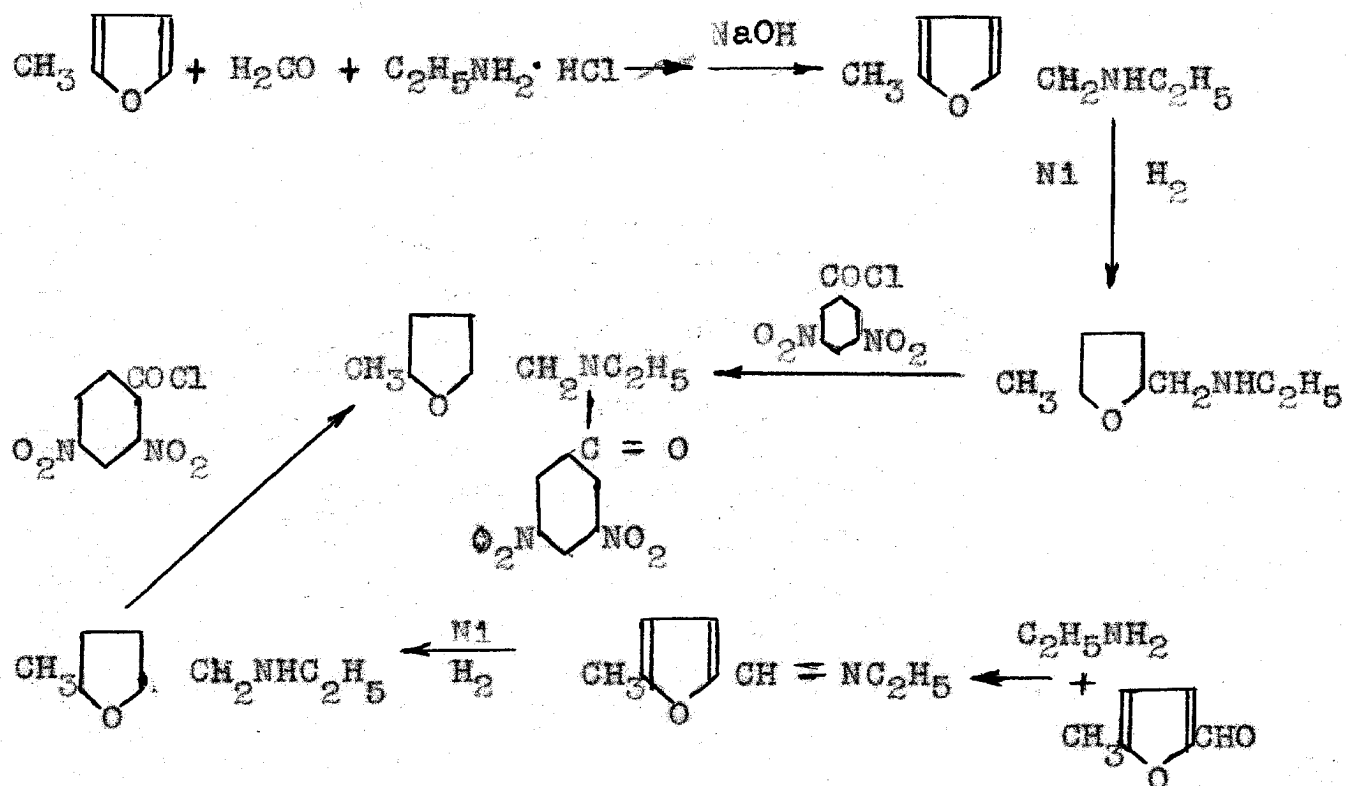
C. Furan Resins

Acid polymerization of methylfuran produced resins with poor aging characteristics and physical properties. A knowledge of the structure of the polymers would be of great aid to research aimed at improving the qualities of these materials.

Methylfuran and furfuryl alcohol were polymerized by dilute hydrochloric acid in an attempt to isolate low molecular weight polymers for structure study. Very complex mixtures were obtained and it appears that the isolation in a pure form of

a simple polymer, such as a dimer or trimer, will prove difficult. It seems probable that valuable information might be gained without isolation of pure forms by ozonolysis studies on the polymer mixtures.

SUMMARY

1. Methylfuran has been produced from furfural in the laboratory in 91% overall yield by vapor phase hydrogenation over a copper chromite catalyst at atmospheric pressure.

2. A small pilot plant has been constructed for vapor phase hydrogenation of furfural to methylfuran. Methylfuran has been produced in 80% overall yield in this unit.

3. In the laboratory 23 g of methylfuran were produced per gram of copper chromite used, while in the pilot plant 23 pounds of methylfuran were produced per pound of catalyst.

4. The complex copper-ammonium chromate should be decomposed at temperatures below 350° in order to obtain a copper chromite catalyst that is active for the vapor phase hydrogenation of furfural to methylfuran.

5. Small amounts of metals such as calcium or barium are necessary to stabilize the chromite catalyst against reduction.

6. The mol ratio of hydrogen to furfural should be greater than 10:1 in order to obtain good conversion of furfural to methylfuran with one pass of the furfural over the catalyst.

7. The catalyst bed temperature is not a critical factor in the hydrogenation of furfural to methylfuran as long as it is maintained in the range of $200-230^\circ$.

8. The vapor pressures of methylfuran have been measured at 15°, 25° and 30°.

9. The total vapor pressures of the **furfural-methylfuran** system have been determined at 20°, 25.6°, and 30°.

10. The vapor-liquid equilibria of the furfural-methylfuran system have been determined at 738 mm.

11. The reaction of methylfuran with formaldehyde and a wide variety of primary and secondary amine hydrochlorides has been found to give the corresponding Mannich bases. The synthesis of 17 new furfuryl amines by this reaction has been described.

12. The reaction of methylfuran or furfuryl alcohol, with formaldehydes and ammonium chloride has been found to give a nitrogen containing polymer which may find uses as an ion exchange resin.

13. Methods have been described for producing light colored resins from methylfuran by uses of acid catalysts.

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