

A FLOW PROCESS FOR THE FISHER-TROPSCH
SYNTHESIS OF HYDROCARBONS

by

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↓

Massachusetts Inst. of Technology
Cambridge, Massachusetts

July 31, 1942

Professor George W. Swett
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Mass.

Dear Sir:

In accordance with the requirements for the degree of Master of Science, I am submitting herewith a thesis entitled "A Flow Process for the Fisher-Tropsch Synthesis of Hydrocarbons".

Yours faithfully,

Muslihittin A. Tunca

260404

A C K N O W L E D G M E N T

I wish to express my appreciation to Professor E.R. Gilliland, of the Chemical Engineering Department, for his constant aid and many helpful suggestions throughout this work. I am also indebted to the Mining Research Institute of Turkey under whose financial aid this work has been carried out.

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I. SUMMARY

Today the oil situation plays a vital role in the economy of civilized countries. Much work has been done in those nations poor in natural oil to find a suitable synthetic process to produce hydrocarbons economically. One of the most successful, the Bergius process, has reached its culmination and the Fisher-Tropsch process seems to be heading toward its complete replacement. But the latter process is still in a very inefficient stage.

This work had for purpose to bring about new developments to this interesting process.

A digest of the literature down to 1902 is made and the development of the process discussed. The most recent and important ones are brought out. The basic principles on which these studies have been carried out are also explained briefly.

A discussion of the reasons for the inefficiency of the Fisher process today is made, based on the literature. The most important ones are considered as being the difficulties in obtaining uniform temperature in the contact mass and the very limited production capacity. Suspending the catalyst in a state of fine particles in a stream of synthesis gas, the so-called jiggling was believed to be a possible solution.

The investigation of the problem was undertaken with

the study of the following questions:

- I. The jiggling properties of catalysts
 - A. Effect of particle size
 - B. Effect of carrier
- II. Study of the activity and life of the catalysts
 - A. Effect of carrier
 - B. Effect of temperature
- III. The effect of the gas rate upon the per cent contraction at optimum temperature
- IV. The effect of temperature upon the per cent contraction
- V. The effect of the gas rate upon the optimum temperature.

From the results obtained experimentally it was concluded that;

- I. Jiggling of particles of Fisher catalyst is very unfavorable with particles smaller than 140 mesh.
- II. Kieselguhr is better as carrier than Fuller's earth, which is better than silica gel, in respect to per cent contraction.
- III. The optimum temperature corresponding to the maximum per cent gas volume contraction is about equal with both Fuller's earth and silica gel as carrier but is lower in the case of Kieselguhr.
- IV. The catalyst with Kieselguhr as carrier is more lasting than with the two other materials.

- V. The loss of activity is caused by temperature effects.
- VI. Contractions as high as 61 per cent can be obtained at gas velocities as high as 20 liters/gm. Co, hr.
- VII. The per cent contraction drops sensibly linearly with increased rate of flow. A 300 per cent increase in rate caused only 19 per cent decrease in contraction.
- VIII. The optimum reaction temperature is higher at higher velocities. It tends to become constant after a certain rate of flow.
- IX. Most of the reaction occurs within a very short distance from the point of entry of the gas.
- X. The catalyst may lose its activity within a very short time due to excessively fast reaction and increase in particle temperature.
- XI. A stable catalyst loses its optimum activity for a lower one.
- XII. Cooling down and heating up again slowly seems to increase the activity slightly.

Further work on the subject was finally recommended and the following suggestions were made;

- I. That investigation be made with the use of a gas with a H_2/Co ratio of 2 to 1.
- II. That recycling the catalyst be carried out in the belief that this will help to keep the catalyst at maximum activity.
- III. That the jiggling process be carried out at pressures of 5 - 20 atmospheres.

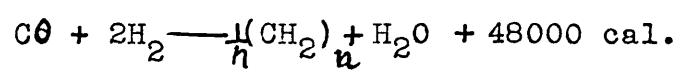
II. INTRODUCTION

Today, the needs of a civilized country in motor fuel have increased to such a degree that it is impossible to provide for them adequately unless sufficient amount of natural oil is easily available. The importance of the oil situation to countries deficient in natural supplies is consequently obvious, especially in war times. As a result intensive studies have been carried out in such countries as Germany, England, Japan, France, Italy, with the purpose of synthetizing hydrocarbons suitable for use as motor fuel, starting from coal, a substance which most of these countries have in large quantities.

A process was developed by Bergius which was relatively well suited to the big scale production of hydrocarbons in the gasoline range. It consists in hydrogenating coal directly, under high temperature and pressure. The gasoline fraction obtained by this process may have an octane number of 75-85 (3) and maybe increased to nearly 100 by addition of small amounts of lead tetraethyl. In spite of these distinct advantages the direct hydrogenation of coal or lignites presents technical difficulties which are far from being eliminated even in the present days. A hydrogenation plant demands not only a very high original investment, but also requires about two years to build. About two thousand men are necessary to run such a plant producing 150,000 tons gasoline a year. (3)

The direct hydrogenation method is also up against considerable metallurgical difficulties. Only a very few steel manufacturing companies are in a position to build the huge reaction towers capable of resisting the effect of high pressure and temperature and the corrosive effect of H_2S and HCl . As a result the cost of these towers is excessive. Finally, the efficiency of Bergius plants is low due to formation of considerable amounts of CH_4 and C_2H_6 from which H_2 has to be obtained catalytically. The process is expensive in itself. For these reasons, the Bergius process is today considered by most authorities as having reached its culmination. In turn, the Fisher-Tropsch process seems to offer many advantages that appear to make it the process of the future.

The Fisher process consists essentially in the catalytic reduction of carbon monoxide to produce mixtures of hydrocarbons. The net reaction to produce the lighter hydrocarbons may be represented by:



These hydrocarbons consist mostly of paraffins in the gasoline boiling range, a lesser amount of fuel oil suitable for Diesel fuel and small quantities of olefins and gaseous paraffins. Their quality and relative amounts may be varied by the choice of the operating conditions and the catalyst.

The gasoline fraction so obtained is of low grade - octane value 55 or lower (3). This is a distinct disadvantage

as compared to products of direct hydrogenation of coal, but the octane value can be made higher by addition of small amounts of lead tetraethyl. By means of reforming the low boiling parts and cracking the heavier ends a high grade gasoline can always be obtained.

The great advantage of the Fisher process lies in the fact that it is carried out either at atmospheric pressure or pressures of 5-20 atmospheres and temperatures not higher than 250°C. Obviously the capital investment of such a plant will be considerably lower than that of a direct hydrogenation plant. It is to be noted that the synthesis from the CO and H₂ obtained from coke combined with the direct hydrogenation of the coal oil distillate formed in coking, has been shown to give nearly twice the yield of gasoline and oil obtained by direct hydrogenation of the same coal. (21)

The yield per kg catalyst, obtained is still very low however and there is yet much progress to be accomplished in the Fisher process.

It was the purpose of this investigation to contribute, in the limits of the short time available, as much as possible to the development of this process of great future.

III. HISTORY AND PREVIOUS WORK

The field of catalytic handling of water gas has become manifold in the last 35 years. Owing to the numerous linking possibilities of carbon with itself, the catalysis between CO and H₂ permits greater variations in the products than are found in most commercial catalysis.

The whole history of the development of the water gas catalysis is that of development of various contacts and reaction conditions.

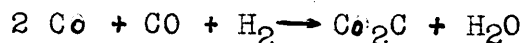
The water gas catalysis began with simple metal contacts at ordinary pressures but elevated temperatures. Other contacts and operating conditions evolved in the course of years. Thus Sabatier and Sendrens (24) began the synthesis of methane in 1902, using various metal contacts especially that of the iron and platinum groups, at temperatures of 200°C. or more. In 1913 the BASF (1) found that at higher pressures and temperatures mixtures of hydrocarbons and various oxygenated organic compounds were formed. In 1923 Fisher (6) obtained a somewhat similar mixture by using iron turnings with alkalicarbonates. He called that product "Synthol". Shortly after, in 1925, the BASF (2) reported selective synthesis of the methanol from water gas with the use of multicomponent catalysts. Not much later, in 1926, Fisher and Tropsch (11) reported for the first time that the metals of the iron group, in especially active state produced mixtures consisting mainly

of hydrocarbons of both paraffinic and olefinic nature.

In the course of the following years a great amount of work has been done by investigators especially in countries short of oil like Germany, Japan, England, etc. Soon after the publication of the first paper on the Fisher-Tropsch process proper by Fisher and Tropsch (11), it was found that the ratio of CO to H₂ in the starting gas mixture had a very definite effect upon the yield and its constitution. It was established that by increasing the ratio H₂:CO, methane formation was favored and the higher hydrocarbons formed were increasingly saturated. A relative increase in CO on the other hand lead to the formation of more unsaturated hydrocarbons (20,5,12,16,8). Fisher (12,7) found that the highest yield is obtained by using a CO:H₂ ratio of 1:2. This has been also confirmed by several other authors (29,32). The same author reported that an increase in temperature results in the formation of CO₂ and CH₄.

Murata and Tsuneoka (26) concluded from a series of experiments that an increase in reaction temperature favors the formation of unsaturateds. In a later paper (20) they show skepticism about these conclusions when they say that it is difficult to draw any definite conclusions as to the effect of temperature on the nature of the product. It is however generally agreed that the optimum reaction temperature, although varying with the type of catalyst used, lies between 150-250°C.

A large number of references are found in the literature relative to the Fisher catalysts. The most comprehensive study on the mechanism has been made by S. R. Crayford (4). According to this author, a metal carbide is first formed in contact of CO with the catalyst, wherein (CH₂) builds up



In the presence of chemisorbed H₂, these will be reduced to CH₄. If however, conditions are such that carbide is formed faster than reduced (CH₂) polymerizes to (CH₂)_n. These large molecules will then be broken up by chemisorbed H₂. A similar theory is also given by S. Watanabe, K. Morikawa, and S. Igawa (33).

In an article in Brennstoff Chemie, Fisher (7) lists the activity of a number of CO, Ni, Fe catalysts. Co catalysts are classed by him as giving the highest yields and having the longest life. Similar statements are made by Tsuneoka and Murata who performed an enormous amount of work both on alloy skeleton and precipitation catalysts (27,20,19,18,28,14). A catalyst prepared by them is particularly interesting for the remarkably high yields they obtained with it. About 180 cc of hydrocarbons were synthesized out of 1 m³ of inert free synthesis gas in a single stage at atmospheric pressure. A value higher than the highest reported in the literature in similar cases. The composition of the contact is given as being 18.85% Co, 18.85% Ni, 7.55% Mn, 7.55% U₃O₈ and 47.2% Kieselguhr by

weight or Co:Ni:Mn, U_3O_8 :Kieselguhr as 50:50:20:20:125.

Names such as Myddleton and Walker (21,22,23), S. Tsutsumi (29,30), G. Kita, Watanabe and Morikawa (32,33) should also be mentioned here for their contributions in connection with Fisher catalysts.

Considerable work has been accomplished on the effect of gas rate, space velocity, length of catalyst bed, time of contact, inerts in the gas mixture, etc. upon the yield and its constitution. It is agreed that for a certain amount of catalyst there is an optimum value of the gas rate which is given by Fisher (10) and Watanabe, Morikawa and Igawa (33) as being 1 lt./hr. gm CO. This figure, however, as well as the optimum space velocity is liable to change with the type of catalyst used. The existence of a definite optimum rate of flow is attributed to the fact that the CO:H₂ mixture has to diffuse through a layer of hydrocarbons to reach the catalyst (33). It is therefore necessary to allow enough time for the diffusion to take place.

According to Murata and Tsuneoka (19), the products will be the more saturated in nature the longer the catalyst bed is. In other words, the longer the time of contact, the stronger the hydrogenation effect. The conclusion to be drawn is therefore that by increasing the gas velocity, the unsaturation can be increased.

The effect of inerts has been studied by Tsuneoka and Fujimara (25). These authors state that inerts below

20 per cent in the original gas have no harmful influence. The relative amounts of the different fractions vary however. Dilution of CH_2 groups due to the presence of inerts results in less polymerization. Thus the gasoline fraction increases relative to a decrease in the oil fractions. Myddleton and Walker (22) found that synthesis in two or more steps gives higher efficiencies. Fisher and Pichler made specific studies on this matter and came to the same conclusions. There is disagreement between these investigators however as to the explanation for the increase in yield. Myddleton and Walker speak of the existence of a true adsorption following Langmuir's equation

$$s = S \left(\frac{ap}{1 + ap} \right)$$

where

s = area covered by adsorbed vapor

S = total surface of catalyst

p = partial pressure of the vapor

a = constant depending upon the temperature

By condensing the products between steps, the partial pressure of the hydrocarbon is decreased meaning a decrease in s and an increase in efficiency.

According to Fisher and Pichler, on the other hand, the increase in efficiency is to be attributed to the elimination of the diluting effect of the hydrocarbons present, thus leaving more chance for the unreacted gas to hit the catalyst and react.

It is felt that the better results obtained in the

multistep synthesis are probably due to both effects. It is also to be added that since the reaction is not completed in a single stage, the heat evolved in one stage is only a fraction of the total. Thus a better temperature control is made possible, adding to the efficiency.

F. Martin (17) reports that 50 per cent of the reaction takes place at the end of $1/3$ of the catalyst length. Lower contacts are therefore necessary to make the reaction go to a reasonable completion, ~~if~~ the synthesis ^{is} made in several steps however, ~~then~~ it is possible to cut appreciably on the length of the catalyst.

The latest development in the Fisher Tropsch synthesis was made with the medium pressure synthesis. In 1937 already S. Tsutsumi (30) noted an increase in yield by working at a pressure of 5 atmospheres. But synthesis at pressures higher than atmospheric was first investigated extensively by Fisher and Pichler (10) who called it "Middel druck Synthese" i.e., "Medium pressure synthesis." The nature of the products obtained this way are not different from those obtained at atmospheric pressures. The relative amounts of the different fractions differ however. The amount of high mol. weight paraffins is higher but according to F. Martin (17) it is possible to decrease the formation of solid paraffins to zero by increasing the reaction temperature from 165°C . to 220°C .

In spite of all these investigations however the actual

state of the Fisher process leaves much to desire from the standpoint of efficiency and relative production capacity. It is hoped that a useful contribution to the better knowledge and development of the Fisher Tropsch process will be made by the present investigation.

IV. DESCRIPTION OF APPARATUS

A sketch of the apparatus used in this present investigation is shown in Figure I. Actual photographs of the whole set-up are also to be found in the Appendix.

In this system, a stream of the synthesis gas or of hydrogen - having for its purpose the reduction of the catalyst - could be obtained out of two high-pressure cylinders respectively through a T connection to the line, by opening or shutting the respective control valves. At first only these valves and a diaphragm type pressure reducing valve were used to control the flow and regulate the pressure, but this proved to be unsatisfactory and two more needle valves were placed in series with the reducer. (In this way, a much easier and more precise control of the flow could be obtained.)

The oxygen contained in the synthesis gas[#] was to be reduced to water in a tube filled with copper gauze as catalyst and heated to 450-500°C. in a resistance type electric furnace. (Not shown in Fig. I). As a measure

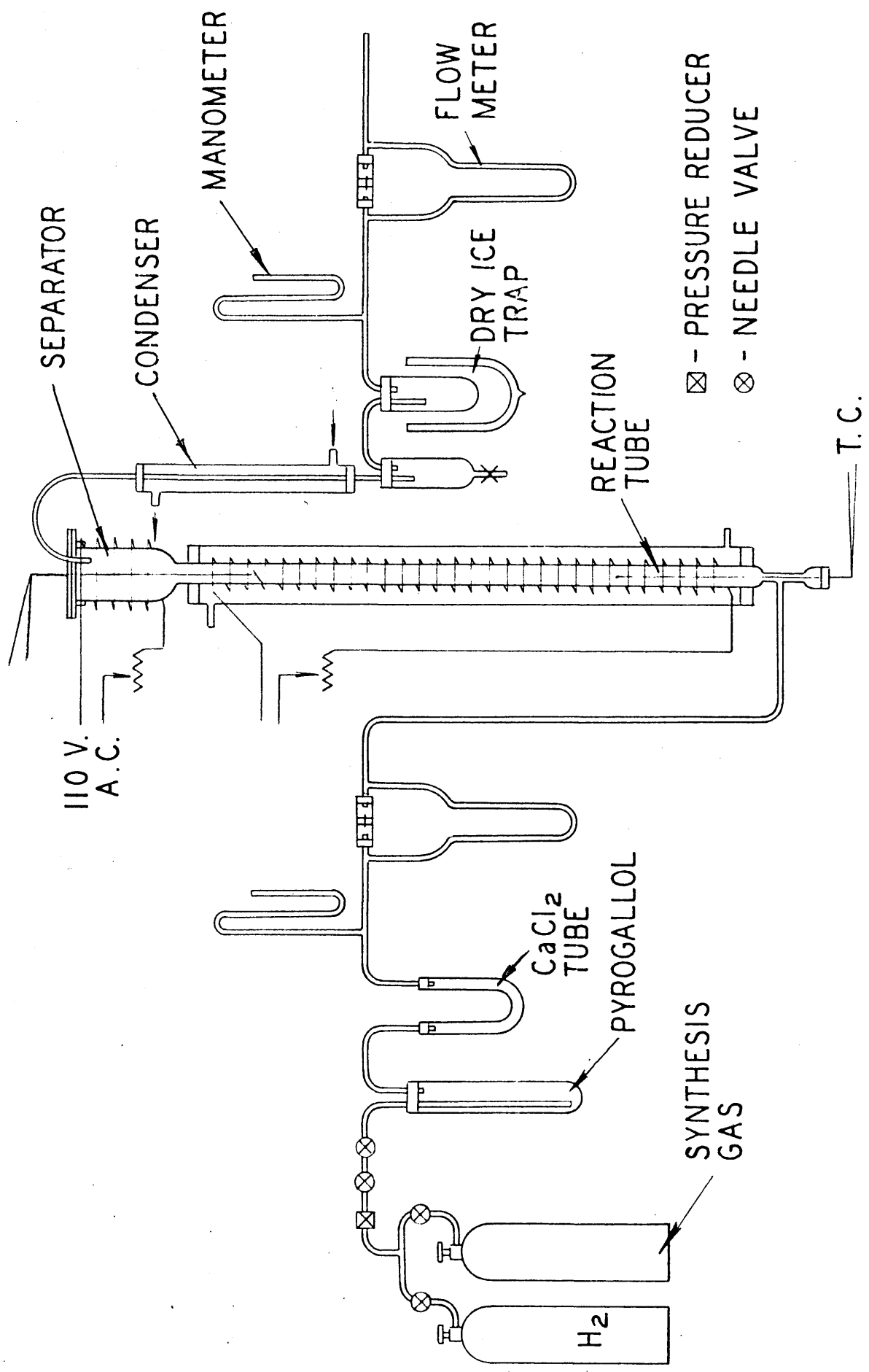
[#] See Appendix for the composition of the gas.

of precaution, however, the gas was then bubbled through an alkaline pyrogallol solution to absorb as much as possible of the last traces of the remaining oxygen.

The water vapor in the gas - from the oxygen reduction, pyrogallol, etc. - was then eliminated in the calcium chloride U-tube. Finally, the gas thus reduced in undesirable constituents to a harmless degree, was metered through an orifice and manometer and entered the reaction tube; "the jigglor". A mercury pressure gage placed before the flowmeter showed any abnormal pressure build-up due to plugging of the lines, etc.

The jigglor itself consisted of a tube 6 ft. tall and 13 mm inside diameter. The bottom narrowed down to about 8 mm inside diameter and formed the high velocity gas neck necessary for keeping the catalyst particles from falling down into the gas inlet, about 10 cm. below the narrowing. The upper part, on the other hand, enlarged into a tube of approximately 1 ft. height and 48 mm inside diameter. It was the gas-catalyst separator. Its top was originally closed with a ceiling of porcelain cement. This was found very unpractical because the cement became too hard and could not be taken off when necessary - cleaning the inside of the reactor. It also made the glass crack at temperatures higher than 200°C. due to its different expansion coefficient. Finally a ring with a flange of

FIGURE I
DIAGRAM OF APPARATUS



brass was made to fit the separator's width and cemented at the top with the porcelain cement. A brass plate was then screwed on with a rubber ring between the two as packing, making any leaks impossible. A thermocouple, with its glass protection tube, was introduced down to about half a foot inside the reactor through a hole in the middle of the plate and fastened to it strongly with cement. A silver soldered brass tube through the plate provided the exit for the reaction products. A thermocouple was also introduced from the bottom up to about a foot and a half inside the reaction tube. The latter was heated to the desired temperature by means of an electric heating coil wound around it uniformly. The temperature was controlled through a slide-wire resistance. This system unfortunately was not satisfactory for the obtaining of a uniform temperature throughout the tube as was found in the course of experiments. However, it could not be changed because of the fact that a jacket was sealed to the tube at both ends with a magnesium oxychloride cement which could not be broken off without harming the apparatus. It was at first believed that the heat of reaction would be more than sufficient to keep the reaction going once started. It was therefore intended to circulate air in the jacket to dissipate the excess heat, but the heat losses were so big

that the present heating coil hardly provided for the necessary temperatures. A magnesia lagging over the jacket was even necessary in the case of catalyst reductions (375-450°C).

The separator which was first covered with magnesia lagging only to keep it hot enough to avoid the condensation of the reaction products was later heated by means of an electric heating coil connected in parallel with the heater of the reaction tube.

The gas exit tube was connected to a water trap and any condensates collected in a graduated funnel, after which further condensates were obtained in the dry ice trap.

The uncondensed gases were finally measured in the flowmeter and passing through a gas sampling bottle went to waste.

An incomplete Orsat apparatus was also used for occasional CO₂ analysis.

V METHOD OF ATTACK

It was pointed out previously that the process of synthesizing hydrocarbons by the catalytic treatment of water gas is still in a very inefficient stage. One can find a score of very important reasons for this inefficiency, mostly of a physical nature.

The reaction $\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ is a very exothermic one and liberates about 48000 calories. On the other hand, it is established that an increase in temperature above an optimum merely favors the formation of methane and carbon monoxide. It is therefore of great technical importance to control it in as close a range as possible, that is, to be able to dissipate the excess heat evolved. For this purpose, many more or less satisfactory contact chambers have been designed. One type used in Germany consists of bundles of tubes in which water or some other cooling material is circulated, and surrounded with the catalyst mass. The gas flows counter-current to the water.

Descriptions of chambers constructed on this basis are made by F. Martin (17) and F. Fisher (7). The latter also gives a list of possible heat dissipating agents which were proven satisfactory in the laboratory.

None of the methods used up to 1939 - start of the war - permit the realization of a desired uniform tempera-

ture inside the contact. Heat conduction from a point in the catalyst to the container walls is relatively poor so that it is not possible to eliminate local temperature variations. The formation of methane is thus increased resulting in a decrease in the more useful products.

Perhaps a more important handicap of the Fisher process is its low production capacity. It is claimed that this is due to a layer of adsorbed hydrocarbons (both true and viscous adsorption) that is always covering the catalyst particles. It is clear that to make any reaction occur, the fresh synthesis gas has to diffuse through the hydrocarbon to come in contact with the catalyst. This diffusion takes a certain time, controlling the rate of flow of the gas. It is also claimed that the rate of reaction is proportional to the rate at which the product leaves the surface of the catalyst. (10) With the present methods in use, the gasoline production of a typical Fisher plant is as low as 30 gms. per kilogram catalyst per hour, according to Berthelot (3).

It should also be added that the more the hydrocarbon stays on the catalyst, the more the chances for its saturation increase, and the life of the contact mass decreases due to wax formation.

It was believed that these handicaps and disadvantages

would be partly or completely eliminated by suspending the catalyst in form of fine particles in a stream of synthesis gas[†] in a vertical column.

By this method, it was felt that the local temperature irregularities occurring inside a fixed catalyst bed would be eliminated. For there will be excellent intermixing of the catalyst, the hot reaction products and the cold incoming fresh gas. It was also felt that a considerably better heat transfer to the tube walls would be obtained as compared to the fixed bed catalyst because of the higher gas velocities to be used for successful jiggling. Not so much heat has to be transferred due to the fact that the incoming gas is cold and takes up as sensible heat a part of the heat liberated. Finally because of the good intermixing, better contact would be secured, viscous adsorption would be lessened, and the rate at which the products leave the catalyst would be perhaps increased due to turbulence. All these would therefore occur in favor of better quality product, higher rate of production and longer catalyst life.

It has been therefore the purpose of this work to study the possibility of realizing improvements described above by applying "jiggling" to the Fisher-Tropsch process.

[†]The process of suspending fine solid particles in a stream of gas will be called "jiggling" in this work.

It should be noted here, however, that the problem as stated is a very vast one and in its entity well beyond the scope of the present work. Certain specific questions of the whole problem have therefore been selected for investigation as being the most vital ones in a tentative and very preliminary study. These may be listed as follows:

- a. Jiggling properties of catalysts
 - I. Effect of particle size
 - II. Effect of carrier
 - III. Effect of gas rate
- b. Study of the activity and life of the catalysts
 - I. Effect of carrier
 - II. Effect of temperature
- c. The effect of the gas rate upon the percent volume contraction at optimum temperature.
- d. The effect of temperature upon the percent volume contraction.
- e. The effect of the gas rate upon the optimum temperature.

The percent volume contraction mentioned above is defined as the ratio of the difference between the rate of the incoming fresh gas and that of the waste gas, over the rate of the incoming gas multiplied by a hundred.

The percent contraction of volume so defined has been used in this investigation as a measure of the reactivity.

It has been chosen among other possible methods, i.e., frequent gas analysis and material balances for its directness and simplicity and the lack of appropriate equipment.

VI. PROCEDURE

The investigation was started by determining the most appropriate particle size of catalyst for best jigging. First very fine particles, of all three catalysts with different carriers, were placed respectively in the column. The gas rate was varied and the best results were observed, first at room temperature, then at 200°C. and higher. Since for maximum efficiency and contact, particle sizes as fine as possible are desired, the next bigger sizes in the Tyler Series were also tried out either homogeneous or in form of mixtures. Thus the most suitable sizes were determined and used hereafter.

In these preliminary experiments no emphasis has been given to keeping accurate record of the gas rates for it was not within the scope of this work to make a quantitative study of jigging and reference for this matter will be made to the work of Scott (31) on jigging. ^{Walker}

The catalyst in the chosen particle size and amount was then reduced in a stream of hydrogen between the temperature ranges of 375°C and 425°C for not more than 5 or not less than 4 hours.

The catalysts used in this work were of the type recommended by Fisher (7) and of composition: 45.9% cobalt, 8.2% thorium oxide, 45.9% carrier (CO: ThO₂; carrier as 100:18:100) Kieselguhr, silica gel, and Fuller's earth respectively constituted the carriers.

Calling A the catalyst on silica gel, B the one on Fuller's earth, and finally C that on Kieselguhr, the catalyst charges used in the experiments had the following particle size distributions:

AI	4.7 gms of 140 mesh unreduced	A
	7.8 gms of 100 " "	" "
AII	7.5 gms of 140 "	" "
	5.0 gm. of 100 "	" "
BI	7.5 gms of 140 "	" B
	5.0 gms of 100 "	" "
BII	8.0 gms of 100 "	" "
	4.5 gms of 140 "	" "
CI	7.5 gms of 140 "	" C
	5.0 gms of 100 "	" "

The sum of 12.5 gms catalyst was chosen because after losing its adsorbed water and being reduced, it corresponds to about 4 gms of cobalt metal which is also the amount used by Fisher and his followers in their work. It was felt that the results would thus be made more comparable with theirs.

The first few runs made with AI were destined chiefly to determine the working characteristics of the apparatus in general and the temperature range at which the reaction begins. At first, the rate of flow was controlled by a single needle valve followed by a diaphragm type pressure reducer. This however proved to be unsatisfactory for close and easy control. Two more needle valves were placed in series with the regulator and before the electric furnace. This setup was found satisfactory. However an occasional adjustment of the last valve - every 20 or 30 minutes -

proved to be necessary due to the fact that the pressure regulator did not provide an absolutely constant downstream pressure.

The procedure consisted thereafter simply in sending the gas into the jigglers at a known rate and at a known temperature for synthesis. The products passed then through a watercooled condenser and any products of condensation collected in a funnel. The remaining gases passed then through a dry ice trap where an additional condensate was collected. The rest of the gases was finally measured in a flowmeter and the per cent volume contraction calculated.

It was also necessary to watch for the temperature. For any additional load elsewhere in the line resulted in a decrease in temperature of the tube, controlled only by a slide-wire resistance.

In any case the temperature was increased very slowly in accordance with Herrington and Woodward's (13) advice. This was done as a measure of precaution in spite of the fact that because of good intermixing of the catalyst with the gas no possibility existed for local increase in temperature to a harmful degree for the catalyst. Something that should be given particular consideration in the case of a fixed bed catalyst.

The catalyst was changed when necessary by drawing off the undesired one from the bottom, opening the top, cleaning the inside if necessary with some glasswool and pouring the new catalyst little by little inside countercurrent

to a stream of hydrogen at a temperature sufficient to dry out the particles. Otherwise they either would stick to the tube walls or form lumps difficult to break up.

Taking these considerations into due account, the following tests were made:

Catalysts AII, BI, BII, were investigated at constant gas rate by varying the temperature to the optimum contraction and holding it constant there. The contractions corresponding to each temperature were calculated and any condensates were measured and observed. Thus, the activity of each catalyst, the effect of temperature upon the per cent volume contraction and the amount of products formed and sometimes in a qualitative way, the nature of the products could be studied for each catalyst.

While with the catalysts mentioned above, the gas rate was kept the same for all runs, it was varied over wide ranges with CI. Thus the effect of the gas rate upon the optimum temperature and the maximum per cent contraction were recorded. The temperature was also increased way above the maximum in order to determine any resulting effects upon the contraction of volume.

These were only made with CI because the phenomena to be observed in those experiments are in general lines common to all the catalysts used here.

At the end, a run was made with the gas rate used in the first run with CI and its activity was thus tested for durability.

VII. RESULTS

The results obtained on the jiggling properties of the catalysts at several particle sizes investigated in the preliminary runs are qualitative. No figures will therefore be given. It should only be said that particles passing through 200 mesh had most unsatisfactory jiggling characteristics. They clung together to form lumps and stuck to the walls of the reactor. Carrying^{out} the jiggling at high temperatures did not bring any improvements. Very satisfactory jiggling was obtained in all cases with particles larger than 200 mesh and of higher density than the fluffy mass used originally without pressing to a hard cake.

As to the quantitative results, they may be listed as follows:

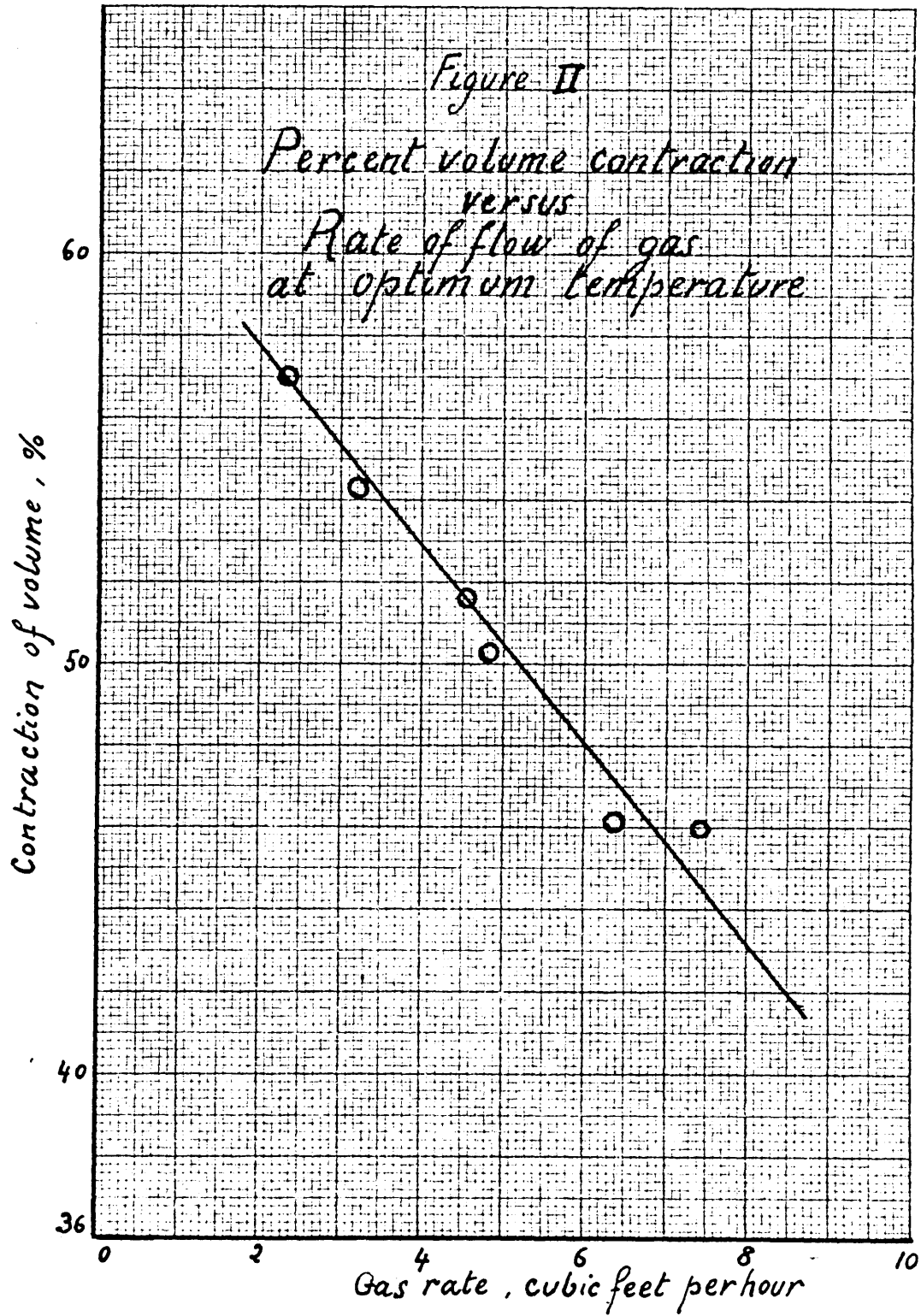
Run No.	Catalyst	Rate of flow ft ³ /hr.	Temperature at bottom °C	Maximum Contraction of volume per cent	Remarks
1	AI	3.8	160 210	0 8	Top temperature 40° lower
2	AI	2.4	205	12	"
3	AI	2.7	230	18	
4			245	30	Liquid condensed in water and dry ice traps. Latter smelling hydro- carbons
5	AII	3.1	250	33.2	Liquids collected smelling hydro- carbons (7cc)
6	AII	3.1	264	27	

Run No.	Catalyst	Rate of flow ft ³ /hr.	Temperature at bottom °C	Maximum Contraction of volume per cent	Remarks
7	BI	3.1	254	45	Liquids collected smelling hydrocarbons activity dropped quickly
8	BI	3.1	258-270	14.5	
9	BI Oxidized at 250°C	3.1	246 up	6.13	
10	BII	3.1	260	35.6	Activity dropped quickly
11	BII reduced anew	3.1	279	35.6	Activity dropped quickly
12	CI	3.1	232	61.3	12.5 cc of water and hydrocarbons collected in 90 min. activity dropped slowly A CO ₂ analysis of the waste gas showed 9% CO ₂
13	CI	3.8	249	50	5 cc H ₂ O + hydrocarbons collected in 30 min.
14	CI	4.55	289	51.6	7 cc H ₂ O + hydrocarbons collected in 30 min.
15	CI	3.1	239	53	
16	CI	3.8	274	51.3	
17	CI	4.55 6.3	291 270	51.6 46.1	
18	CI	2.32 3.1 4.8 4.8 6.32 6.32 7.4 7.4	259 254 254 270 249 279 259 296	57 54.2 50.0 50.3 44.6 46.1 37.0 46.0	

The results obtained are illustrated by plots in Figures II, III and IV. These are made from data obtained with the catalyst CI only since enough data could not be obtained with the other ones as explained in "Discussion of Results."

Figure II

Percent volume contraction
versus
Rate of flow of gas
at optimum temperature



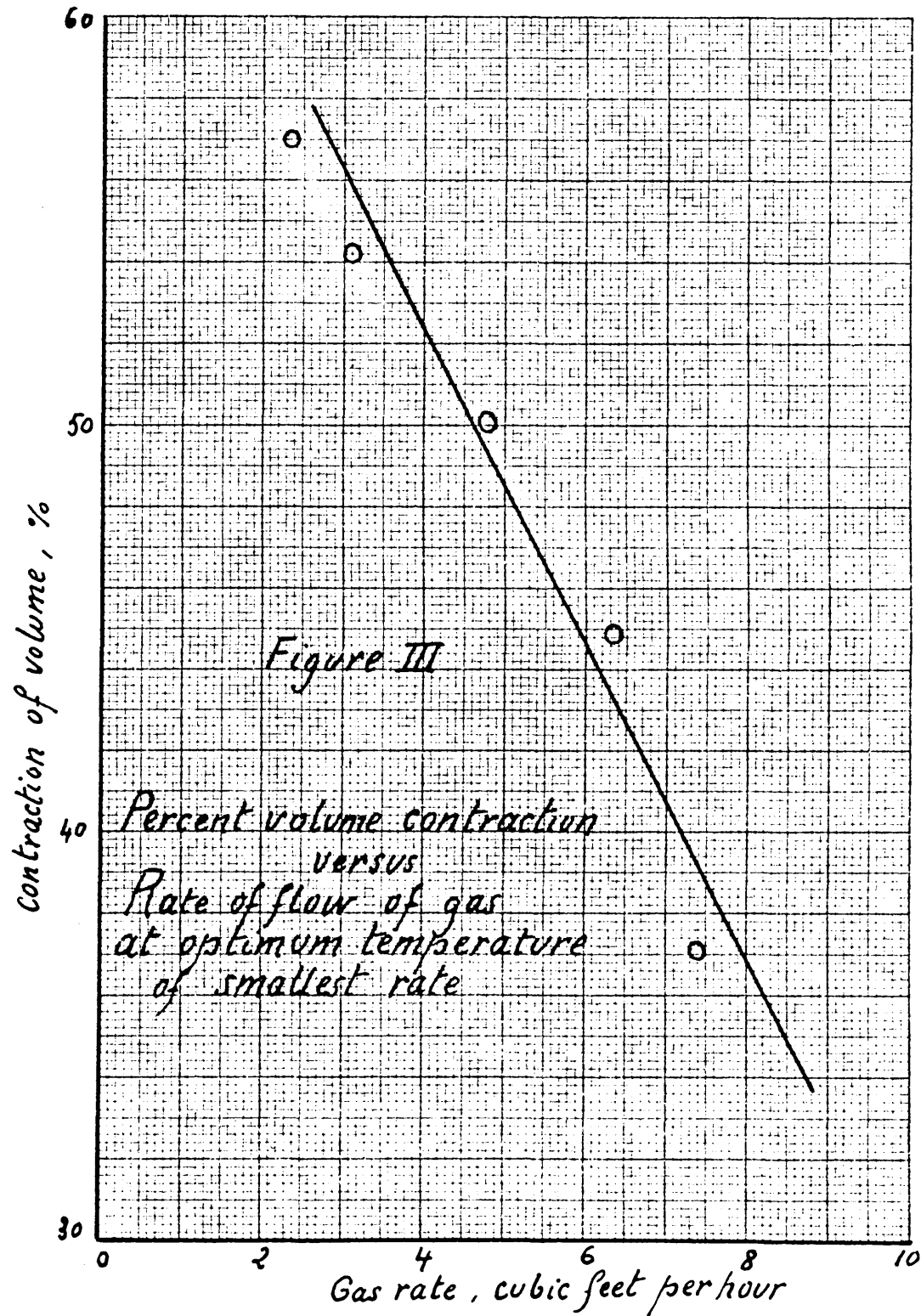
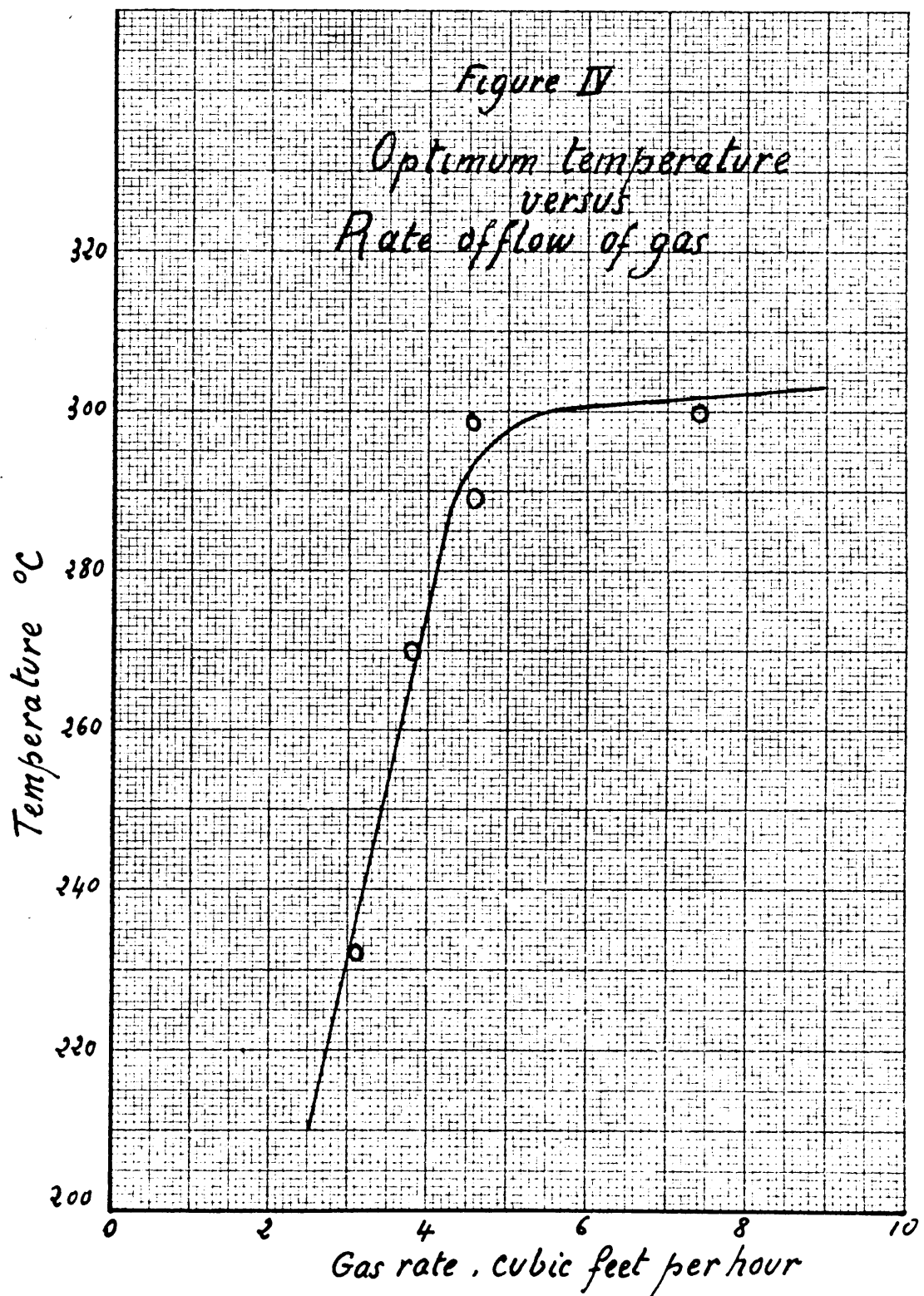


Figure IV

Optimum temperature
versus
Rate of flow of gas



VIII. DISCUSSION OF RESULTS

Because of the limited amount of time and especially materials and equipment that were available for the investigation of such a subject as the application of jiggling to the Fisher-Tropsch process, entirely new as a method, this work unfortunately stayed within a very limited scope. Experiments had to be made much on a cut and try basis, which made even so much ^{more} difficult the drawing of conclusions. It is also regrettable that although the catalysts used were of the same type Fisher and his co-workers used, the synthesis gas, due to unfortunate circumstances was made of a composition very unfavorable to the formation of easily condensable hydrocarbons. It was $H_2/CO = 2.80$ as against $H_2/CO = 2$ recommended as being the most favorable by Fisher and others. This made very difficult the comparison of the actual data with those found in the literature.

It should also be noted that not too much emphasis has been laid upon the true accuracy of the temperatures recorded, for although the trends in temperature variations were of highest importance, it was felt that the individual temperatures were not so, due to the fact that these may vary from one type of catalyst, and one operating condition to the other. An error of $10-12^{\circ}C$ on temperature readings is therefore to be accounted for. In most cases only readings of the bottom thermocouple have been recorded. Because most of the reaction occurred within a short distance

from the bottom of the tube, the temperature in the lower part of the column was always 40-50^o C higher than the one recorded in the top thermocouple. Since it was not possible with the actual design of the apparatus to obtain a uniform temperature lengthwise throughout the column, the bottom temperature has been taken as the reaction temperature. An accuracy within 3 per cent at the most for low and 2 per cent for the high velocities is to be expected, on the other hand, in the orifice readings.

For the sake of simplicity, the discussion will follow first the questions of jiggling properties of the catalysts.

It was reported by Tsuneoka (27) that the best hydrocarbon yields were obtained using catalysts of particle sizes from 1-2-4 mm diameter. Smaller particles were found less suitable probably because they favored formation of local chimneys and ducts hindering efficient contact. In the present case however this could not happen. For this reason the smallest possible particle size was considered most advantageous for allowing greatest contact of gas with catalyst.

About 2 gms. of unreduced catalyst on Kieselguhr of size smaller than 140 mesh were introduced and jiggling was tried at room temperature with a gas velocity sufficient for steady suspension. After a few minutes however there was almost no jiggling in the column. Most of the particles had clung together and formed big balls that settled at the bottom. The rest stuck to the tube walls and would

not come out even on mechanical shock.

It was then thought that particles of originally larger sizes might do better and a mixture of 2 gms. 140 mesh, 4 gms. 100 mesh, 4 gms. 65 mesh, as well as a mixture of 4 gms. 140 mesh, 4 gms. 100 mesh, 2 gms. 65 mesh were tried. Formation of lumps and sticking to the walls again occurred.

The catalyst was then dried out for 48 hours in an electric oven at 120°C and 10 gms. of a 200^{mesh} fraction experimented upon. There was no improvement what so ever as far as jiggling properties were concerned. It is therefore concluded that the lump forming and sticking is due to the minute Kieselguhr particles that, through their ramified structure, cling together to larger sizes. This is confirmed by the facts that the same experiments, made with 200 mesh pure silica gel gave most satisfactory results. On this basis, all three catalyst types were pressed to a hard cake in an hydraulic press, broken up to small pieces and separated to the desired sizes in standard Tyler series screens. The hard particles so obtained when not smaller than 140 mesh did not in any case form lumps or stick to the walls. In the long run, the larger particles disintegrated slowly and the minute particles formed this way were seen to cling to the walls. These were only a small percentage however and could easily be broken lose by knocking softly on the hopper. It is believed that the sticking is of electrostatic nature

mostly although at some places it is mechanical due to grease etc. as shown by the fact that the particles are so strongly held. This latter was avoided by heating the jigglers to 400°C and passing a stream of air in it to burn all possible grease.

Although in the case of synthesis with a fixed catalyst bed, the reaction is said to start at around 150°C and be at optimum between 170-200°C, it was not found so in the present case. In a trial run with catalyst AI and a rate of 3.8 ft.³/hr. no volume contraction could be observed at 140°C. Past 160°C however, the bottom thermocouple showed a temperature 40°C higher than the top one indicating the occurrence of reaction. The temperature then increased to 210°C bottom and 175°C top, where only about 8 per cent contraction could be observed (run 1).

The rate of flow was then decreased to 2.4 ft.³/hr. and at 205°C bottom temperature, the volume contraction after two hours reached 12 per cent. The top and bottom thermocouple temperature difference was again 40°C.

At a gas rate of 2.7 ft.³/hr. and a temperature of 230°C the contraction reached 18 per cent after three hours, (run 3). Finally at the same gas input, the temperature was increased to 245°C and the contraction increased to about 30 per cent. In the same time, a liquid was seen to condense in the water condenser and collected in the graduated funnel. An additional condensate

was obtained in the dry ice tube, which contrary to the one obtained in the water trap smelled strongly of hydrocarbons. Oil drops could also be seen. However, the contraction soon decreased and enough condensate could not be collected for analysis.

That the synthesis through jiggling occurs at considerably higher temperatures than those reported in the literature is probably due to the fact that in the present case the recorded temperature is the true temperature of the catalyst-gas mixture as against the temperature of the outside wall in all the experiments on the orthodox Fisher process in the laboratory. It is believed that the temperatures inside a catalyst bed are probably as high as the ones observed here.

At 3.1 ft.³/hr. and 250°C, AII showed a contraction of 33.2 per cent. Ninety minutes after reaching that value, the contraction had dropped to about 21 per cent. After 2-1/2 hours it was not higher than 14 per cent (run 5).

After having allowed the jigglers to cool down, another run was started in order to determine the possibility of bringing back or approaching the original activity by increasing the temperature slowly above the previously recorded optimum. It is seen from the data that a contraction of about 27 per cent was reached (run 6) at about the same temperature as in run 5. A further increase in temperature merely decreased the

activity again. By bringing it down to the former optimum, the contraction was not at all increased. This shows clearly the evil effect of high temperatures upon the activity. It might be that when the optimum temperature is reached, the reaction goes so fast that the heat liberated temporarily boosts the catalyst temperature too high, causing the loss of its activity. Soon an equilibrium sets up however and the activity stays constant at a level slightly lower than the original non-lasting maximum.

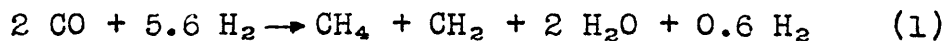
It is not possible however to explain the behaviour of BI on this basis. In run 7 although a maximum contraction of 45 per cent definitely higher than for AII was obtained at the same temperature, it dropped in about 10 minutes sharply to about 11 per cent. The same technique of cooling down and bringing it to the right temperature gave no more than 14.5 per cent contraction (run 8).

This suggested the possibility that the loss of activity might be due to the catalyst being coated instantaneously by a layer of hydrocarbons formed on account of the exceedingly fast reaction. The catalyst was therefore heated for 4 hours at 250°C in a stream of air, to test this possibility. But the contraction obtained in a subsequent run (run 9) with synthesis gas was almost nil, pointing to the conclusion that the assumption was not well founded.

BII which had a higher percentage of 100 mesh particles than BI allowed a maximum contraction of 35 per cent as against 45 per cent for BI. The temperature corresponding to that figure was slightly higher than for BI. But the loss of activity after a short time occurred the same way as for BI (runs 11, 12).

From the considerations above it can perhaps be safely stated that although silica gel as carrier gives a more stable catalyst, one with Fuller's earth constitutes a considerably more active one. Since the quality of the hydrocarbon yield in a Fisher synthesis is claimed to be very much dependent upon the working temperature (28), both silica gel and Fuller's earth seem to be equal on that matter.

Kieselguhr on the other hand seems to hold the definite advantage of allowing a considerably lower optimum temperature (run 12). The contraction of 61 per cent observed was the highest obtained yet. Unfortunately the activity started dropping slowly and was about but 42 per cent after 50 minutes. Assuming that the reaction goes merely according to the equation



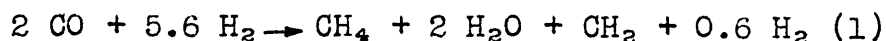
in which case the contraction would be 79 per cent, the value of 61 per cent can still be considered a remarkably high figure for a space velocity of about 350* as against

*This figure is one calculated on the volume of the whole tube. Since the reaction occurred within about a foot from the bottom and there was almost no suspension of particles above the middle at that rate, the true space velocity should be about 1500.

100 usually used by Fisher.

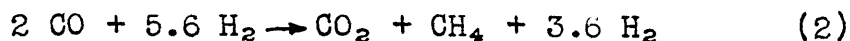
However, it may be stated that the above reaction is not the only possible one. During the 1-1/2 hour that elapsed from the time the contraction reached 50 per cent until it was 49 at the end, about 12 cc of water + about 1/2 cc oil were collected, or approximately 90 cc/cu m. of H₂O and 4.0 cc/cu. m. of oil.

If only the reaction:

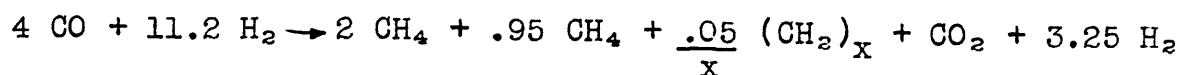


occurred, the theoretical amount of water formed would be 180 cc per cu. m and the oil should amount to 70 cc per cu. m or 82 gms. (assuming a density of 0.85). Taking the average per cent reacted over 1-1/2 hour as 50 per cent, the water condensed should have been about 125 gms/cu. m.

It is certain that the discrepancy can be explained from the occurrence of the reaction:



as shown by the fact that a gas sample taken at around the maximum contraction contained about 9 per cent CO₂ (unfortunately a complete analysis could not be made because of lack of adequate equipment). Since 90 cc H₂O/cu. m gas were collected, only half of the cubicmeter gas reacted according to 1. The oil represents about 5 per cent of what should have been (70 cc) therefore the 95 per cent must have been further hydrogenated by the hydrogen from 2. The overall reaction would then be:



which would give a contraction of about 54 per cent. Taking into account the nitrogen which was contained in the original gas, the percentage CO_2 in the non-condensable gases would be 12.5 per cent which is close enough to the experimental value of 9 per cent.

Although the above considerations cannot be taken as irrefutable facts, they seem to indicate strongly that the reaction has been almost complete or very nearly so. This is not unreasonable because as a result of perfect contact opportunities which are lacking in the fixed catalyst/^{bed}system, the maximum amount of gas can hit the catalyst and because of the exceedingly high gas velocity, the reaction products can leave the surface more easily, two conditions which are essential for completion of the reaction.

A series of runs were made with different rates of flow of the gas with the purpose of determining the effect of rate of flow on the contraction and the optimum temperature. As can be seen from Figures II, III, the per cent contraction shows a sensibly linear drop with an increase in the gas rate or space velocity. It is remarkable and very encouraging however that an increase of more than 300 per cent in the rate of flow causes the contraction to decrease to only 46 per cent or about a decrease of 19 per cent based on the 57 per cent contraction at $2.32 \text{ ft.}^3/\text{hr.}$

The plot of optimum temperatures versus rate of flow (Figure IV) increases first linearly then from around 5 ft.³/hr. stays seemingly constant. A plot of the per cent contraction versus the rate of flow at approximately the optimum temperature corresponding to the lowest rate of flow is also of interest. For it shows the per cent loss in contraction if for reasons outlined before low temperatures are desired in spite of high gas rates. Over a 300 per cent increase in the latter, not more than 35 per cent loss in contraction was observed which is much less than ever hoped by any investigator of the classical Fisher method. These facts definitely seem to point to the powerful potentialities of the jiggling process as applied to the Fisher synthesis.

It is also noteworthy that after the first run at the rate of 3.1 ft.³/hr. (12) two other similar ones were made one after 13, 14 and one after 16, 17, and 18 in which it is clearly seen that the activity became higher than at the end of run 12 and remained nearly constant thereafter in spite of all the increase in temperature in the other runs and all the reaction that took place equivalent to a continuous run of 7 days under Fisher's conditions, (1.1/hr.gm. Co). The optimum temperature however increased from 232°C in run 12 to 237°C in run 15 and 254°C in run 18 for the same rate. This is also in agreement with the reports of Fisher (7) and Tsuneoka (25,26,27) on that matter who say that the

temperature has to be shifted higher with time.

It should perhaps be worth mentioning at this moment a few qualitative observations made during the experiments. After run 3 was over, it was seen that the upper part of the hopper, which was not at a temperature higher than 60°-70°C, was covered inside by a thin film of heavy oil or wax-like material. Further heating to more than 150°C was not sufficient to evaporate it. The same phenomenon was not observed anymore at higher temperatures and gas rates than in run 3. Adding that apparently more oil could be seen in the condensates of runs made at comparatively low temperatures rather than high, one could perhaps draw the conclusion in agreement with experiments by several other authors that high temperatures tend to favor the formation of lower boiling hydrocarbons down to methane.

Finally as a general conclusion to the whole discussion of the preceding pages, it is felt that because of the remarkably good reactions obtained at gas rates at least 20 times higher than those used by other investigators in the field (20 l/hr. gm. Co to 1 l/hr. gm. Co) it would not be very unconservative to state that jiggling the catalyst as fine particles in the synthesis gas presents potentialities not yet encountered in the application of the Fisher-Tropsch process.

IX. CONCLUSIONS

In the light of the results obtained in this investigation, the following conclusions are drawn:

- I. Jiggling of particles of Fisher catalyst is very unfavorable with particles smaller than 140 mesh.
- II. Kieselguhr is better as carrier than Fuller's earth, which is better than silica gel, in respect to per cent contraction.
- III. The optimum temperature corresponding to the maximum per cent gas volume contraction is about equal with both Fuller's earth and silica gel as carrier but is lower in the case of Kieselguhr.
- IV. The catalyst with Kieselguhr as carrier is more lasting than with the two other materials.
- V. The loss of activity is caused by temperature effects.
- VI. Contractions as high as 61 per cent can be obtained at gas velocities as high as 20 liters/gm CO, hr.
- VII. The per cent contraction drops sensibly linearly with increased rate of flow. A 300 per cent increase in rate caused only 19 per cent decrease in contraction.
- VIII. The optimum reaction temperature is higher at higher velocities. It tends to become constant after a certain rate of flow.
- IX. Most of the reaction occurs within a very short

distance from the point of entry of the gas.

X. The catalyst may lose its activity within a very short time due to excessively fast reaction and increase in particle temperature.

XI. ^Astable catalyst loses its optimum activity for a lower one.

XII. Cooling down and heating up again slowly seems to increase the activity slightly.

Finally it can be safely stated that the process of jiggling as applied to the Fisher Tropsch syntehsis is a very promising one.

X. RECOMMENDATIONS

From the results obtained in this work and the conclusions drawn thereof it is clear that the process investigated seems to be very promising and further studies on this matter are highly recommendable. In order to facilitate such work the following suggestions are made:

- I. That investigation be made with the use of a gas with a H_2/CO ratio of 2 to 1.
- II. That recycling the catalyst be carried out in the belief that this will help to keep the catalyst at maximum activity.
- III. That the jiggling process be carried out at pressures of 5-20 atmospheres.

A P P E N D I X

XI. APPENDIXPreparation of the Synthesis Gas

The synthesis gas which had the composition

67.2% H₂

24.0% CO

1.5% O₂

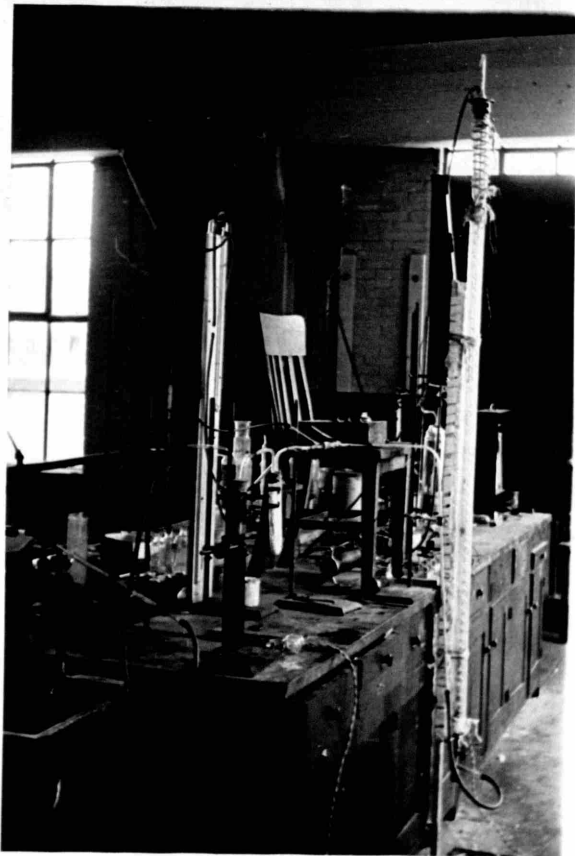
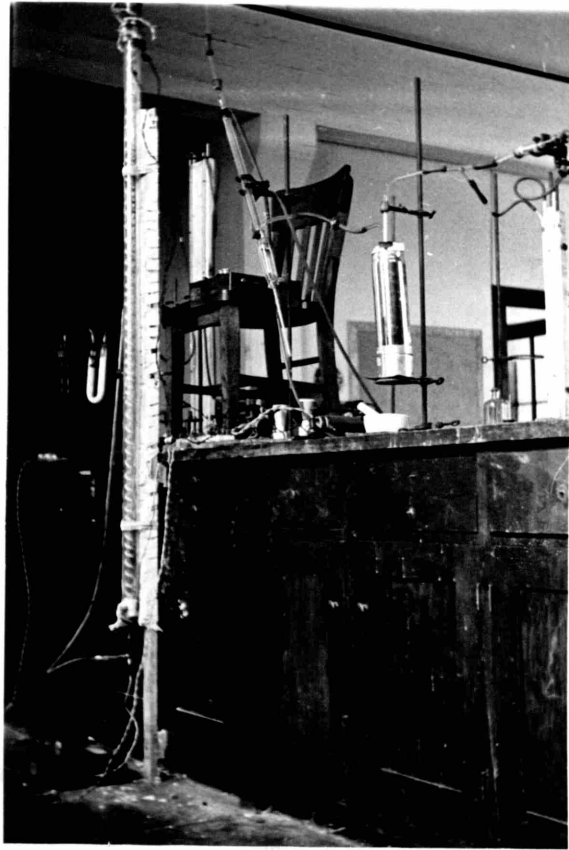
7.3% N₂

was prepared by compressing into a known amount of H₂ contained in a cylinder the desired amount of CO. This latter was prepared by the decomposition of formic acid by concentrated sulfuric acid according to a modification of the method of Petavel.

Preparation of the catalysts

The catalyst of composition Co:ThO₂:carrier in the proportion of 1:0.18:1 related to Cobalt was prepared as follows according to Fisher.

247 gms. of Co(NH₃)₂, 6 H₂O and 24 gms. of Th(NO₃)₄, 12 H₂O were dissolved in about 750 cc cold water and 50 gms. carrier. Fullers earth, silica gel, Kieselguhr, respectively in a fine powdered state were added. The mixture was then neutralized by enough K₂CO₃ as required stoichiometrically to precipitate the metals as carbonates. The mass was then heated to boiling and the precipitate collected on a Buchner funnel. After thorough washing with hot water the precipitate was heated to 130°C. for 24 hours in an electric oven and was then ready to be caked-up, sized up, and reduced for synthesis.



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ORIGINAL DATA

Run Number	Catalyst	Bottom Therm.C. Reading M.V.	Bottom Temp. °C	Inlet Flow M. Cm H ₂ O	Inlet Flow rate fts/hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate fts/hr	Volume Con- traction%	Time from start Min.	Duration of run Min.	
I	A _I	7.32	180	14	3.8	17	3.8	0	Initial	60	
			210	14	3.8	15	3.5	7.9	Initial		
II	A _I	8.3	205	6.6	2.4	8.2	2.4	0	Initial	180	
				6.6	2.4	6.5	2.1	12.5	Initial		
III	A _I	9.3	230	8.4	2.7	7.0	2.2	18.5		180	
IV	A _I	9.92	245	8.4	2.7	5.5	1.89	30		120	
V	A _{II}	1.1 10.12	27	10.0	3.1	12	3.1	0	Initial	180	
			250	10.0	3.1	11.5	3.0	10	Initial		
				10.0	3.1	6.5	2.07	30	33.2		
				10.0	3.1	8.5	2.45	120	21.0		
				10.0	3.1	9.5	2.65	150	14.0		
				10.0	3.1	9.5	2.65	180	14.0		
VI	A _{II}	1.1 6.8 8.6 9.6 9.8 10.1 10.3 10.7 10.9 11.1 11.2 10.7	27	10.0	3.1	12	3.1		Initial	180	
			166	10.0	"	11.5	3.65				
			212	"	"	11.2	2.95				
			237	"	"	10.2	2.8				
			241	"	"	9.4	2.65				
			246	"	"	9.0	2.6				
			254	"	"	7.4	2.3				
			264	"	"	7.2	2.25				
			269	"	"	7.4	2.3				
			270	"	"	8.4	2.45				
			276	"	"	8.8	2.55				
			264	"	"	8.9	2.56				
								27	40		
						70					
						100					

ORIGINAL DATA

Run Number	Catalyst	Bottom Therm., C. Reading M.V.	Bottom Temp. °C	Inlet Flow M. Cm H ₂ O	Inlet Flow Rate ft ³ /hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate ft ³ /hr	Volume Conversion %	Time from start Min.	Duration of run Min.	
VII	BI	1.1	27	10	3.1	12	3.1	0			
		5.9	145	"	"	11.8	3.05				
		7.0	171	"	"	11.6	3.01				
		7.9	194	"	"	11.6	2.98				
		8.9	219	"	"	11.3	2.95				
		9.9	244	"	"	9.2	2.6				
		10.2	251	"	"	6.2	2.05				
		10.3	254	"	"	5.0	1.70	45		10	
		10.1	246	"	"	10.0	2.75	11			
		10.3	254	"	"	10.5	2.85				
		10.8	266	"	"	10.0	2.75			120	
VIII	BI	1.1	27	10	3.1	12	3.1	0			
		10.5-11.1	258-270	10	3.1	9.5	2.65	14.5		330	
IX	BI Oxidized at 250°C	1.1	27	10	3.1	12	3.1	0			
		10.1	246	10	3.1	11.0	2.91	6.13			
		Increased	Increased	"	"	"	"	"			
X	BII	1.1	27	10	3.1	12	3.1	0			
		10.5	255	"	"	7	2.2				
		10.7	260	"	"	6	2.0	35.6			
		10.7	260	"	"	9.2	2.6	16			
XI	BII	1.1	27	10	3.1	12	3.1	0			
		11.5	279	"	3.1	6	2.0	35.6			
		Varied for max. cont.	279	"	3.1	9.4	2.65	14.5			

ORIGINAL DATA

Run Number	Catalyst	Bottom Therm.C. Reading M.V.	Bottom Temp. °C	Inlet Flow M. Cm H ₂ O	Inlet Flow Rate ft ³ /hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate ft ³ /hr	Volume Con- traction %	Time from start Min.	Duration of run Min.
XII	CI	1.1	27	10.0	3.1	12	3.1	0		
		8.2	202	"	"	9.15	2.58			
		8.5	209	"	"	7.3	2.25			
		8.8	217	"	"	4.85	1.75			
		9.1	224	"	"	4.85	1.75			
		9.1	224	"	"	4.6	1.7			
		9.1	224	"	"	4.4	1.65			
		9.1	224	"	"	4.22	1.62			
		9.1	224	"	"	3.9	1.53			
		9.1	224	"	"	3.65	1.47			
		9.4	232	"	"	3.3	1.37			
		9.4	232	"	"	3.6	1.3			
		9.4	232	"	"	2.6	1.2	61.3	32	
		9.4	232	"	"	3.0	1.3			
		9.4	232	"	"	3.3	1.37			
		9.4	232	"	"	3.5	1.44	54.2	42	
		9.5	234	"	"	3.9	1.53			
		9.5	234	"	"	4.0	1.55			
		9.49	233	"	"	4.22	1.53		54	
		9.4	233	"	"	4.5	1.67			
		9.3	229	"	"	4.7	1.72			
		9.3	229	"	"	4.6	1.7		69	
		9.4	232	"	"	4.85	1.75		74	
		9.4	232	"	"	5.1	1.8	42.0	84	
		9.2	227	"	"	5.25	1.84		90	90
XIII	CI	1.1	27	14	3.8	17	3.8	0		
		9.9	244	"	"	5.8	1.95			
		9.3	229	"	"	6.0	2.0			
		9.6	231	"	"	5.9	1.98			
		9.6	237	"	"	5.8	1.95			
		9.9	244	"	"	5.8	1.95			
		10.0	247	"	"	5.9	1.98			
		10.1	249	"	"	5.7	1.9	50		
		10.2	251	"	"	5.7	1.9	50		30

ORIGINAL DATA

Run Number	Catalyst	Bottom Therm.C. Reading M.V.	Bottom Temp. °C	Inlet Flow M. Cm H ₂ O	Inlet Flow Rate ft ³ /hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate ft ³ /hr	Volume Con- traction %	Time from start Min.	Duration of run Min.
XIV	C I	1.1	27	19.0	4.55	22.5	4.55	0		
		10.7	260	"	"	8.0	2.4			
		10.45	254	"	"	8.2	2.42			
		10.6	257	"	"	8.0	2.4			
		10.7	260	"	"	7.8	2.35			
		11.1	270	"	"	7.8	2.35			
		11.2	272	"	"	7.2	2.25			
		11.3	274	"	"	7.4	2.27			
		11.5	279	"	"	7.5	2.4			
		11.9	289	"	"	7.0	2.2	51.6		
		12.1	291	"	"	7.0	2.2			
		12.3	299	"	"	7.0	2.2			
		12.7	311	"	"	7.0	2.2			
		10.8	262	"	"	7.8	2.35			
10.3	254	"	"	8.0	2.4					
XV	C I	1.1	27	10	3.1	12	3.1	0		
		9.5	231	"	"	3.7	1.48			
		9.7	239	"	"	3.7	1.48			
		9.7	239	"	"	3.6	1.45	53		
		9.6	237	"	"	3.8	1.5			
		9.6	237	"	"	4.5	1.67			

30

ORIGINAL DATA

Run Number	Catalyst	Bottom Therm.C. Reading M.V.	Bottom Temp °C	Inlet Flow M. Cm H ₂ O	Inlet Flow Rate ft ³ /hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate ft ³ /hr	Volume Con- traction %	Time from start Min.	Duration of run Min.	
XVI	CI	1.1	27	14	3.8	17	3.8	0			
		9.3	229	"	"	5.9	1.98				
		9.5	231	"	"	5.8	1.95				
		9.9	244	"	"	5.6	1.92				
		10.0	247	"	"	5.6	1.9				
		10.3	254	"	"	5.5	1.92				
		10.5	259	"	"	5.5	1.9				
		10.6	257	"	"	5.5	1.9				
		10.7	260	"	"	5.5	1.9				
		11.1	270	"	"	5.4	1.85				
		11.3	274	"	"	5.4	1.85		51.3	35	
		11.6	281	"	"	5.5	1.9				
		11.8	290	"	"	5.5	1.9			45	45
XVII	CI	1.1	27	19.0	4.55	22.5	4.55	0			
		12.5	306	"	"	7.0	2.2				
		11.5	279	"	"	7.3	2.25				
		11.2	272	"	"	7.5	2.3				
		12.1	291	"	"	7.1	2.2	51.6			
		12.3	299	"	"	7.0	2.2				
		12.7	311	"	"	7.0	2.2				
		13.1	321	"	"	7.0	2.2		57.6	25	25
		11.1	270	34	6.3	14.0	3.45	46.1		35	35

ORIGINAL DATA

Run Number	Catalyst	Bottom Therm.C. Reading M.V.	Bottom Temp. °C	Inlet Flow M. Cm H ₂ O	Inlet Flow Rate ft ³ /hr	Outlet Flow M. Cm H ₂ O	Outlet Flow Rate fts/hr	Volume Con- traction %	Time from start Min,	Duration of run Min.
XVIII	C _I	10.5	259	6.5	2.32	2.0	1.1	57		
		10.3	254	10.0	3.1	3.5	1.35	54.2		
		10.3	254	21.0	4.8	8.0	2.42	50.0		
		11.1	270	21.0	4.8	7.8	2.40	50.3		
		10.1	249	32.0	6.32	14.6	3.47	44.6		
		9.9	244	"	"	15.5	3.6	41.5		
		9.4	232	"	"	14.5	3.45	44.8		
		11.5	279	"	"	14.0	3.36	46.1		
		10.5	259	42	7.4	23.5	4.66	37.0		
		10.7	260	"	"	23.5	4.66	37.0		
		11.1	270	"	"	20.5	4.3	41.9		
		11.5	279	"	"	19.5	4.16	43.8		
		12.2	296	"	"	18.5	4.0	46.0		
12.3	299	"	"	19.0	4.1	44.6				

Condensates collected:

The figures given here are only approximate readings and estimates.

Run	Water trap c.c.	Dry Ice trap c.c.	Total	Duration of run	Oil Estimated c.c.
V	5	2	7	180	
VIII		2	2	330	
XII	8	4.5	12.5	90	0.5-1
XIII	4	1.0	5.0	30	
XIV	6.5	0.5	7.0	30	

In all cases oil drops were seen to float on the water or form a white emulsion especially in the dry ice collector. In most cases the amount was so little as to make even an estimate insignificant.

Calibration of Instruments

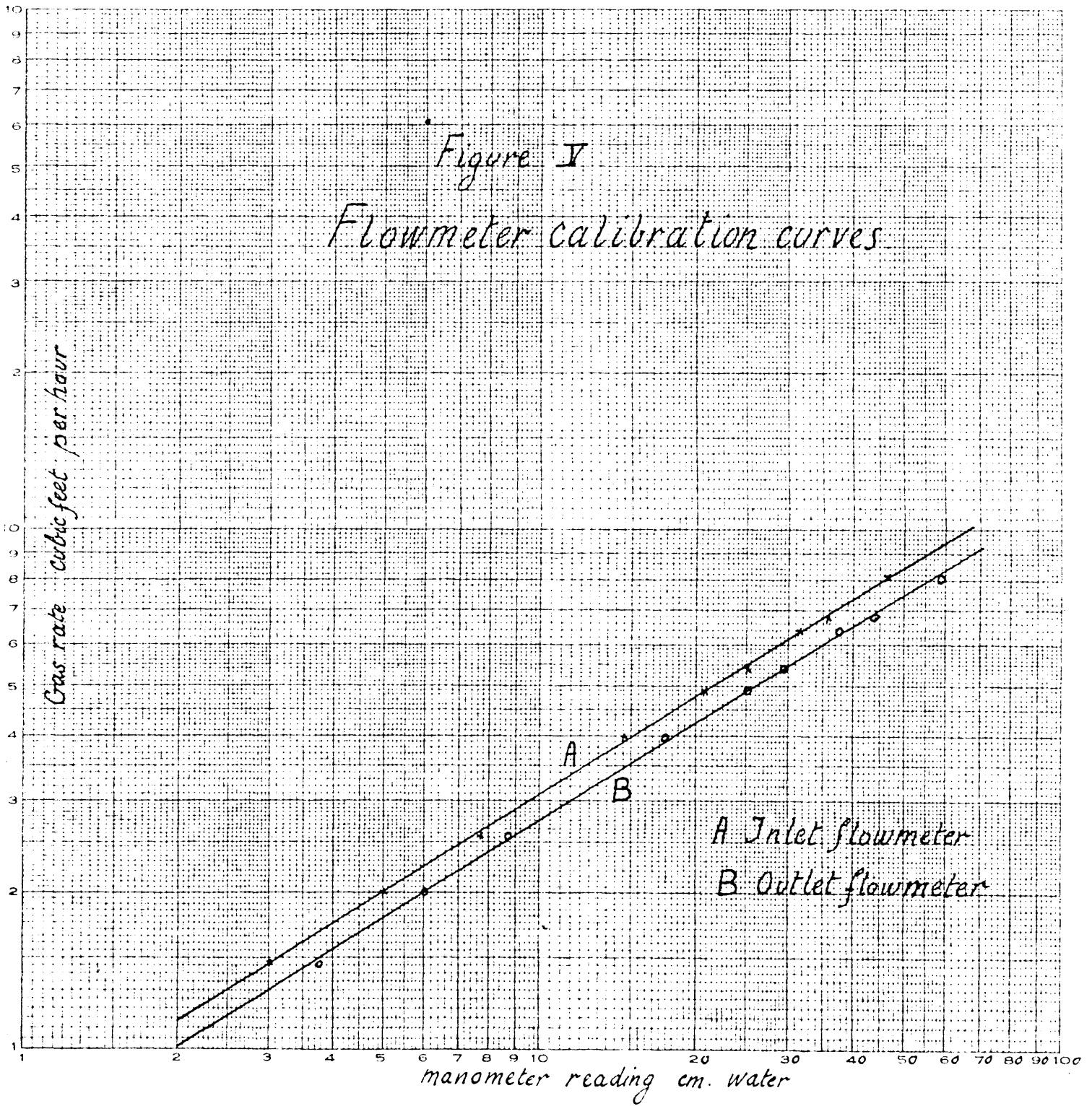
Flowmeters

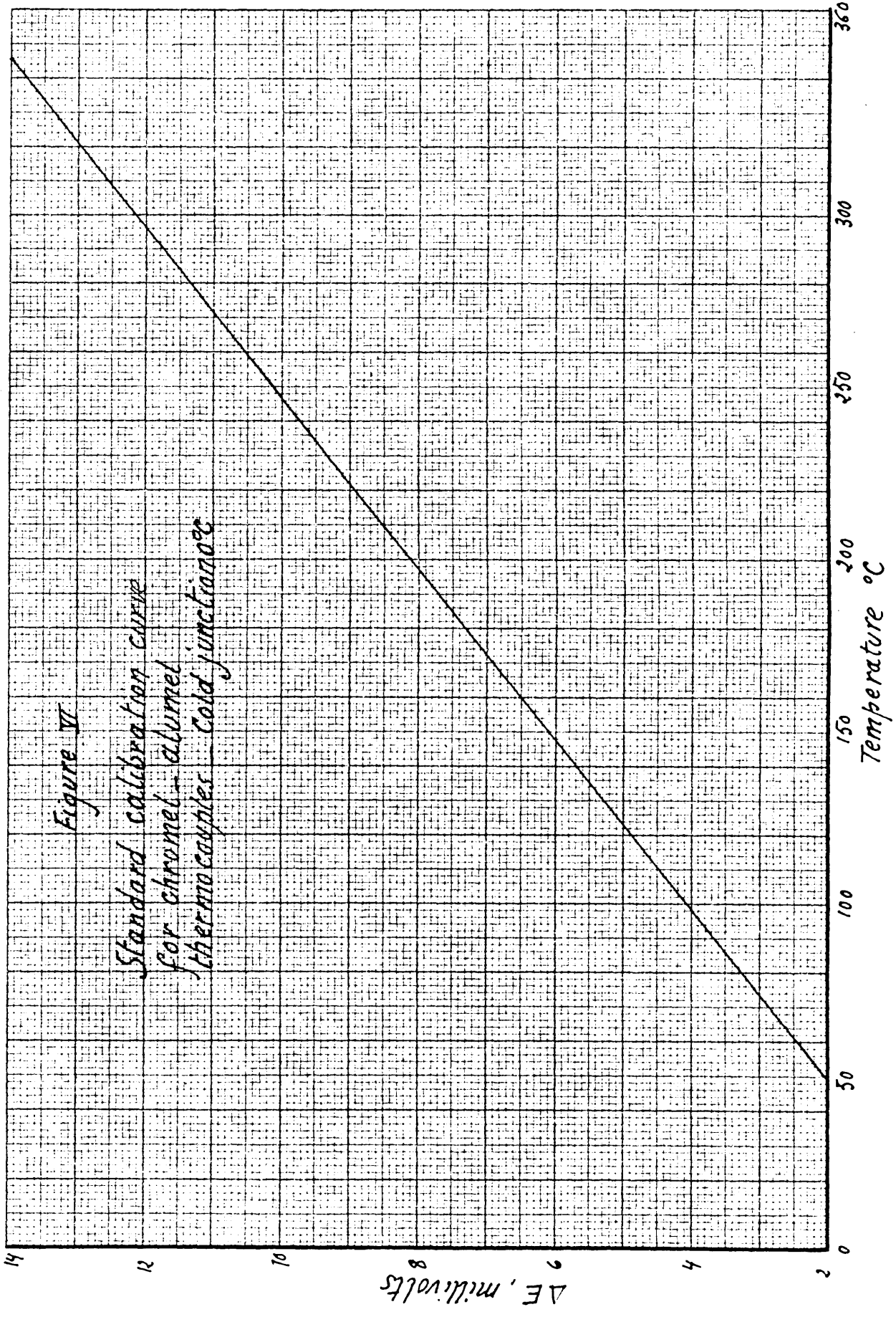
The flowmeters consisted of short capillaries stuck in rubber stoppers placed inside 25 mm tubings. The calibrations were made by comparison with a standard Wetttestmeter of 6 ft³ capacity.

Thermocouples

Since a high accuracy was not desired on the temperature readings, the thermocouples, made of chromel and alumel wires, gage N=28, were not calibrated. Instead, the standard calibration plot of the wire manufacturers was used.

Figure V
Flowmeter calibration curves





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