THE FISCHER-TROPSCH SYNTHESIS

The development of methods and apparatus,
and preliminary studies on catalysts.

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by

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Table of Contents

List of Figures

I INTRODUCTION

The discovery of petroleum and its applications have been largely responsible for the great industrial development of this century. So large has been the consumption (and no decrease in the future can be expected) that some oil authorities have predicted a definite shortage within a period of forty years. Extensive exploration is under way to discover new oil fields but it is felt that the real solution lies in the development of synthetic fuels and supplementary reserves.

Even a preliminary examination of supplementary reserves of liquid fuels in the form of oil shales and sands, and coal, discloses quantities of products that in principle remove for generations to come any possibility of a shortage. The problem is not one of scarce raw materials but one of economics, to provide liquid fuels from coal, for example, at a cost not substantially different from present costs based on petroleum.

In the past few years, there has been a growing interest in this problem. This is particularly true of those countries with limited or no oil resources. Spurred on by an endeavor to become economically self-sufficient, Germany has been leading the field in research and commercial development. Japan, Britain, and the United States, however, are now taking an increasingly active interest in the possible production of synthetic petroleum.

At the present time, two important processes are receiving considerable attention.

1) Berguis Process - a catalytic hydrogenation of coal under high pressures and temperatures.

2) Fischer-Tropsch Process - an indirect catalytic hydrogenation of coal and other carbonaceous materials.

Both processes present excellent possibilities and both have reached the commercial stage of development. However, only the latter process will be considered in this report.

The Fischer-Tropsch synthesis consists of the catalytic hydrogenation of carbon monoxide at medium pressures (5 - 15 atm.) into a mixture of gaseous and liquid hydrocarbons, suitable for the manufacture of fuels. Comparatively low temperatures are employed

(190° to 250°C)- depending upon the catalyst. The synthesis gas, a mixture of CO and H_2 often known as water gas, is produced by the incomplete oxidation of coal, coke, and other carbonaceous materials, such as natural gas.

The production of synthetic hydrocarbons from water gas was first carried out by F. Fischer and H. Tropsch in 1925 - 26 (17). Working at atmospheric pressure and at temperatures of 250° - 300°C, they obtained a product which was principally aliphatic hydrocarbons, containing little or no oxygenated compounds. Their research was so fruitful in the next few years that in 1933 the Ruhrchemie A - G undertook the construction of a plant at Holten, Germany, with a capacity of 1000 tons per year. Much progress was made in the years following. By the end of 1936, five plants were completed or under construction, boosting the production of primary oils to 145,000 metric tons per annum (30). Germany continued to increase its production of synthetic fuels until, in 1940, an annual production of 1,000,000 tons of Fischer-Tropsch liquids was reported (31). Undoubtedly this figure was increased substantially during the war years.

In Japan, by 1938, two plants had been reported giving an annual output of 150,000 tons.

Later information revealed that the erection of three new plants had increased the annual production by 260,000 tons. Small scale plants have been built in both France and Britain.

The extensive development of the Fischer-Tropsch synthesis has been promoted in Germany, not particularly by economic, but by nationalistic motives. An investigation by the U.S. Senate (27) into the economics of this process indicates the relative costs of gasoline produced by two methods.

1) Fischer-Tropsch synthesis

a. from coal - 19.2¢/gal. with the present European design.

b. from natural gas - 8.8¢/gal. with the present design. However a cost of only 4.8¢/gal. is possible if large scale production were carried out using American technology and natural gas at less than 5¢ per 1000 cu. ft.

2) Petroleum Refining

- 5.3 - 5.5¢/gal. with present day methods.

While the production of synthetic fuels from natural gas could, under the most favorable circumstances, compete economically with that from petroleum, it cannot be considered as a long time solution to the problem. Any real solution lies in the use of coal as the primary raw material. The resources of natural gas

are of the same order of magnitude as petroleum and further the economic and social value of natural gas as an industrial and domestic fuel may rule out its extensive use as a chemical raw material.

The Fischer-Tropsch process has attracted the interest of several research organizations in the United States. At present the Bureau of Mines, U.S. Department of the Interior, is vitally interested in its development and is planning the construction of several pilot plants. Research work is also being carried out in a number of oil companies (the most important of which are probably the Standard Oil of New Jersey and the Gulf Oil Co.) but information about their progress is unavailable.

Canada, up to the present time, has shown little interest in the Fischer-Tropsch synthesis. However, in 1944 the Research Council of Alberta initiated a program of research in this connection. This question is of particular interest to Alberta which is enormously rich in reserves of coal and natural gas, the basic raw materials for the manufacture of synthetic fuels. Important industrial development of this process would be of immense economic value to this province.

In the research and development of the Fischer-Tropsch process, the following general problems must be solved:

1) Industrial development of laboratory operations. This is a problem common to all new processes. Economic design and operation depend upon the availability of fundamental data on the process. Much work remains to be done in this field.

2) Heat exchange. Since the reaction is highly exothermic, and since the catalysts are very sensitive to temperature, means must be devised to dissipate the heat. At the present time, the allowable space velocities (and hence gas velocities) are low, resulting in poor heat transfer. Consequently thin layers of catalyst must be used to properly dissipate the heat. All this means comparatively large amounts of steel per unit of catalyst i.e. unit of production.

3) Development of catalysts. This involves the preparation, conditioning, maintenance, and evaluation of new and more effective catalysts. Improvement of catalysts can lead to elimination of the heat exchange problem. It is with the development of catalysts that the present investigation is primarily concerned.

The theory of catalysis is as yet poorly developed and the problem can be attacked only upon an empirical basis. Long term tests under conditions approximating commercial production are necessary to properly evaluate a catalyst. This testing is an integral part of any long range program of fundamental research on the whole question of catalyst development.

Research on Fischer-Tropsch catalysts at the University of Alberta was begun in the summer and fall of 1944 and only the preliminary work has been done on the problem. This involved the construction and assembly of the experimental equipment, the solution of the operational difficulties, and the initial tests upon a few catalysts.

In the course of this investigation, several problems were encountered, which are related, but which have no direct bearing upon the catalyst testing. Two in particular, might be mentioned:

1) Preparation of the synthesis gas

2) Design and calibration of capillary flow-meters. They are of such general interest that it was felt that they should be included in an Appendix of this report.

Preliminary experiments were also carried out on the short-time testing of Fischer-Tropsch catalysts

in a static system at atmospheric pressure. A brief discussion of this phase of the project is included in the Appendix.

II LITERATURE REVIEW

Since its original discovery in 1926, the Fischer-Tropsch synthesis has received wide-spread attention throughout the world, with extensive investigations being carried out largely in Germany but with important contributions from Japan, Russia, England and the United States. As a result, the literature on this process is extensive. Most of the original papers have been published in foreign journals and, except for their abstracts, have not been consulted. In view of the importance of the process, however, many of these papers have been translated and reprinted in available journals. In addition, the information has been brought up to date by several comprehensive reviews (18, 23, 30). While the following literature review does not profess to be complete, it is believed that the major contributions have been included.

The production of hydrocarbons from water gas was pioneered in 1913 by Sabatier (28). He found that finely divided nickel catalyzed the reduction of carbon monoxide to methane according to the following reaction:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

However, no higher hydrocarbons were obtained.

In the same year the Badische Anilin and Sodafrabrik organization patented a process (4) in which saturated and unsaturated gaseous and liquid hydrocarbons, alcohols, aldehydes, acids and ketones were produced from water gas. The reaction took place at elevated temperatures and pressures (300° - 400° C, 100 - 200 atmospheres) over a methanal catalyst impregnated with alkali and oxides of cobalt, osmium or zinc.

In 1913 Franz Fischer and Hans Tropsch (16), on passing water gas over an alkali iron catalyst at 400 - 450°C and 100 - 150 atmospheres, obtained a mixture of aliphatic alcohols, aldehydes, ketones, acids and esters. This product was called "Synthol". It was not until three years later, however, that these two workers reported (17) the famous synthesis which bears their name. By operating at lower pressures and temperatures, and by using alkali-free

iron and cobalt catalysts, they obtained a product (given the name "Kogasin") which consisted almost entirely of hydrocarbons ranging from ethane to solid paraffin.

Since the original announcement, research workers in many countries have studies this synthesis and its implications. Attention has been devoted chiefly to the following phases of the process - the development of new and more active catalysts; the determination of the optimum operating conditions for existing catalysts; and the study of the mechanism of the reactions involved. These will be dealt with in turn.

Catalysts and their Properties.

Many catalysts have been suggested for the Fischer-Tropsch synthesis. On the whole, however, the main constituent of these catalysts is one or more metals from the Eighth Group of the Periodic Table (i.e. Ni, Co, and Fe) usually in the metallic form.

Before any fundamental research on Fischer-Tropsch catalysts is possible, it is first necessary to know the distinguishing characteristics of these catalysts - their desired properties and their faults. Komarewsky and Riesz (23) state that Fischer-Tropsch catalysts must comply with the following requirements:

1) Ability to form a carbide from carbon-monoxide

2) Hydrogenating ability

3) Polymerizing ability

All metals in the Eighth Group satisfy the first two, and, to a certain extent, the third condition. These investigators further suggest that multi-component or "complex-action" catalysts are the most suitable.

Although Fischer and Tropsch employed an iron catalyst in the original synthesis, most of their later work was carried out on cobalt and nickel catalysts. The following table shows the yield and life of some of the catalysts which they had studied up to 1936 (9).

Table I

Yield and Life of Some Fischer-Tropsch Catalysts

Catalyst	Yield g/meter of synthesis gas	Life till decrease to 80% of original activity
Iron:		
Fe Cu Mn Silicagel 0.4% K_2CO_3	30-35	8 days
Fe Cu on Kieselguhr	28	8 days
Nickel:		
Ni Th on Kieselguhr	100	30 days
Ni Mn Al on Kieselguhr	105	45 days
Cobalt:		
Co Th on Kieselguhr	110	60 days
Co Th Kieselguhr decomposed	105	25 days
Co Mn on Kieselguhr	105	Min. 30 days
Co Ni alloyed (Si)	85	12 days
Co Th Cu on Kieselguhr	105	60 days

It is seen that the Co-Th-Kieselguhr catalyst appeared to be the best at that time. However, in 1943, Fischer and co-workers (15) report that further studies have shown that a nickel-manganese-alumina catalyst was clearly superior.

Other investigators have been actively engaged in the development of new catalysts. Although attempts have been made and are being made to develop short time, positive test methods, there has been no success, and

to date this problem can be attacked only empirically. The value of a catalyst can be assessed only after long continuous tests under conditions approximating commercial operation. Cobalt and nickel catalysts have received the most attention and are consequently more developed than the iron catalysts. However, the relatively high cost of cobalt and nickel has prompted many research workers to study and develop the latter.

I. G. Farbenindustrie A.-G. has patented the so-called "Iso" process, using a robust iron catalyst, operating at 200 psi. and 300°C. This is probably a fused iron oxide catalyst which has been reduced at 850°C. Little is known about this process but development in Germany had apparently reached the commercial stage. Recent information (private) suggests, however, that this process is not yet successful.

The action of promoters on Fischer-Tropsch catalysts is obscure and the only guide being followed is that of trial and error. Foster (18) has reviewed some of the catalysts which have been suggested. The promoters used include alkali and alkaline earth metal oxides, copper, thoria, and the oxides or sulphides of uranium, chromium, tungsten, aluminium, and manganese. Other proposed promoters are found in the patent literature but the latter contains little information of value.

Napthali (26) has offered explanations for the action of some of these promoters. Copper facilitates the action of the catalyst by lowering the temperature necessary for the reduction of carbon monoxide. It is effective with iron and cobalt but not with nickel. Small quantities of alkali in iron catalysts favor wax formation. Thorium, manganese, and similar metals, when precipitated together with the contact mass, appear to function by distorting the metal surface enhancing the activity. Space lattice distortion changes the inter-atomic distance to permit cross linkages, thus affecting the chain length and the iso-normal paraffin ratio.

In general, cobalt catalysts are promoted by thorium or by rare earths while iron catalysts are promoted by copper. The best carrier or support for cobalt catalysts is kieselguhr. Iron catalysts are not supported since all known carriers to date exert only a detrimental effect.

In line with the general theory of solid catalysts, there is evidence to indicate that the synthesis takes place only at a comparatively few active centres on the surface of the catalyst. Even in the best Fischer-Tropsch catalysts, these few active centres become deactivated rather rapidly. The following possibilities have been suggested for

the loss of activity of cobalt catalysts:

1) Wax formation on the surface of the catalyst - reversed by hydrogen treatment at 200°C.

2) Oxidation of the active centres by water - reversed by hydrogen treatment at 400°C.

3) Carbiding - irreversible.

Underwood (31) has reported that, under optimum operating conditions, the catalyst life is from four to six months. This is only approximate since life depends upon manner of operation, period and manner of reactivation, minimum yield allowed and economics. For instance, Fischer (15) states that a nickel-manganese-alumina will remain active one to two years provided that it is regenerated periodically. In general, however, the life of Fischer-Tropsch catalysts is relatively short and it is desirable to lengthen it.

It might be mentioned that while cobalt catalysts can be regenerated by a hydrogen treatment (at either 200°C or 400°C depending upon the circumstances) this is not possible for iron catalysts. If for any reason, the latter loses its activity, it cannot be reactivated. Permanent loss of activity for both cobalt and iron catalysts has been attributed to the loss of active centres through volatilization as carbonyls.

Closely allied with the problem of deactivation is the question of poisoning. Fischer-Tropsch catalysts are characterized by their high susceptibility to poisoning, particularly by minute quantities of sulphur. Herington and Woodward (21) have investigated the effect of small quantities of hydrogen sulphide on a Co-Th-kieselguhr catalyst. The first addition of hydrogen sulphide caused a marked increase in the yield of liquid hydrocarbons. This continued until more than 8 milligrams of sulphur had been added per gram of catalyst. Further addition caused a drop in total hydrocarbon yield but this could be offset by raising the reaction temperature. The addition of hydrogen sulphide in quantities over 34 milligrams of sulphur per gram of catalyst resulted in a continuous decrease in activity until complete poisoning was reached. However, even as little as 10 milligrams of sulphur per gram of catalyst is sufficient to prevent the periodic regeneration of the catalyst. Sulphur poisoning is irreversible. In commercial operation the maximum tolerance for sulphur content is 0.1 grain per 100 cubic feet. Myddleton (24) has reported on efforts to develop sulphur resistant catalysts but the results have not been conclusive.

Fischer-Tropsch catalysts are also poisoned by minute quantities of oxygen gas. The latter appears

to attack the active catalyst centers preferentially. However, cobalt catalysts which have been poisoned in this way can be reactivated by a hydrogen treatment at 400°C.

Operating Conditions for Fischer-Tropsch Catalysts

The various operating conditions-temperature, pressure, space velocity, and composition of synthesis gas - all have a marked effect on the behavior of Fischer-Tropsch catalysts. Fischer and co-workers have done considerable work on this phase of the problem in an effort to determine the optimum operating conditions for commercial plants.

Fischer-Tropsch catalysts are very sensitive to temperature - the maximum range of variation being 15 centigrade degrees. Storch (30) reports that, even for the most active cobalt catalysts, the reaction rate is very slow below 175°C and above 225°C and the production of liquid falls off sharply, with methane formation predominating. The best cobalt catalysts operate at a temperature of 195 - 200°C. Nickel-manganese-alumina catalysts, as developed by Fischer (14), operate between 190° - 210°C. As the catalyst slowly loses its activity during operation, the temperature has to be raised slightly. Higher temperatures favor methane formation with a corresponding loss in

yield of liquid hydrocarbons and furthermore causes the catalyst to become irreversibly poisoned, possibly due to carbon formation. In this connection, Hofer's observation (22) that the upper temperature limits of the Fischer-Tropsch synthesis and the lower temperature limits of carbon formation (i.e. from the metallic carbide) very nearly coincide, may be of significance. For iron catalysts, the optimum temperature is around 250°C but with higher temperatures, carbiding and carbonyl formation deactivate the catalyst irreversibly.

The synthesis pressure affects both the yield and type of product, and the life of the catalyst. Earlier work by Fischer and Tropsch (16) has shown that high pressures (100 - 150 atmospheres) favored the formation of "synthol" or oxygenated compounds. On reducing the pressure to 20 atmospheres or less, the reaction produced hydrocarbons almost exclusively. Fischer and Pichler's curves (13) showing the effect of pressure on total and fractional yield of products using a Co-Th-kieselguhr catalyst are reproduced in Figure I.

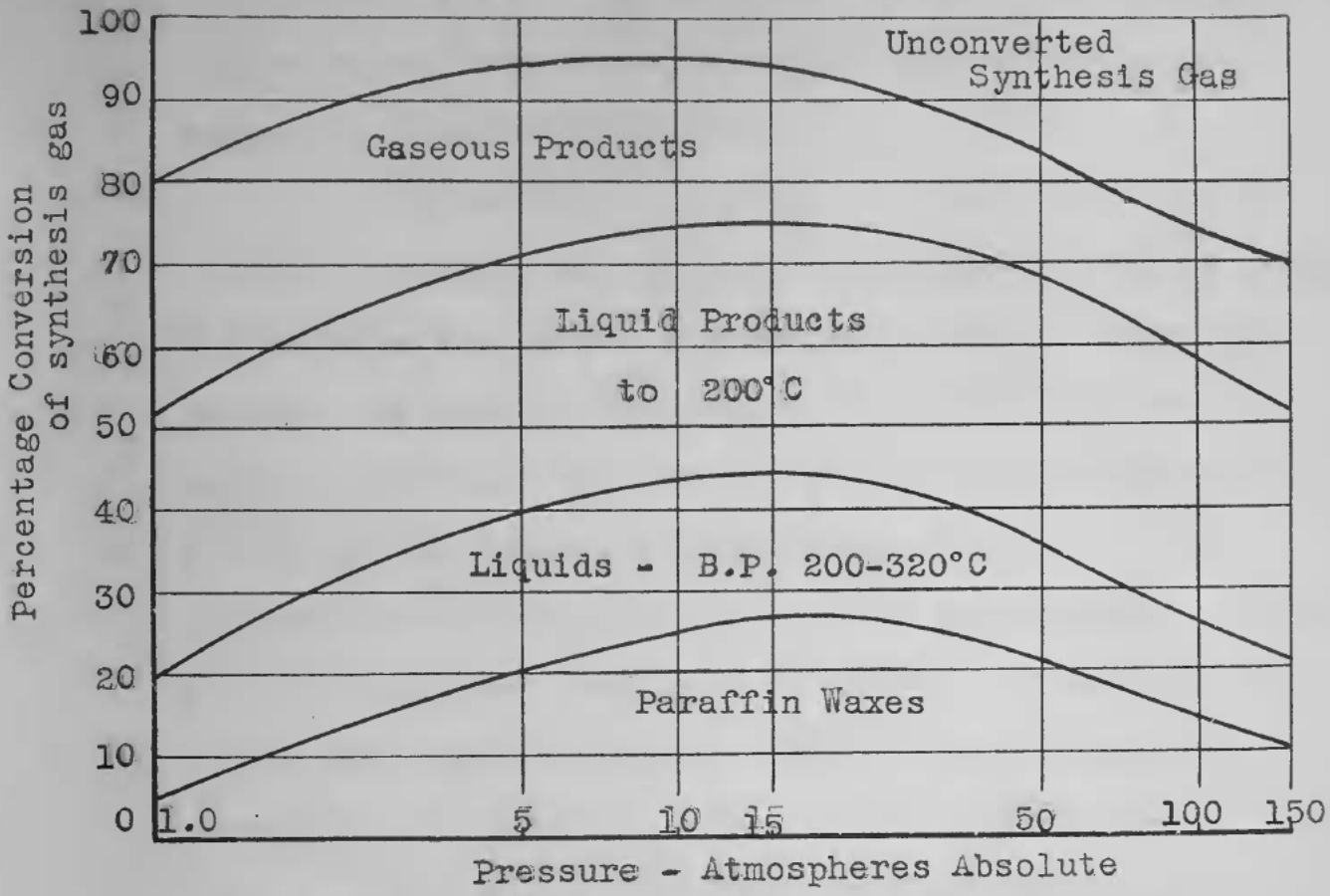


Figure I = Effect of Pressure on Hydrocarbon Yields

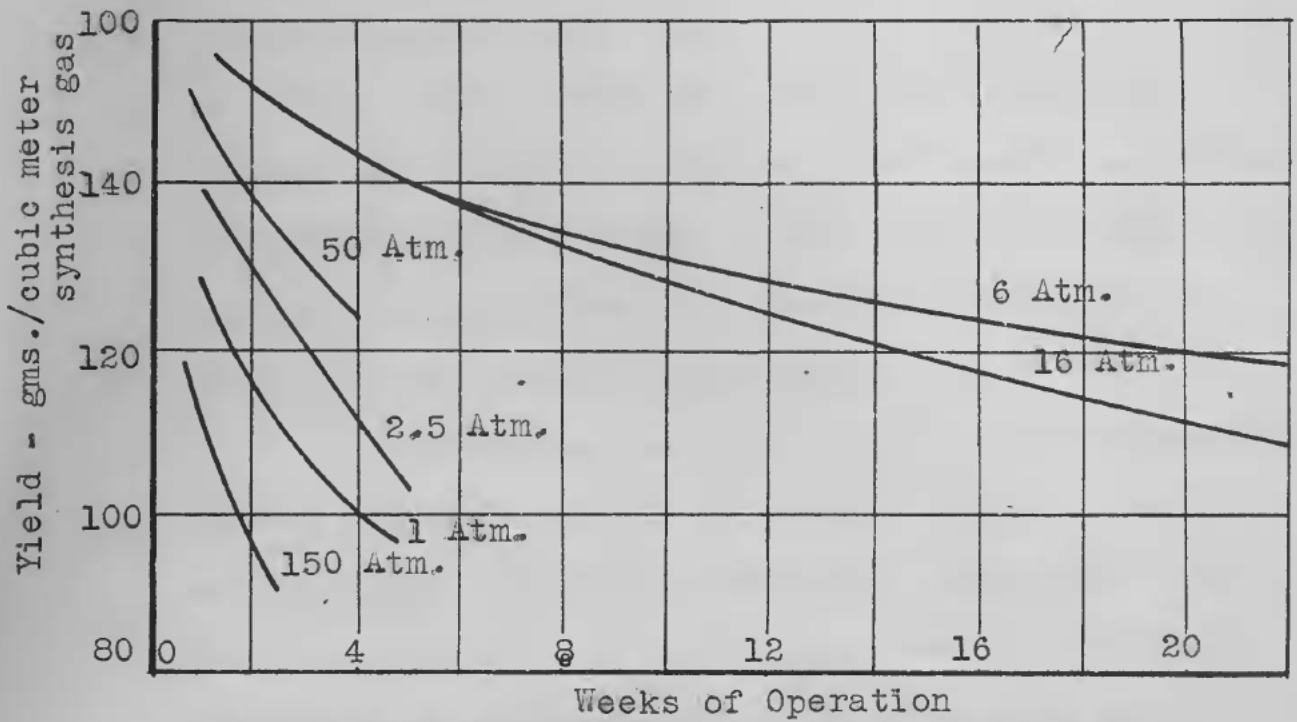


Figure II-- Effect of Pressure on Catalyst Life

A pressure of 5 - 15 atmospheres gives the greatest degree of conversion and also the highest yield of solid and liquid hydrocarbons.

The effect of pressure on the durability of a cobalt catalyst was shown by Fischer and Pichler (12). The results are shown in graphical form in Figure II. At both low and high pressures, the effectiveness of the catalyst decreases markedly in the first few weeks. A pressure of 5 - 15 atmospheres appears to be the optimum for maintaining the life of the catalyst. These results have been confirmed with iron. Komarewsky and Riesz (23) report, however, that these pressures are unsuitable for operating with nickel catalysts.

The space velocities employed are in comparison with catalysts for other syntheses, extremely low, being, in general practice, in the range of 100 - 150 per hour. This leaves much room for improvement. Fischer and Pichler (12) have investigated the effect of varying the throughput on the yield of liquid hydrocarbons obtained from a Co-Th-kieselguhr catalyst. Their plotted results are shown in Figure III.

At the maximum point in the space-time-yield curve, the yield of oil is only 60 grams per cubic meter of gas indicating incomplete conversion. If one-pass operation is practiced, such yields are probably not economical. Aside from this, another

factor limits the space velocities. Since the reaction is strongly exothermic, a high space velocity presents a serious heat exchange problem. If the heat of reaction cannot be dissipated effectively, this causes local heating of the catalyst, resulting in the sintering and deactivation of the active centres. German industry has attempted to solve the heat transfer problem by using a relatively inert catalyst, high space velocities, and recycling. However, the formation of gaseous inert products (CH_4, CO_2) leads to serious recycling difficulties. Two stage operation appears to be the compromise (30, 31).

Figure III - Effect of Varying Throughput on Degree of Conversion and Space-Time-Yields

Fischer and co-workers (15) have studied the effect of varying the $CO:H_2$ ratio in the synthesis gas. They recommend that the stoichimetrical mixture containing 33.3% CO and 66.6% H_2 is the most desirable one, giving the maximum yield of products per cubic meter of raw gas per unit time. In addition this ratio gives the highest degree of conversion to liquid hydrocarbons.

The reaction rate decreases as the $CO:H_2$ ratio rises above this optimum. The yield of liquid products increases as does the unsaturation. On the other hand, a low $CO:H_2$ ratio results in a greater degree of conversion and more saturation. The effect of the $CO:H_2$ ratio can be somewhat minimized, however, by the proper selection of a specific reaction temperature - this temperature being higher for CO rich gases than for H_2 rich gases.

Inert gases like nitrogen have only a diluent effect and do not affect the reaction materially.

Type of Products

The type of products obtained in the Fischer-Tropsch process depend upon both the operating conditions and the catalyst employed. The effect of varying the operating conditions has already been qualitatively shown. The products obtained from the

two general types of catalyst (iron; and cobalt, nickel) show considerable differences. Most of the literature deals with cobalt catalysts; data on iron catalyst products are relatively scanty.

Napthali (26) has reported that cobalt catalysts give a more saturated product than the iron. Fischer (11) using a cobalt catalyst obtained the following primary product or Kogasin.

Table II

Analysis of Kogasin

Fraction	B.Pt. °C	% by Wt.	% of Olefins
C_3 and C_4	Below 30	8	50
gasoline	30 - 200	60	30
Diesel Oil	Over 200	22	10
Paraffin Wax		10	

Kogasin is largely composed of straight chain saturated and unsaturated hydrocarbons. The gasoline fraction constitutes 60% of the total product but has a low octane number.

On the other hand, the U.S. Bureau of Mines (32) find that at 7 atmospheres, and using a cobalt catalyst, the product had the following approximate composition by weight:

Percentage	Fraction
10	C_3 and C_4
20	40 - 150°C B.Pt.
30	150 - 370°C B.Pt.(Diesel Cut)
40	above 370°C

These sets of data should be regarded as only illustrative of the type of product obtained. The character of the various fractions have been revealed by several investigators (26, 30, 32). The diesel oil cut may be removed by simple distillation. It is of good quality, having a high cetane number due to the straight chain character of the hydrocarbons in this fraction. The paraffin wax differs in properties from that obtained from petroleum but can be put to the same uses. It is characterized by a high melting point and contains relatively high proportions of long straight chain hydrocarbons. The gasoline fraction may be increased by reforming and cracking the primary product in conventional petroleum plant equipment. The octane number can also be raised by these methods. Egloff, Nelson and Morrell (7), by means of thermal treatment and catalytic polymerizations, obtained 84.3% of 66 octane gasoline from a kogasin oil which originally had an octane number of only 20.

Little is known about the product from iron catalysts except that a higher percentage of olefins (and hence a higher octane number) is found in the primary product.

The development of new catalysts to direct the reaction towards specific products has been recently reported (6). Of particular interest is the so-called "iso-synthesis" in which iso-paraffins are produced directly. High octane gasoline fractions are obtained which may be converted to aviation fuel.

The literature reveals the wide versatility of the Fischer-Tropsch synthesis. A large variety of products is possible through the proper choice of catalysts and operating conditions.

Mechanism of the Reaction

The overall chemical reaction over Ni, Co catalysts differs from that over Fe catalysts mainly in the by-products produced. Along with hydrocarbons the latter yield CO_2 while the former give principally H_2O. The reactions - assuming formation of paraffin hydrocarbons only - may be represented by the following equations.

1) For the Co and Ni catalysts

$$nCO + (2n+1)\ H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

2) For the Fe catalysts

$$2n\ CO + (n+1)\ H_2 \longrightarrow C_nH_{2n+2} + nCO_2$$

This difference in behaviour has been one of the main difficulties in the determination of the reaction mechanism. Much research has been done on this question and several theories have been advanced.

In 1926 F. Fischer and H. Tropsch (17) following their initial production of paraffin hydrocarbons from water gas postulated that the catalytic process involves the formation of a carbide, rich in carbon (Fe_3C_4 or Fe_2C_3) which is later converted to methylene groups. The overall effect may be represented by:

$$3\,CO + 3H_2 \longrightarrow CO_2 + H_2O + 2CH_2$$

The methylene groups polymerize in the presence of hydrogen to form the paraffinic compounds. An Fe - Co contact mass was used in their investigation and, as a result, both CO_2 and H_2O were present. In a later paper Fischer (10) reiterated his initial idea but suggested an alternative. He stated that the methylene groups first polymerize to extremely high molecular weight hydrocarbons. These are subsequently cracked into compounds with high vapour pressures and carried off the catalytic surface. The actual mechanism is suggested as follows:

$$CO + Me \longrightarrow MeC + MeO$$

$$MeC + MeO + 2H_2 \longrightarrow 2Me + CH_2 + H_2O$$

However, it is probably more correct to assume that the original carbide is merely reduced to a lower

carbide rather than to the metal. No attempt was made to explain the CO_2 formation.

In an endeavour to explain the formation of oxygenated compounds, Elvin and Nash (8) advanced in 1926 an alternative theory. The hypothetical formation of methanol is postuluted as the intermediate reaction for obtaining both hydrocarbons and oxygenated compounds (acids, alcohols, ketones and aldehydes). This, however, is not supported by thermodynamic considerations. This theory has found some support with Japanese investigators (3).

The presence of carbides in catalysts was confirmed by experiments (22) involving the carbiding and reduction of the three metals, Ni, Co and Fe. Up to certain critical temperatures, when treated with CO, all three form metallic carbides which can be reduced completely, giving CH_4 as a product. Above these temperatures (which are but slightly higher than the optimum for the synthesis) elementary carbon is formed which, by carrying away active centres and producing irreducible residues, tend to poison the catalyst. There is evidence to indicate that the carbides are the real catalyst bodies.

Craxford (1, 2) in supporting and developing Fischer's carbide theory, has presented a detailed mechanism of the reaction. He argued against the

formation of hydrocarbons by simple carbiding and reduction as expressed by the following reactions:

1) $2Co + 2CO \longrightarrow Co_2C + CO_2$

2) $Co_2C + H_2 \longrightarrow CH_2 + 2Co$

First, both reactions are too slow to account for the rate of the overall reaction:

3) $CO + H_2 \longrightarrow CH_2 + H_2O$

Secondly over Co catalysts the production of H_2O cannot be explained by equations 1) and 2).

As a result of experiments involving the rate of ortho-para conversion of hydrogen on the surface of an active Co-Th-kieselguhr catalyst, Craxford concluded that the reaction forming hydrocarbons proceeds by way of molecular H_2. The following steps in the reaction (shown diagrammatically in Figure IV) have been suggested:

1) CO is chemisorbed to the surface and reduced by molecular H_2 to form the carbide.

2) The carbide is reduced by H_2 to form methylene groups.

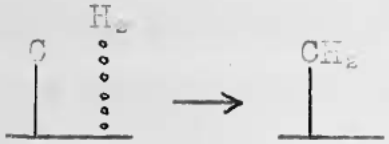
3) In the presence of large amounts of chemisorbed H_2, the methylene groups are immediately reduced to methane; with smaller amounts long chain hydrocarbons are formed.

Legend: ..... Van der Waal Adsorption
——— Chemisorption

(1) Chemisorption of CO

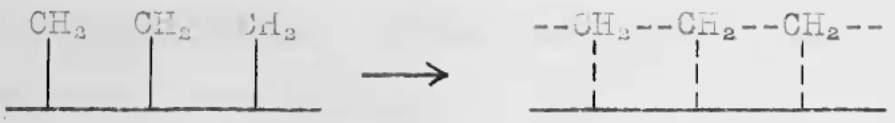
Reduction of Chemisorbed CO by H_2 to give Carbide

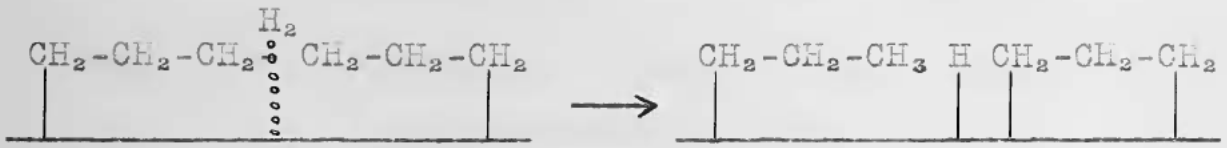
(2) Reduction of the Carbide to Chemisorbed Methylene



(3) a. Presence of a Large Amount of Chemisorbed H_2

b. Presence of a Small Amount of Chemisorbed H_2





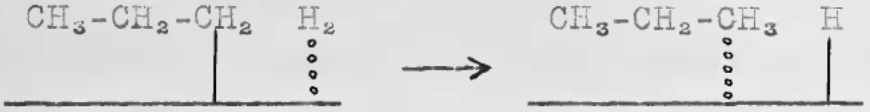


Figure IV - Mechanism of the Synthesis of Hydrocarbons (Craxford)

This mechanism supports Fischer's idea of the formation of high molecular weight hydrocarbons subsequently followed by hydrogenation or 'cracking'. Further experiments involving the breaking down of ethane, propane, and butane (mixed with the requisite amount of H_2) into CH_4 over a freshly reduced Fischer catalyst substantiated this view.

While Co catalysts are usually considered very active for the water gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

the primary oxygenated compound is water rather than CO_2. No other explanation for this phenomenon is given other than to assume the reaction is inhibited by the operating conditions of the Fischer - Tropsch synthesis. When the temperature is raised to 250 - 300°C, CO_2 is again produced exclusively, with no hydrocarbons save methane.

To conclude then, while the Craxford mechanism is valuable, it is nevertheless complicated and is so far limited to Co catalysts.

Herington and Woodward (21) conclude that the Fischer - Tropsch catalysts possess two types of active centres:

(a) Type A (probably cobalt carbide) which is responsible for the formation of methylene groups.

(b) Type B (probably cobalt metal) which is responsible for the adsorption of H_2 to liberate the products from the catalytic surface.

Myddleton (25) has offered an explanation for the difference in the by-products with Ni, Co, and Fe catalysts on the basis of the chemical bonding of the CO to the surface. With dual bonding to adjacent atoms (as in the case of cobalt and nickel) H_2O is produced whereas with single attachment (as with Fe) CO_2 is produced. Further experimental evidence is needed to support this claim.

In general, the carbide theory, advanced by Fischer and developed by Craxford, appears to be the most acceptable at the present time. This mechanism has been developed primarily for Co catalysts and little work in this connection has been done with Fe catalysts. It is almost certain, however, that the formation of iron carbides plays an important role in the mechanism of the latter.

III EXPERIMENTAL EQUIPMENT

The Fischer-Tropsch process is composed of essentially two distinct stages - the preparation of the synthesis gas and its conversion into suitable hydrocarbons. The description of the equipment may also be divided in this manner. The preparation of the synthesis gas will be described in detail in the Appendix. The emphasis in this section will be placed on the equipment used in the actual synthesis.

Catalyst testing is carried out on a pilot plant basis and the equipment is operated continuously for long periods - extending into several months. The following requirements must be satisfied - the passage of water gas at extremely low space velocity (100-150 per hour) over a catalyst column at medium pressures (100 psi.) and temperatures (200° - 250°C) with good control in general but particularly with respect to temperature.

Much of the present design, the reaction converter, and the recovery system in particular, has

been based on the experience of the U.S. Bureau of Mines (Department of the Interior) Pittsburg, Pa. However, at the University of Alberta, much more automatic control (especially in the control of gas flow) had to be incorporated into the design. This was necessary because only a comparatively small staff was available for work on this project. There are six individual catalyst testing units, each of which may be operated nearly automatically, and independentlyof each other.

(a) General Flow Sheet

Before giving a detailed description of the individual pieces of equipment, a short discussion of the general flow sheet (Figure V) will be first presented. This will afford an overall picture of the whole process and will bring out the relationships between the various pieces of equipment. Only a brief descriptive paragraph on the synthesis gas production will be given here.

Methane and oxygen, in the volumetric ratio 2 : 1, are passed simultaneously into gasholder A, the flow being measured by two capillary type flowmeters. The mixed gases are passed at a controlled rate over a nickel catalyst heated to 1000°C in the electric furnace B. Here the conversion into synthesis gas occurs, the

main reaction being

$$2\ CH_4 + O_2 \longrightarrow 2\ CO + 4\ H_2$$

The exit gas is purified (of H_2S and CO_2) by a caustic scrubber C and is then stored in gasholder D. This low pressure gas is compressed to 100 psi. guage and held in the high pressure storage tank E. The pressure here is maintained constant by automatic control, the movement of a Bourdon tube actuating a relay and magnetic switch in the power supply to the compressor. High pressure synthesis gas, after being dried in the alumina dryer F, is passed into a header common to all six units.

The gas flow to each unit is indicated by the pressure drop across a capillary-tube flowmeter, the pressure drop being indicated on a mercury manometer, equipped with high, low and intermediate contacts. The manometer contacts are part of an electrical circuit which operates a motor driven control needle valve G, designed to keep the flow constant within narrow limits. The gas passes into the reaction chamber of the converter H containing a column of catalyst. The catalyst bed (approximately 16 inches in length) is supported inside a $\frac{1}{2}$ inch iron pipe. The catalyst temperature is held constant by a liquid boiling at constant pressure in a jacket surrounding the reactor. This outer jacket forms part of a closed system which also includes the water-cooled reflux

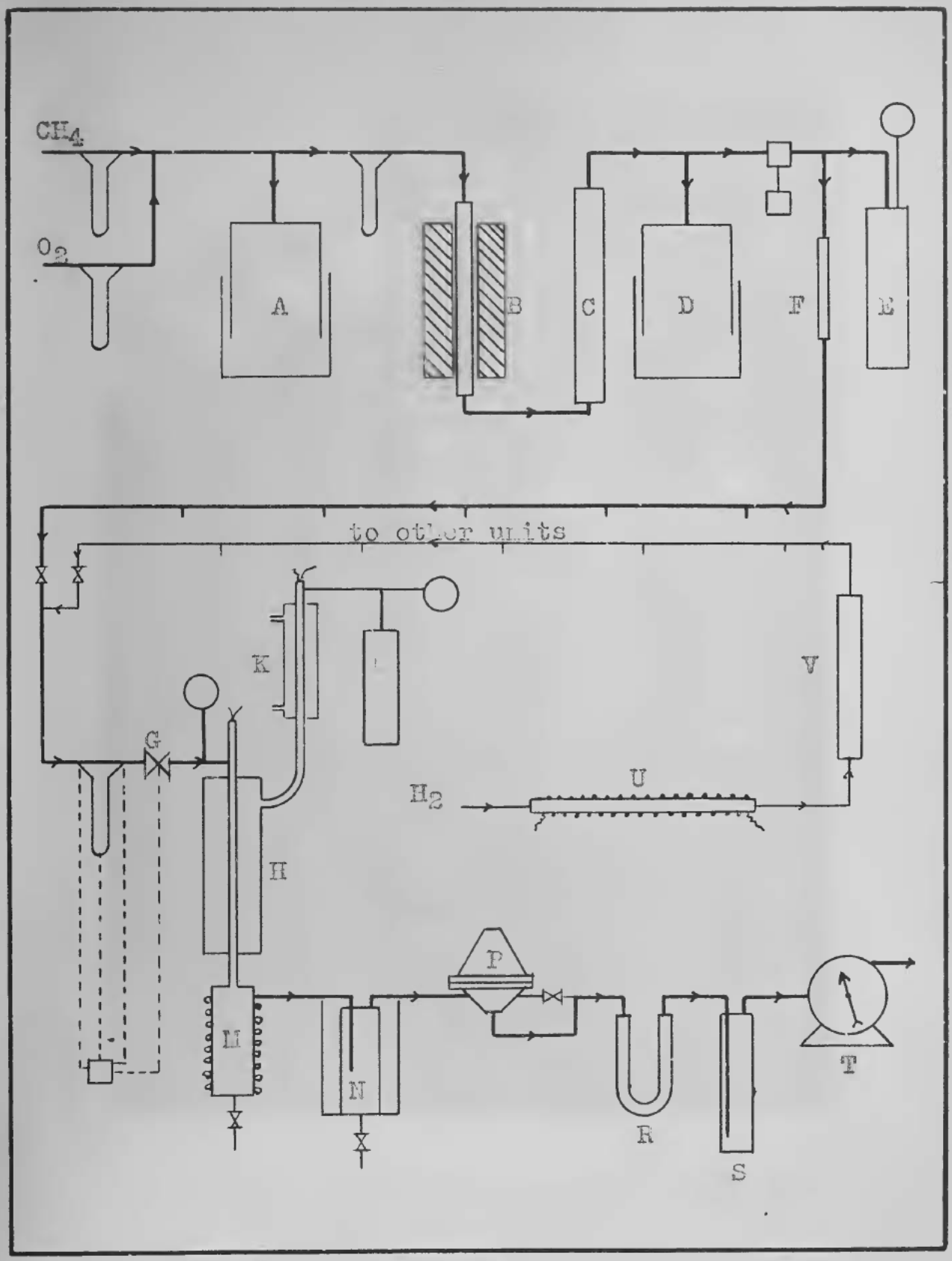


Figure V - General flow sheet for testing of Fischer-Tropsch catalysts.

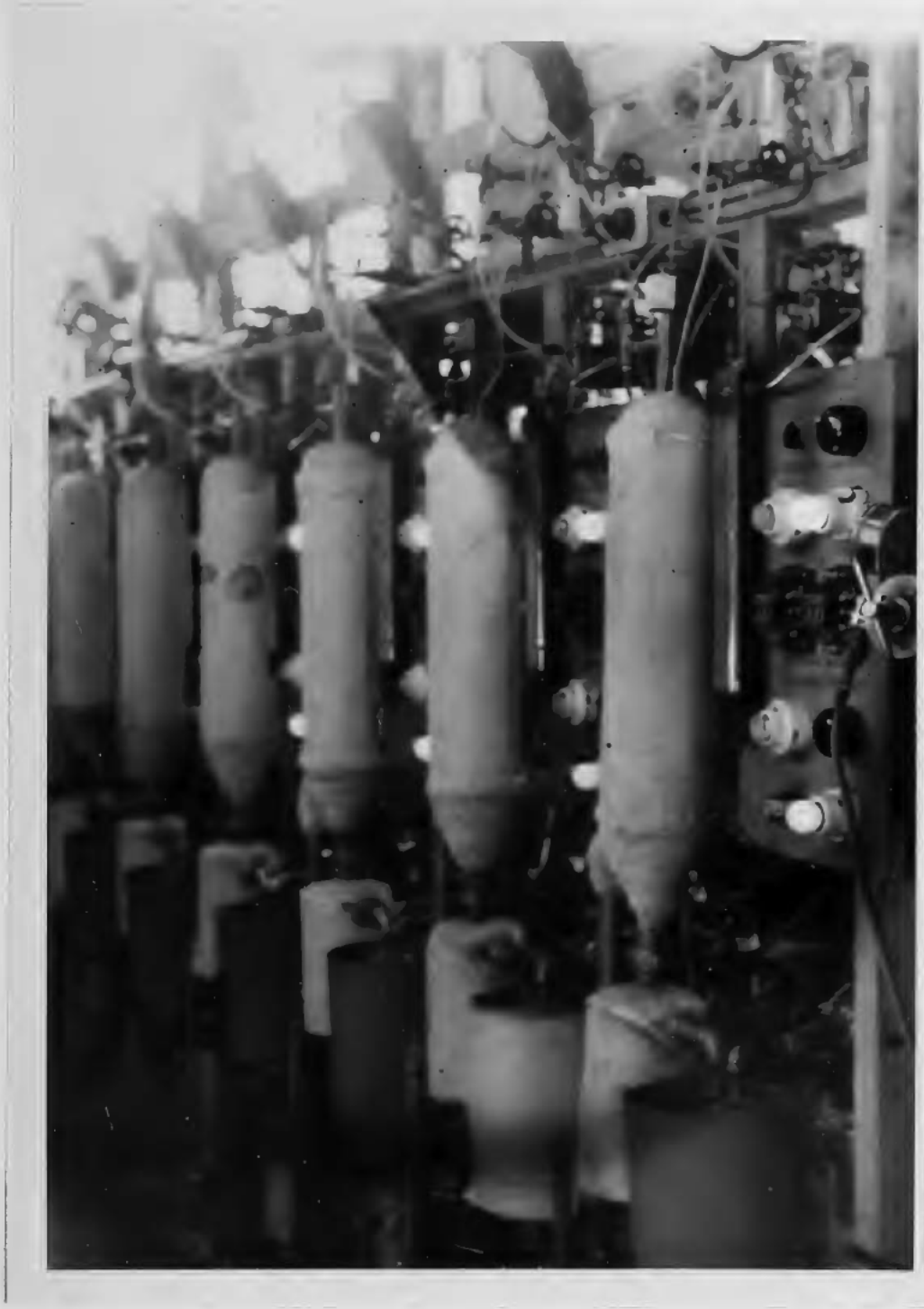


Figure VI - Front View of Catalyst Testing Units

Figure VII - Main Panel Board and
Equipment for Synthesis Gas Preparation

condenser K and the ballast chamber L. The temperature of the boiling liquid is changed by varying the pressure of an inert gas in this system.

The liquid and solid products of the synthesis are partially separated and collected in the two pots M and N. The hydrocarbons with boiling points higher than 100°C (at 100 psi.) are collected in a steam-coil-jacketed pot M; the hydrocarbons with boiling points between 0°C and 100°C (at 100 psi.) in the ice-jacketed pot N. Pressure is maintained constant in the unit by a back pressure regulator P. The gaseous products, in passing through this valve, are reduced from 100 psi. to about atmospheric pressure. Water and carbon dioxide are removed by a calcium chloride dryer R and a caustic scrubber S respectively. The volume of the residue gases is measured by a Precision Wet Test Meter T.

For purposes of reduction and reactivation of the catalyst, and for the maintainence of a reducing atmosphere over the catalyst during "shut-downs", a hydrogen supply is included in the flow sheet. Hydrogen from a high pressure storage cylinder is discharged at a controlled rate and at pressures slightly above atmospheric through a two stage pressure-reduction valve. Passage of the hydrogen over metallic copper at 250° - 300°C in the furnace J serves to remove any

oxygen, while activated charcoal in the scrubber V preferentially adsorbs any high molecular weight gases, leaving relatively pure hydrogen gas. A common header services all units.

(b) Description of Synthesis Equipment

This section is not intended to give a detailed description of all the major pieces of synthesis equipment used in these investigations. General descriptions will be given of common equipment and details will be given only for equipment that presents new design or new unique features. The equipment required in the preparation of the synthesis gas will be discussed in the Appendix. Special features incorporated into the design to control the experimental conditions - temperature, pressure and rate of flow - will be dealt with in the next subsection on "Instrumentation and Controls.".

Since the Fischer-Tropsch process involves the synthesis of gas under pressure, two types of storage are required - a low and high pressure storage. A conventional water-seal type gasholder D serves as the low pressure reservoir (Figure V) and a pressure tank E as the high pressure reservoir.

Gasholder D has a capacity of approximately 15 cu. ft. and the floating drum is counter-balanced

to maintain a gas pressure of about one inch of water. Two safety devices, in the form of upper and lower limit switches, have been incorporated into the design. The lower limit switch consists of a "microswitch" and is attached to the outer fixed drum of the gas-holder. It is actuated by the floating drum when it reaches its lower position and breaks the electrical circuit of the compressor motor, thus eliminating the possibility of water being drawn accidentally into the gas compressor. The upper limit switch consists of a microswitch attached to the top of one of the gasholder guides and is actuated by the floating drum when near the full position. A warning bell is sounded and steps are taken to reduce or discontinue synthesis gas production.

The high pressure reservoir E consists of a standard compressed air receiver, approximately 15 inches in diameter and 60 inches long, of about 6 cu. ft. capacity. The pressure is indicated by a Bourdon tube pressure guage and is maintained constant to within 0.5 to 1 psi. by means of an adapted Mercoid Pressure Control operating on the compressor motor circuit.

The gas is compressed by a small single-acting compressor with a 2 inch stroke and a $1\frac{1}{4}$ inch piston. It is fitted with a solid plunger-type

piston, an external packed gland, and poppet type valves. There are no piston rings. Lubrication is supplied by gravity through the intake valve. The compressor, driven by a $\frac{1}{2}$ h.p. 1700 r.p.m. induction motor through a belt drive, operates intermittently, always under pressure, transferring the gas from the gasholder to the pressure storage in response to the mercoid control. A check valve in the discharge line allows the compressor to be unloaded and prevents leakage from the high pressure storage.

The Al_2O_3 drier F is a two foot length of 2 inch standard iron pipe, filled with dehydrated alumina and is wound with a heating coil, the whole being encased in 85% magnesia pipe insulation. Water is removed from the synthesis gas at room temperature. The heating coil permits the reactivation of the alumina at a temperature of 300°C.

The six converter units, identical in both design and construction, are connected to common headers but isolated one from the other so that the operating conditions may be varied in each. They are constructed of standard-weight, butt-weld iron pipe and standard malleable iron pipe fittings. Each unit consists of principally three sections: (1) the catalyst chamber (2) temperature control system (3) liquid product recovery system. A

drawing of the converter and its accessories is shown in Figure VIII.

The catalyst tube A is a ½ inch standard pipe 27 inches long. Screwed on the upper end is the catalyst chamber head B, machined from a 2 inch hexagonal steel bar. A thermocouple well C of ¼ inch steel tubing, screwed into the head, extends the length of the chamber. Provision is also made in the head for the introduction of the catalyst into the converter. A piece of 3/8 inch pipe D with a fine wire screen welded to its upper end, is screwed into the lower end of the column and serves as a support for the catalyst. The gas enters the unit through a ¼ inch pipe E and passes down through the catalyst bed. Connection is made to a Bourdon-type pressure guage by means of a ¼ inch tee which also serves as a connection for the gas feed line.

A heating jacket F, 20 inches long of 2½ inch standard pipe with ¼ inch steel plate ends, is welded to the catalyst tube. A liquid, heated electrically by a resistance coil encircling the jacket, is kept boiling within the jacket maintaining the catalyst tube at a constant and uniform temperature. The boiling temperatures are controlled by the pressure in the heating jacket. The temperature of the liquid is observed by means of a thermocouple inserted in the

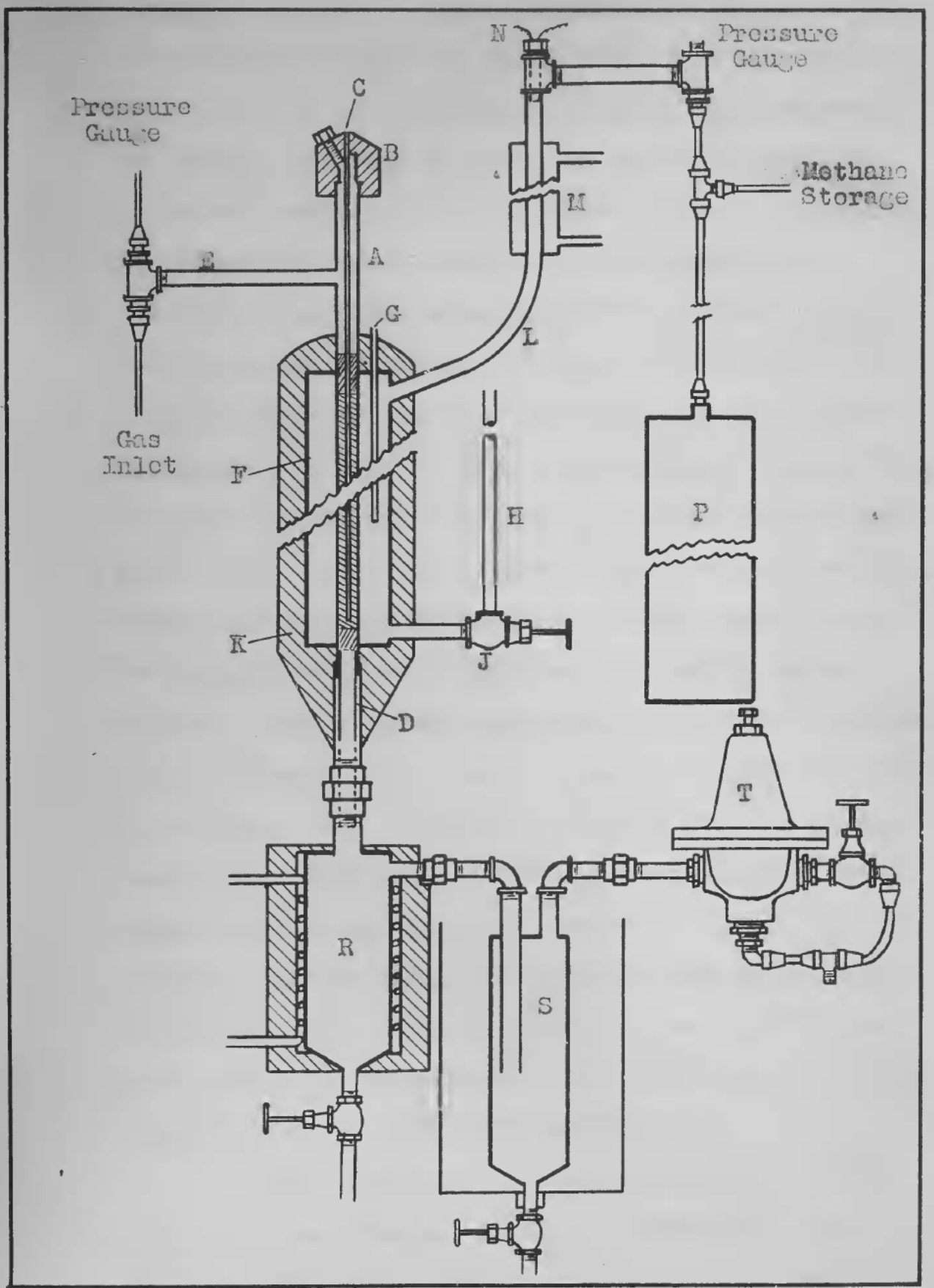


Figure VIII- Converter Unit Assembly.

thermocouple well G. The liquid level is indicated by an open end sight gauge H. When necessary the valve J shuts off connection between the chamber and the gauge, allowing pressure or vacuum to be built up in the former and allowing the latter to be drained. To prevent excessive heat loss, the jacket and catalyst column are covered with 85% magnesia pipe insulation K with asbestos cement at each end. A ½ inch pipe L with its upper end enclosed by a water condenser M is connected to the jacket and serves as a reflux column for the boiling liquid. At the upper end of this column is a Fenwal thermoswitch N which breaks the heating circuit if the hot vapours rise too high, in case of failure of the cooling water supply. Here also are connections to: (1) a compound Bourdon tube pressure gauge (range of 30 in. Hg vacuum to 60 psi.) (2) a ballast tank made from an 18 inch length of 3 inch pipe and (3) a natural gas header common to all six units and connected to a high pressure gas storage. The liquids used in the converters depended upon the temperatures required, and were tetralin, dowtherm and a paraffin oil of initial boiling point of 360°C (700 mm Hg).

The recovery of liquid products is accomplished in two stages - in steam-heated and ice-jacketed condensers R and S resulting in a rough

separation of heavy waxes and low boiling hydrocarbons. Both pots made from 2½ inch pipe, 7 and 8 inches long, are only slightly different in design. Condenser R has several turns of ¼ inch copper tubing encircling it and is insulated with 85% magnesia pipe insulation. Steam passing through the copper tubing maintains the temperature at approximately 100°C. Both pots are equipped with ¼ inch drain valves to permit the removal of the liquid products. Pipe unions, connecting the pots to one another and to the adjoining equipment, enable the removal of either one of the condensers.

The residue gases are bled off continuously by the Cash back-pressure control valve T. These are standard Cash model 1935, size ½", in which the makers replaced the usual bronze seat by a metal-composition seat. The control desired, from 100 - 0 psi. gauge, and the small quantities of gas flowing necessitated experimentation with the seat. The material known as "vulcanized fibre" was found most suitable, giving perfect control without drifting and complete shut-off. It is probable that the valve floats continuously when passing the small amount of gas involved.

The expanded gases are treated for removal of water and carbon dioxide, the residue gases after

measurement by a standard Precision Wet Test Meter being discharged to the atmosphere. Water is adsorbed in calcium chloride in Schwartz ground glass stoppered U-tubes; carbon dioxide is removed in a standard potassium hydroxide solution contained in a fritted glass type gas washing bottle (500 cc). Two driers and two scrubbers in parallel, suitably connected by stop-cocks so that either drier or scrubber can be used, make up this phase of the system. A continuous gravity-type gas sampler (not shown on the general flow sheet), placed immediately before the gas meter, gives a representative sample of the residue gases. The rate of sampling is regulated by a capillary placed in the liquid discharge. A 10% Na_2SO_4 and 10% H_2SO_4 solution is used as the confining liquid.

Saran tubing (a vinylidene chloride plastic) is used for connections between the various pieces of the equipment. Its strength (at low temperatures only) and its flexibility make it an ideal conduit particularly where many short circuitous leads are required. Saran tubing and fittings are used to connect together the header, the flowmeter, the mercury manometer, the control valve, the catalyst column and the pressure gauge in the high pressure synthesis gas stream. They also form an integral part of the temperature control system, connecting the methane leader and the ballast tank to the main assembly.

(c) Instrumentation and Control

The electric power required for operation is supplied to a main panel board and from here to the individual units. The instrumentation of the main panel board is shown in Figure IX (a). Power from a 110 volt line passes through a two pole line switch A to the various units. A fuse B inserted in the line protects the power supply. Across this supply and in parallel are a light C and a relay D which together serve as an alarm system. When the power is on, the light glows and the relay is actuated, opening the battery circuit containing the bell E. A power failure causes the light to go out and the bell to ring. The other bell F is common to all six convertors and rings when the automatic temperature and pressure controls on any of the units fail to function properly. The latter alarm is also connected to a microswitch G, which is actuated whenever the gasholder for the synthesis gas rises too high.

The thermocouple system is shown in Figure IX (b). The cold junction H, the constantan header K, and the potentiometer L are common to all units. Individual copper leads are used for each thermocouple. These are connected to the main circuit through a pair of single gang eleven position rotary switches M and N.

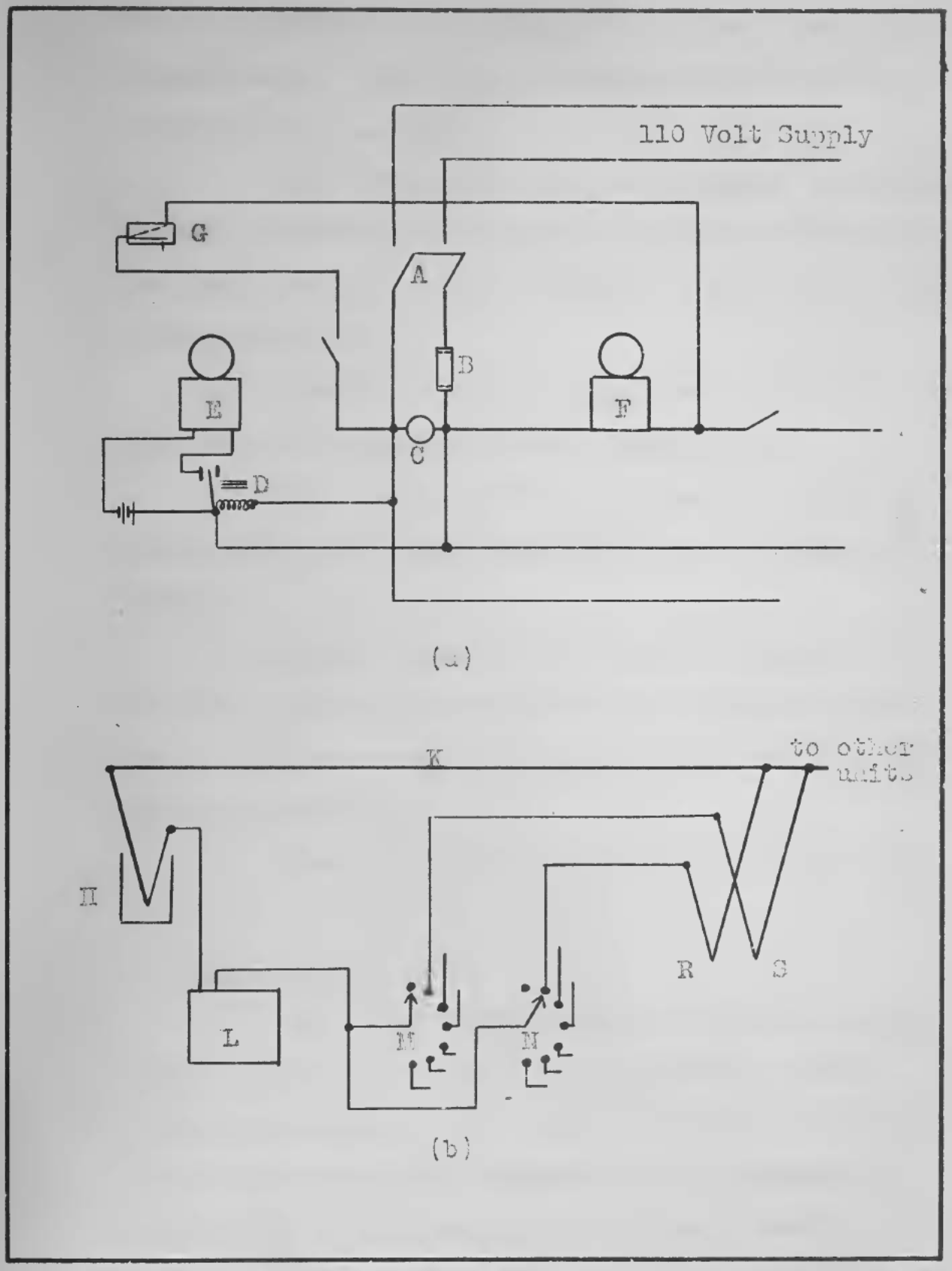


Figure IX - Main panel board (a) Electrical supply and alarm system. (b) Thermocouple system.

One rotary switch connects the thermocouples giving the catalyst bed temperatures; the other, the jacket temperatures. Each set of thermocouples (R and S) is connected as shown.

Each individual unit is designed to maintain certain predetermined operating conditions continuously for long periods of time. There are three main operational controls:

1) Automatic control of synthesis gas flow. This flow must be steady and easily measurable.

2) Temperature control - the maximum range of deviation in catalyst temperature is 15 centigrade degrees.

3) Pressure control - a constant pressure of 100 psi. must be maintained in the reaction system and at the same time the residue gases must be bled off continuously.

These controls will be discussed in turn.

1. Flow Control

The chief difficulties of automatic flow control arose as a result of the extremely small flows encountered. A gas space velocity of 150/hour (normally used in the Fischer-Tropsch synthesis) corresponds to an absolute flow of only about 0.4 cc./sec. for the volume (70 cc.'s) of catalyst space

used, when measured at the operating pressure of 100 psi. gauge. The literature reveals no previous attempts to use automatic flow control on such low rates.

For automatic control, there must be a primary measuring instrument which will respond quickly to changes in the rate of flow. This response must then operate a control instrument to correct the flow. In this case, the measuring instrument is a capillary type pressure flowmeter. A diagrammatic drawing of the latter, together with a description of its design and calibration will be shown in the Appendix. It is sufficient at this point to state that the rate of gas flow is indicated by a pressure drop across the capillary, this being measured by a mercury manometer.

The instrumentation and wiring is shown in Figure X (a). The two mercury arms of the Merriam 3-contact manometer A are connected to an electrical circuit operating a small electric motor B. The latter is a 1/50 H.P. reduction gear motor, induction type, delivering 29 r.p.m. on the output shaft. The driving mechanism of the valve stem is linked to the motor shaft by a 24 to 1 worm and worm wheel, the valve drive rotating at 1.2 r.p.m.

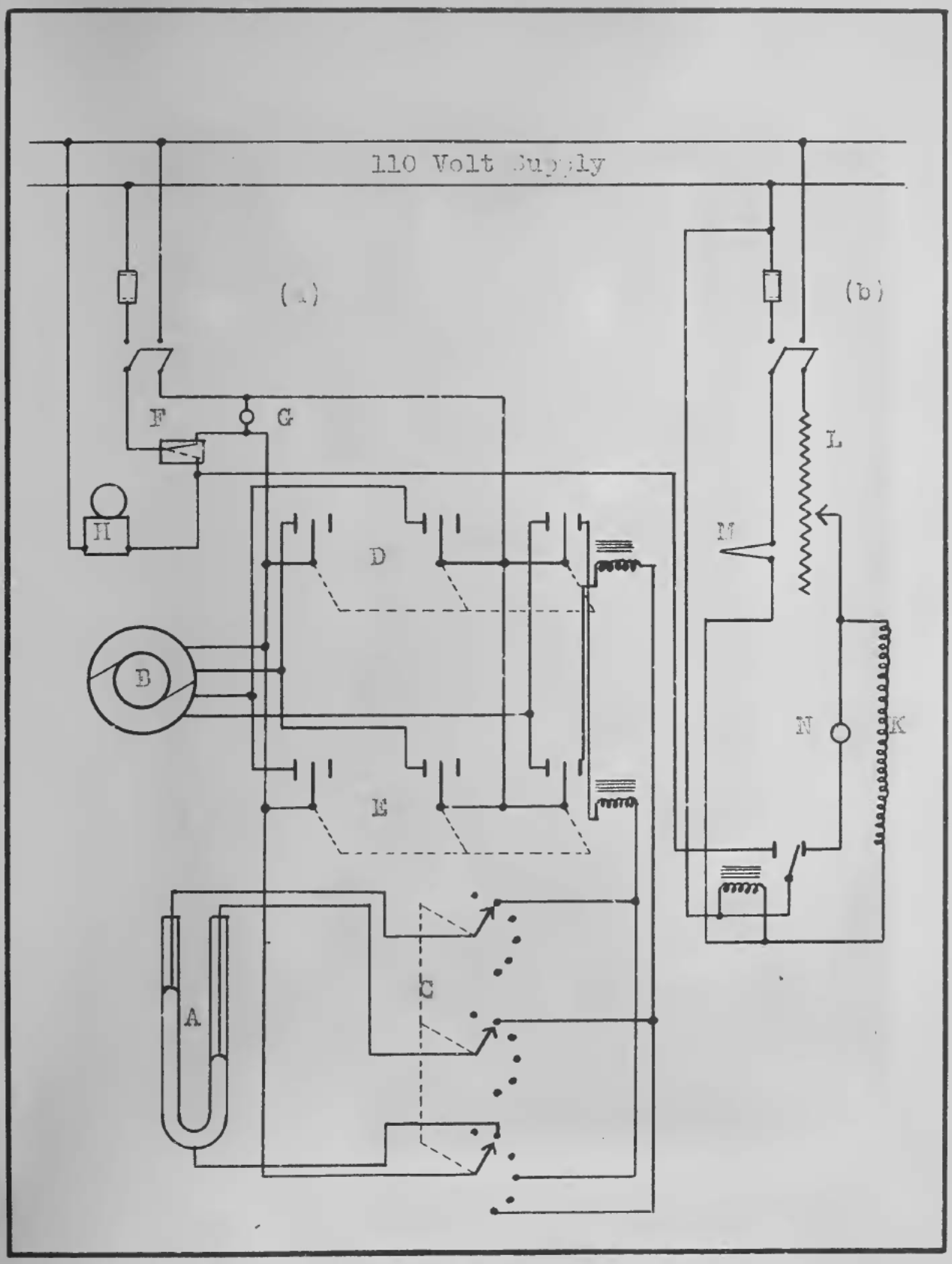


Figure X - (a) Electrical circuit for flow control.
(b) Electrical heating circuit.

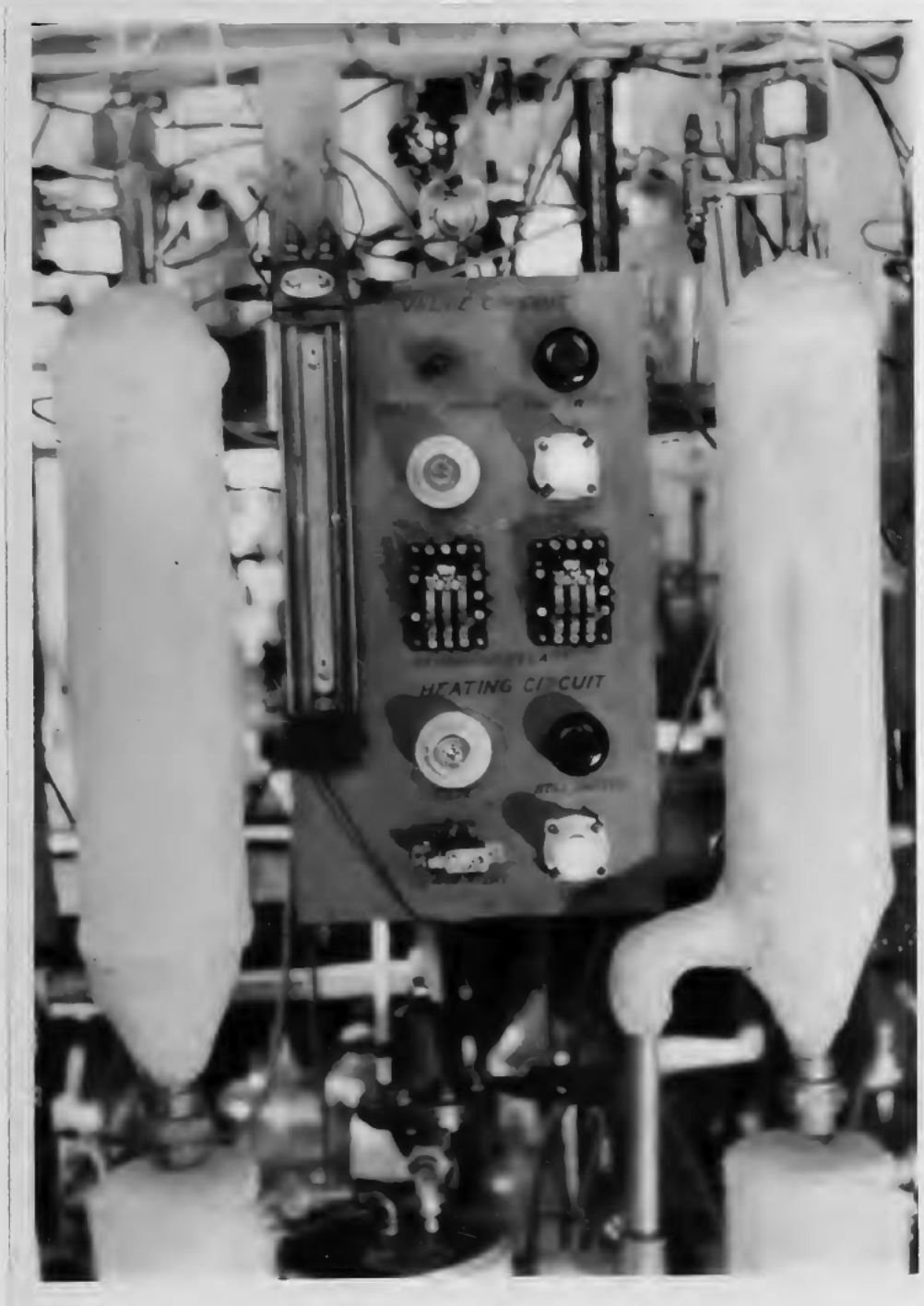
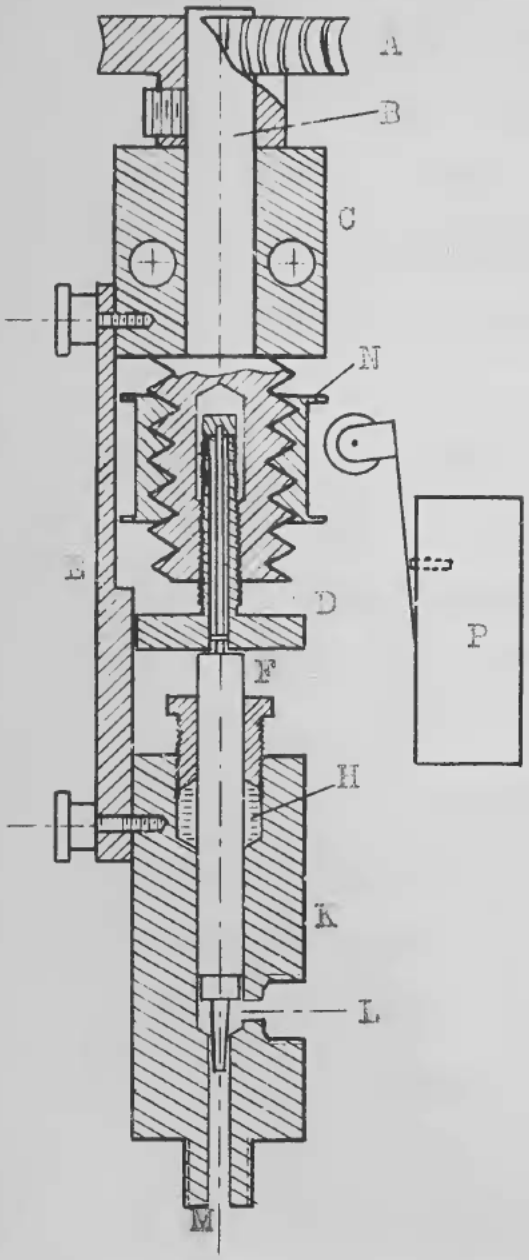


Figure XI - Front View of Single Converter

The motor, the control valve, and the flowmeter are all mounted on an angle iron, which is in the form of an inverted L. Their spatial relationships are indicated in a photograph - Figure XII.

The valve and mechanism are illustrated in Figure XIII. The brass valve drive shaft B is mounted in a steel bearing block C. Female threads (24 to the inch) at its lower end connects the drive shaft to a brass thrust shaft D. The latter, with one of its hexagonal sides bearing against the brass bar E, is prevented from rotating. For every revolution of the drive shaft, there is imparted to D a vertical movement of approximately 1/24 of an inch. This is in turn transmitted to the steel valve stem F. The needle of the latter has a very small taper of only 0.034 (inches /inch), thus permitting fine control. There is, however, a definite lag (fixed by means of the threaded nut on top of the valve stem) between the action of the motor and the response of the valve stem. This lag improves the control characteristics of the valve by matching the lag in the flowmeter-manometer system. A gland G and the packing H keep the valve pressure-tight. The valve body K is machined from a $1\frac{1}{4}$ inch hexagonal brass bar. The synthesis gas enters at L and leaves at M, making the valve self-cleaning.

Figure XII - Control Valve and Flowmeter Block



Scale: 1" - 1½"

Figure XIII - Flow Control Valve.

There is provision made to prevent the valve from binding in either the extreme open or closed positions. The drive shaft B operates a brass cam N. This cam is machined from a $1\frac{1}{2}$ inch hexagonal brass bar and has internal threads, four to the inch, fitting similar threads on the drive shaft B. Rotary motion is prevented by the brass bar E. As the drive shaft turns, the cam moves up or down. At either extreme of its travel, the cam actuates the microswitch P, breaking the motor circuit and ringing the warning bell.

The motor operating circuits are fed through an operating switch C (Fig.Xa) - a 3 gang, 6 pole, rotary type. Only three poles are used, each alternate pole being open. In two of these three switch positions, the motor is operated manually to either open or close the valve. In the third position, the relays D and E and the manometer A are brought into the circuit and the motor is operated by automatic control. These reversing relays are connected such that the circuit through one actuates the field of the other. Thus when one is open, the other is necessarily closed and short circuits are prevented. A fuse further protects the motor and circuit.

Considerable difficulties have arisen with the control value, due largely to the smallness of the

flows involved. The slight coasting of the motor, the lag in response of the mercury manometer, the inertia of the mercury are all important factors when dealing with such low rates of flow and were overcome in part by test and experience.

Upon actual trial runs, it was found that the maximum allowable pressure drop across the control valve were only about one pound per square inch. If this value were exceeded, the mercury in the manometer started to hunt i.e. it continued to oscillate over a range of several inches. With a high pressure drop across the valve, the valve stem operated in a nearly closed position, resulting in a proportionately large percentage of throttling per increment of vertical motion. If the pressure drop was less than one pound per square inch, however, the control was excellent. The valve stem quickly found, and remained at, the equilibrium position corresponding to the existing flow and pressure.

It became clear that satisfactory automatic flow control required that the pressure variation in the supply reservoir be not more than a pound per square inch. This was accomplished by means of pressure actuated, position relays located in the relay circuit of a magnetically operated compressor starting switch. The movement of the Bourdon tube (in an adapted mercoid

pressure control gauge attached to the reservoir) is magnified and translated into a lateral motion of a metal contact strip. The latter moves between two electrical contacts which, in turn, are connected through two relays to the magnetic switch relay. As the pressure in the reservoir drops, one contact is made starting the compressor. As the pressure is raised, the other contact breaks the circuit, stopping the compressor. The supply pressure was maintained constant within half a pound per square inch. The service required of the compressor motor is a difficult one. A future design would involve improvements in the flow control valve and continuous compressor operation with control by an unloading device.

2. Pressure Control

In normal operation, the pressure in the system must be kept at 100 psi. gauge. This is done using a Cash type 1935 back pressure regulator. This can be adjusted to maintain the desired pressure differential between the system and the discharge - in this case 100 psi. Other pressures can be used but only if the same for all converters. Improvement in the flow control value to the extent necessary to permit wide variations in pressure between converters does not seem possible. Back pressure regulators

between the synthesis gas header and the individual units would be the solution.

3. Temperature Control

Temperature control is obtained by the method devised by Downs. The temperature of the catalyst tube is kept constant by an outer jacket of boiling liquid. Three liquids have been used - dowtherm when operating at 250°C, tetralin at 200°C and for activations, a paraffin fraction having an initial boiling point of 360°C. The electrical heating circuit is shown in Figure X (b). The outer jacket is heated by a resistance coil K, (total resistance of 20 ohms) which is connected in series with a rheostat L. The heat input to the jacket is manually controlled to be slightly above that required to keep the fluid boiling, the vapors being condensed in a water-jacketed condenser. Connected to the latter is a ballast chamber whose purpose is to eliminate surges due to changes in the vapor position. The volume of the ballast is about ten times that of the condenser.

The temperature of the boiling liquid is controlled by varying the pressure in the condenser system. An inert atmosphere of methane is maintained above the liquid. Pressures greater than atmospheric are obtained from a high pressure methane storage;

vacua from a water pump. It is possible to vary the pressure in the system from 26 inches of mercury vacuum to 40 psi. gauge. For dowtherm this corresponds to a temperature range of 180°C to 330°C, and for tetralin 130° - 280°C.

There are two thermocouples in each converter - one in the boiling liquid, the other in the catalyst bed. The latter may be adjusted to give temperature readings throughout the whole length of the catalyst bed.

An alarm mechanism is incorporated into the electrical heating circuit to prevent the liquid from boiling out of the jacket. This may arise from one of two causes: the stoppage of the water flow or the supply of too much heat to the boiling liquid. A reversible thermal switch M in the top of the condenser is set to break contact in the heating circuit at 70°C. If any hot vapors reach the top, the thermoswitch opens breaking the circuit. The light N goes off and the bell rings. Thus in the event of water failure, the action of the thermal switch would prevent any undue temperature rise and, by intermittent action, maintain approximate temperature control.

There is no warning bell if the heating coil burns out but there is an increased brightness in the signal light.

IV CATALYSTS AND THEIR PREPARATION

In these investigations five catalysts in all were tested. Except for two of these, very little is known of their preparation. Two catalysts, a Co-Th and a Ni-Mn, were prepared by the Harshaw Chemical Co. of Cleveland, Ohio, and a third was an ammonia iron base catalyst supplied by the Alberta Nitrogen Products Ltd. of Calgary, Alberta. The other two catalysts, one of pure iron and the other iron-copper, were prepared by an under-graduate student (29) as part of another project, following the procedures laid down by the U.S. Bureau of Mines.

The Bureau of Mines No. 10 Iron catalyst was prepared according to methods developed by the U.S. Bureau of Mines. Two solutions were made up separately at 70°C. Solution I consisted of 1012 grams of C.P. $Fe(NO_3)_2 \cdot 9H_2O$ dissolved in 3 litres of distilled water; solution II was 571 grams of C.P.K_2CO_3 dissolved in a litre of distilled water. With both solutions at 70°C, solution II was added slowly to I over a period

of 20 minutes. The temperature of the mixture was to be maintained at 70°C throughout the preparation. The slurry was made up to 6 litres, the supernatant liquid decanted. The slurry was again made up to 6 litres, the supernatant liquid again decanted. This was to be repeated until the nitrate concentration was less than 1 part in 16,000 as indicated by a diphenylamine test. Nitrate in larger concentrations turns a diphenylamine solution a distinct blue. According to instructions sixteen decantations should have been sufficient but, in practice, even after thirty decantations, the wash water gave a weak nitrate test. At this point washing was considered complete.

The precipitation and washing was carried out over a period of a week, during which time the temperature of the slurry may have varied over a range of 10 - 15 degrees. It is thought that this long period of digestion may have had a detrimental effect upon the catalyst.

The slurry was filtered in a large Buckner filter and washed several times on the filter paper. The cake was placed upon a porous plate and allowed to dry slowly at room temperature for five days, open to the atmosphere. It was then placed in an electric oven. The temperature was raised slowly to 1500C over a period of five hours and held for an additional 24

hours. The dried catalyst was ground to pass through a 50 mesh sieve. A yield of 193 grams was obtained. Nine grams of small flake graphite was added as a lubricant and the catalyst was pelletted into small tablets 7/32 inches in diameter and 3/32 inches thick. The graphite has no catalytic action; it is inert.

The second catalyst, Bureau of Mines No. 24 Fe-Cu, was prepared by the co-precipitation of $Fe(OH)_2$ and $CuCO_3$ from a sulphate solution with K_2CO_3. It was prepared in a manner almost identical with that of the iron catalyst above. Similar solutions were used, the only difference being that solution I with the same iron concentration had $CuSO_4$ added to give an Fe-Cu ratio of 4:1. Precipitation and washing was the same except that the slurry was blown 10 - 15 minutes with air before each decantation. Some of the iron is oxidized to the ferric state. Sixteen decantations were performed. The catalyst was mixed with graphite and pelletted.

Nothing is known of the two Harshaw catalysts, A5 and A124, except that cobalt and nickel are the bases with thoria and manganese respectively as promoters. The pellets were in the form of cylinders, 3/32" diameter and 1/8" long.

The ammonia catalyst is prepared by fusing iron oxide, prepared from "drum scrap" steel sheet,

with suitable promoters, crushing and screening the resultant mass to $\frac{1}{4}$" - 3/8" mesh. The exact procedure is not known. The following analysis of this ammonia catalyst was supplied by the maker:

SiO_2 - 1.4%	MgO - trace to 0.2%
K_2O - 1.7%	CuO - trace to 0.2%
Al_2O_3 - 1.7%	Fe - 67.7%

For present purposes, this catalyst was crushed again and that portion retained between 6 and 10 mesh sieves tested as a Fischer-Tropsch catalyst.

V ANALYTICAL METHODS AND OPERATIONAL TECHNIQUES

The procedure followed in testing the catalysts was based primarily on the U.S. Bureau of Mines technique. These methods were developed empirically and slight deviations are permissible provided that a careful record is kept at all times of the experimental conditions. In general, the methods of handling the iron type and the cobalt type catalysts differed considerably.

After the units had been tested and the leaks reduced to a negligible quantity, the catalyst chambers were filled with catalyst pellets, forming a column approximately 16 inches long and 0.6 inches in diameter. In some cases porcelain chips were used to support from below and cover the top of the catalyst bed, primarily to insure uniformity of temperature over the length of the catalyst column.

Reduction and Conditioning of the Catalyst

The system was first flushed with hydrogen and the rate of flow adjusted to give a space velocity of 20 - 25/hour. (Space velocities are based on the volume of the empty catalyst chamber, not on the actual volume of the catalyst). In the first experiments, a slow stream of methane passing through the outer jacket constituted the heating medium. The heat supply was controlled manually with a rheostat. The temperature of the catalyst bed was raised quickly to 100°C and then slowly over a period of 20 hours to 360° - 380°C. During this time, the jacket temperature was kept 20 - 30 centigrade degrees above the catalyst temperature, insuring the proper rate of heating. Reduction was completed by holding the catalyst temperature at 360° - 380°C for 4 hours.

There were two difficulties encountered in the use of a methane heating medium. First, it was difficult to raise the catalyst temperature at a uniform rate and secondly, there was a considerable temperature differential over the length of the catalyst column, the top and bottom portions being 30 - 40 centigrade degrees cooler than the middle. For these reasons, in the later experiments, a high boiling point liquid was used in the outer jacket as the heating medium. This liquid was the residue

obtained after distilling off all the lighter fractions (up to 375°C) from a gas oil or petrolatum.

The conditioning procedures for iron and for cobalt catalysts were quite different. In the former case, after reduction, the temperature was reduced to 220°C and synthesis gas at 100 psi. and space velocity of 150/hr. was admitted, replacing the hydrogen. The temperature was adjusted to give a contraction of 13% * (20% in the case of a water gas having a $CO:H_2$ ratio of 1:1). When it became steady at this value, the temperature was raised slowly over a period of 48 hours to 250°C or to a temperature such that the contraction was approximately 40%. The catalyst was now completely conditioned and ready for operation. After a cobalt catalyst had been reduced, it was allowed to cool to 160°C and synthesis gas admitted at one atmosphere and space velocity of 100/hour. The temperature was adjusted to give 20% contraction and held for 4 hours. The temperature was raised until 30% contraction and again maintained for 4 hours. This was repeated until a 60% contraction was reached. The most active cobalt catalysts operate at

* % contraction =

$$\frac{\text{Vol.of Feed Gas - Vol.of } CO_2 \text{ - free Residue Gas}}{\text{Vol. of Feed Gas}} \times 100\%$$

approximately 190°C. The synthesis gas pressure was raised to 100 psi. and production started with an initial contraction of about 70%.

Method of Operation

When the automatic controls were functioning properly, the operation of the process (as distinguished from the analytical work involved) required comparatively little attention. All the units were started on production Sunday midnight and operated continuously until Saturday morning. During week-ends, the temperature of the catalyst was lowered 15 centigrade degrees and a slight but positive flow of hydrogen maintained over the catalyst. A normal weekly run was approximately 125 hours. At the end of the week, the liquid and solid hydrocarbon products were removed from the pots, weighed, and stored for analysis.

Iron catalysts were operated with a gas space velocity of 150/hour for the first four weeks and 100/hour thereafter. Cobalt catalysts utilized a space velocity of 100/hour throughout their whole life.

Good iron catalysts maintain their activity for periods of months, while cobalt catalysts become slowly deactivated (noted by a decrease in the per-

centage contraction). Low temperature reactivations of the latter were carried out periodically, usually once a week. The pressure was allowed to fall to atmospheric and the synthesis gas replaced by hydrogen. The temperature was raised 15 degrees above operating temperature and hydrogen passed over the catalyst at a space velocity of 200 - 300/hour for two hours. The unit was put on production again by cooling to operating temperature and replacing the hydrogen by synthesis gas at 100 psi.

Iron catalysts are never reactivated.

Aside from the analyses, the work of the operator normally consisted of the following: (a) the preparation of the synthesis gas, (b) a periodic checkup of the recovery system, especially with regards to the operation of the scrubber and the residue gas proportional sampler, (c) check on the proper functioning of the automatic controls, and (d) periodic readings of the experimental conditions. In the project's initial stages, however, considerable difficulties were encountered in setting up the various operational controls (particularly in the regulation of the gas flow) and this, together with the maintenance of the equipment, required a large part of the operator's time.

Flowmeter readings were recorded every hour (and the contraction calculated) while temperature and pressure readings were taken every three or four hours. By means of these and other operating data, it was possible to follow the progress of the catalyst testing and to note any changes in the experimental conditions. A sample operating sheet is shown on the next page.

Analyses and Material Balances

Examination of the flowsheet indicates one feed and three product streams. The synthesis and residue gases flowed continuously while the light and heavy liquid products were removed from the ice-jacketed and steam-jacketed pots once a week. Overall material balances, therefore, had to be based upon at least a week's operation.

The synthesis gas was analyzed once every two or three days in a standard Burell Gas Analysis Apparatus. The percentages of CO_2 (by KOH), H_2 and CO (by oxidation over CuO) were determined directly, N_2 by difference. A careful check was kept on the H_2:CO ratio which ideally is 2:1 but in actual practice ran slightly higher, around 2.03.

The residue gas contained water vapor, CO_2, hydrocarbons (CH_4, C_2H_6, C_3H_8), N_2, and unconverted

Exp't No. - 2
Catalyst - Pure Fe (B. of M. # 10)
Weight - 92.8 gms.

OPERATING SHEET
F - T

Date: July 7/45

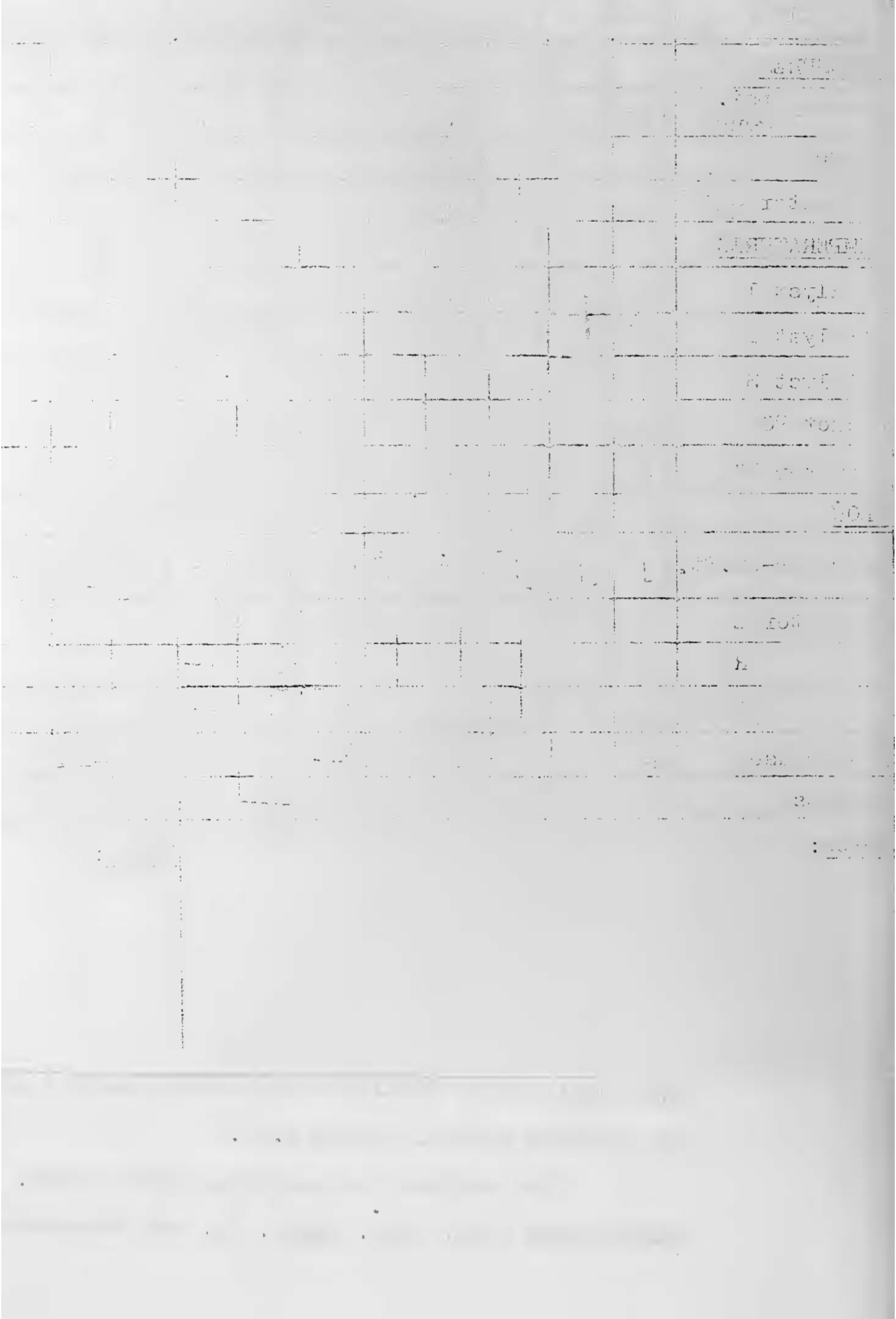
Reactor No. - 5
Nominal Pressure - 100 psi.
Nominal Temperature - 265°C
Nominal Flow Rate - 9.40 L/HR.

Time	8 AM	9	10	11	12	1 PM	2	3	4	5	6	7	8	9	10	11	12	1 AM	2	3	4	5	6	7
PRESSURES																								
Reactor psi. gauge	100+			100.5				101				101			101			100.5				100.5		
Jacket psi. gauge	33.3			33.5				33.8				34.0			34.0			34.0				33.8		
Barometer mm. Hg	701			701				702				702			702			702				702		
TEMPERATURES																								
Catalyst 1	267			267				268				268			268			268				267		
Catalyst 2	265			265				266				266			266			265				265		
Catalyst 3	257			257				257				258			257			256				257		
Jacket °C	265			265				266				266			266			266				265		
Gasmeter °C	68			69				72				75			75			72				70		
FLOW																								
Gasmeter-cu.ft.	1.6550	1.9710	2.0865	2.3005	2.5190	2.7395	2.9590	3.1780	3.3920	3.6145	3.8340	4.0530	4.2705	4.4870	4.7010	4.9155	5.1335	5.3610	5.5800	5.8006	6.0180	6.2350	6.4586	6.6775
Flowmeter L	1.97			1.98				2.00				1.99			1.98			2.01				1.96		
" R	1.95			1.96				1.97				1.97			1.96			2.00				1.95		
" Total	3.92			3.94				3.97				3.96			3.94			4.01				3.91		
% Decrease	36.8			37.0		36.4		36.6		35.8		36.0			36.6			36.1		36.3		36.6		
Samples							5CA93						5R31						5CB44					

Notes:

Notes:

Notes:



H_2 and CO. The water was removed by a $CaCl_2$ U-tube drier, and determined by weighing. It was necessary to weigh these driers only once a week since the water content of the residue gases was comparatively low. The CO_2 was removed by a caustic scrubber, and determined by titration. The scrubber liquid consisted of 250 cc's of a 3N solution of KOH. Only half of the total strength of the KOH could be effectively utilized since, beyond that point, some CO_2 passed unabsorbed through the scrubber. An aliquot part (10 cc's) of spent solution was titrated against 1N HCl to both the phenolphthalein and methyl orange end points. The difference represented the molar equivalent of CO_2.

A proportional sampler collected a daily 2-litre sample of carbon dioxide-free residue gas. This sample was analyzed in a Burell Apparatus for CO_2, H_2 and CO (over CuO), hydrocarbons (burning with oxygen over a hot platinum wire) and N_2 (by difference). The hydrocarbon content was expressed in terms of methane and ethane although it was realized that some higher hydrocarbons may have been present.

The liquid products collected each week were allowed to accumulate until in sufficient quantities to be analyzed. In both of these fractions, considerable water was present which was removed in a

separatory funnel. The liquids were filtered to remove solid impurities.

The water in each case was tested for the following:

a) acidity - by titration with a weak solution of NaOH.

b) a distillation to detect the presence of alcohols and other low boiling fractions.

c) density - accurately by density bottles.

The oil fractions collected were tested for:

a) density

b) aniline point - to determine the degree of unsaturation.

c) refractive index.

d) an A.S.T.M. distillation, modified because of the small quantities involved.

The wax fraction was tested only for density.

VI EXPERIMENTAL RESULTS

Since the present investigation involves the testing of specific catalysts, each must be reported separately with respect to treatment and results. Five catalysts were tested:

1) Pure iron
2) Iron-copper
3) Promoted iron (ammonia)
4) Cobalt-thoria
5) Nickel-manganese

The reduction, conditioning, behavior, and yields will be discussed for each catalyst.

The feed or synthesis gas, common to all units, was found to have the average composition:

CO_2	0.3% by volume
H_2	64.4%
CO	31.5%
N_2	3.8%
H_2/CO	2.04:1

This gas was used in the testing of all catalysts and the daily variation was on the average not more than about 2%.

During the course of the experimental runs, it was suspected that the feed gas may have contained some catalyst poisons, either oxygen or sulphur. Sensitive tests failed to detect the presence of either. In testing for oxygen, the feed gas was passed over white phosphorus, freshly distilled and deposited from the red allotrope. No luminescence was visible indicating the absence of oxygen in quantities greater than one part in a million (20). In testing for sulphur, it was assumed that, if present, sulphur would occur as hydrogen sulphide. A measured quantity of gas (several cubic feet) was passed through a caustic scrubber, the solution acidified and titrated with an 0.005 N-I_2 solution using starch as an indicator. Close agreement of the titration of the sample and a blank indicated a negligible amount, at the most, of sulphur in the gas.

1. Iron Catalyst (Bureau of Mines #10)

Source of catalyst - prepared at the University of Alberta.

Weight of catalyst - 71.5 gms.

Volume of chamber occupied by catalyst - 62.2 cc.

Reduction: The catalyst temperature was brought up slowly over a period of 20 hours to 360 - 380°C in an atmosphere of hydrogen. This temperature range was maintained for 4 hours. Heating was by transfer across a slow stream of methane passing through the outer jacket. Although the middle three quarters of the catalyst column was at 380°C the top and bottom portions were as much as 50 degrees lower.

Conditioning: On reducing the catalyst temperature to 225°C and admitting synthesis gas at 100 psi. gauge, no apparent contraction occurred. The temperature was raised in 5 degree increments over a period of 48 hours to 250°C. The conditioning then proceeded as follows:

Temp. °C	Percentage Contraction	Total hrs. operation
250	13%	78
254	18%	86
260	20%	92
268	Initially 30% increasing to 38%	

Operation: In order to maintain the necessary contraction, operation was carried on at 268°C, even though this temperature is higher than that recommended by the Bureau of Mines. Table III shows the operating

conditions and contractions for each successive week of testing.

Table III

Weekly Operation with the pure Iron Catalyst

Week No.	Temp. °C	Space Velocity hrs.$^{-1}$	Contraction %	Flow Control
1		Activation		
2	269	150	39	Good
3	269	150	38	Good
4	265	150	35	Good
5	265	150	35-40	Unsteady
6	253	150	25	Good
7	265	150	35	Good
8	266	100	55	Good
9	266	100	52	Fair

Reactivation and Operation: Although the catalyst was giving the proper contractions, it was evident that this was due mainly to the methane formation and the water gas shift reaction. At the end of nine weeks, the catalyst was given a high temperature reactivation. Hydrogen at one atmosphere and space velocity of 20 - 25/hour was passed through the

catalyst bed. The temperature of the latter was raised quickly to 360°C and held for 4 hours.

After reactivation, synthesis gas at 100 psi. was admitted and the unit operated at 250°C for two more weeks. Although contractions were high, there was no increase in liquid hydrocarbon yields and it was decided that no useful purpose would be served in further continuing the test.

Yields The yields of the various products are shown in Table IV.

Table IV

Weekly Yield of Products from the pure Iron Catalyst
gms./cubic metre of gas at N.T.P.

Week No.	Liquid Fraction Heavy	Liquid Fraction Light	Off - gas CH_4	Off - gas C_2H_6	Off - gas CO_2	Off - gas H_2O
1	Activation					
2	0.2	7.7	41	62	*	3.9
3	0.8	9.8	40	43		28.6
4	1.4	9.4	29	48		6.8
5	1.7	9.1	26	48		18.8
6	5.1	5.4	21	11	108	14.8
7	1.4	8.0	31	44	180	22.2
8		4.9	38	32	153	26.9
9		1.2	35	34	145	14.7
	Reactivation					
10	0.1	6.5	55	22	222	38.0
11	3.6	5.9	46	24	154	25.4

* Figures are unavailable for the first few weeks since much CO_2 was passing through the scrubber unabsorbed.

Analyses: Four distinct products from the synthesis were analyzed namely, the residue gas, the light liquid fraction, the heavy liquid fraction, and the water.

a) The residue gas had the following average composition (CO_2 unadsorbed):

Component	Volume Per cent
CO_2	19.1
H_2	55.3
CO	5.4
CH_4	8.8
C_2H_6	5.6
N_2	4.8

There were no significant trends in the gas composition during the course of the catalyst testing except that, after the high temperature reactivation, the gaseous hydrocarbons and carbon dioxide content increased slightly.

b) The light liquid fraction analyzed as follows:

1) Density at 25°C - 0.7164 gms/cc.
2) Aniline point - 66.9°C.
3) Refractive index - 1.4112
4) Distillation - see Figure XIV
5) Odour indicates possible oxygenated compounds.
6) Average molecular weight - 130.

c) The heavy liquid fraction showed the following properties:

1) Density at 25°C - 0.7734.

2) No solid products precipitated in this fraction at room temperature.

d) The water had the following characteristics:

1) Density at 25°C - 0.9968 indicating practically pure water.

2) Traces of acids: Acid normality - 0.004.

3) Traces of a low boiling point liquid on distillation.

Discussion of Results

1) Even at the beginning of the testing, there were positive indications of the poor behaviour of this iron catalyst. These may be listed as follows:

a) Formation of appreciable quantities of water - not usually expected from active iron catalysts.

b) Low yields of liquid hydrocarbons - about a sixth of the yields obtained by the U.S. Bureau of Mines.

c) Comparatively high yields of gaseous hydrocarbons indicating the methane reaction.

d) High CO_2 production, indicating the water gas shift reaction.

e) In order to obtain the contraction normally expected from this catalyst, operating

temperatures 15° - 20° higher than those reported as optimum in the literature were required.

There is a possibility that the inactivity of the catalyst may have been due to poisoning either by sulphur or oxygen. However, delicate tests have failed to reveal the presence of either in the synthesis gas. In the case of sulphur poisoning, unless there is a comparatively high concentration of hydrogen sulphide in the feed gas (which is unlikely), the poisoning should take some length of time. In the initial stages, the literature reports that the liquid hydrocarbon yields actually increase. However, this catalyst was inactive from the very beginning. Initial oxygen poisoning is unlikely but a possibility.

Some parts of the catalyst may have been improperly reduced. However, this is insufficient to account wholly for its poor behavior.

The third possibility is that the catalyst was originally inactive due to contamination in its preparation. Further, the long time of digestion (several days) may have affected the physical condition of the catalyst, perhaps in the state of subdivision.

2) Until the eighth week the total liquid yields remain substantially constant, at which time they dropped sharply with a corresponding increase in

methane production. The few original active centres were apparently deactivated either by poisoning, carbiding or carbonyl formation.

3) High temperature reactivation failed to restore the activity of the iron catalyst. This is in agreement with the literature. The subsequent high contractions are due almost entirely to methane formation and the water gas shift reaction.

4) The liquid hydrocarbon products were entirely oil. No wax was precipitated.

5) Correlation of the aniline point and the average molecular weight indicates that the light liquid product contained some unsaturated and possibly some cyclic compounds. The refractive index tends to substantiate this.

2. Iron-Copper Catalyst (Bureau of Mines #24)

Source of catalyst - prepared at the University of Alberta.

Weight of catalyst - 76.3 gms.

Volume of chamber occupied by catalyst - 58 cc.

Reduction: This catalyst was reduced in the same way as the iron catalyst described previously, i.e. at 360 - 380°C for 4 hours in an atmosphere of hydrogen. The same difficulties were encountered.

Conditioning: Synthesis gas at 100 psi. was admitted at (catalyst temperature of 223°C. The progress of the conditioning is recorded below:

Temp. °C	Percentage Contraction	Total hrs. operation
223	0	
230	11	16
237	16	34
245	20	58
250	25	62

Despite the low contraction, it was decided to operate in the region of 250°C, since the literature reveals that at slightly higher temperatures carbiding and carbonyl formation quickly deactivate the catalyst.

Operation: Operation proceeded at a pressure of 100 psi. gauge and a gas space velocity of 150/hr. The results are shown in tabular form below:

Table V

Weekly Operation with the Fe-Cu Catalyst

Week No.	Temp. °C	Contraction %	Flow Control
1	Activation		
2	250	23-25	Fair
3	250	22-25	Fair
4	255	29-31	Fair
5	255	25-35	Unsteady
6	255	30-40	Unsteady

The contraction is apparently temperature sensitive. The unsteadiness of flow during the last two weeks of operation obscured the contraction but indications point to increasing contraction.

Reactivation and Operation: At the end of the sixth week, in an endeavour to improve its activity, the catalyst was given a high temperature reactivation at 360°C for 4 hours. Although the resulting contraction was higher (58 - 60%), there was no improvement in the liquid hydrocarbon yield. It was concluded that the catalyst had been permanently deactivated. Testing was discontinued.

Yields: The yields per cubic meter of synthesis gas of the variour fractions for each successive week are shown in Table VI.

Table VI

Weekly Yields of Products from Fe-Cu Catalyst
gms./cubic metre of gas at N.T.P.

Week No.	Liquid Product		Off-gas			
	Heavy	Light	CH_4	C_2H_6	CO_2	H_2O
1	Activation					
2	6.6	5.8	8.0	11.0	53.7	25.3
3	5.6	5.3	9.3	9.7	62.6	24.7
4	6.2	7.7	26.2	20.1	86.2	23.1
5	5.1	2.9	22.4	32.8	89.5	
6		3.7	32.5	23.1	154.5	3.7
	High Temperature Reactivation					
7		5.5	19.6	40.8	197	28.6
8		8.9	17.4	37.6	149	19.0

Analysis of Products: (a) Table VII shows the change in composition of the residue gas during the catalyst testing.

Table VII

Composition of Off-Gas from Fe-Cu Catalyst
- Volume % -

Week No.	CO_2	CH_4	C_2H_6	CO	H_2	N_2
1	Activation					
2	4.4	1.8	1.3	24.3	63.0	5.2
3	5.4	2.2	1.2	24.8	63.1	3.3
4	8.7	6.3	2.6	18.4	62.1	1.9
5	11.9	7.6	5.8	14.0	57.9	2.8
6	20.3	9.4	3.5	13.3	51.3	2.2
	High Temperature Reactivation					
7	29.7	5.8	6.6	4.8	50.0	3.1
8	22.8	6.1	6.9	4.4	57.6	3.2

(b) The light liquid fraction analysed as follows:

1) Density at 25°C - 0.7537 gms./cc.

2) Aniline point - 63.2°C.

3) Refractive index - 1.4189.

4) Distillation - see Figure XIV.

5) Odour - suggestive of oxygenated organic compounds.

6) Average molecular weight - 130.

(c) The heavy liquid fraction exhibited the following properties:

1) Density at 25°C - 0.7856 gms./cc.

2) White solid at room temperatures.

(d) The water showed the following characteristics:

1) Density at 25°C - 0.9840 gms./cc.
(Pure water - 0.9940 gms./cc.)

2) Traces of acid: Acid normality - 0.004.

3) Traces of a low boiling point liquid on distillation.

Discussion of Results:

1) The overall behavior of the Fe-Cu catalyst was very similar to that of the pure iron with respect to water formation, low yields of liquid hydrocarbons, high yield of gaseous hydrocarbons, high carbon dioxide production, and lower contraction than that normally expected at the operating temperatures. The low activity of this catalyst may be explained in the same manner as above.

2) As testing proceeded, the activity of the catalyst decreased continuously. Table VI shows the progressive decline in liquid and solid product yields and the increase in production of carbon dioxide and gaseous hydrocarbons. It is clear that the reactions favoring the water gas shift and methane formation became predominant after a few weeks' operation.

3) As before high temperature reactivation failed to improve the activity of the catalyst.
4) Approximately half of the condensible hydrocarbon product was solid wax at room temperature.
5) The aniline point and average molecular weight indicated some unsaturation in the light product.

3. Iron base Ammonia Catalyst.

Source of catalyst - Alberta Nitrogen Products Ltd.
Weight of catalyst - 187.6 grams.
Volume of chamber occupied by catalyst - 75 cc.

Reduction: Reduction with hydrogen was the same as that for the other four catalysts. The temperature was raised over a period of twenty hours to 362°C and maintained for four hours. In the final stages, a high boiling point gas oil was used as the heating medium and no difficulties were encountered in maintaining a fairly constant temperature throughout the whole catalyst bed.

Conditioning: Temperatures were lowered to 220°C and conditioning was commenced at 100 psi. gauge pressure. At 249°C a contraction of 3% was obtained which remained unchanged even with temperatures as high as 292°C. The test was then discontinued.

Yields: No liquid products, either water or oil, were obtained. Only a small amount of methane in the residue

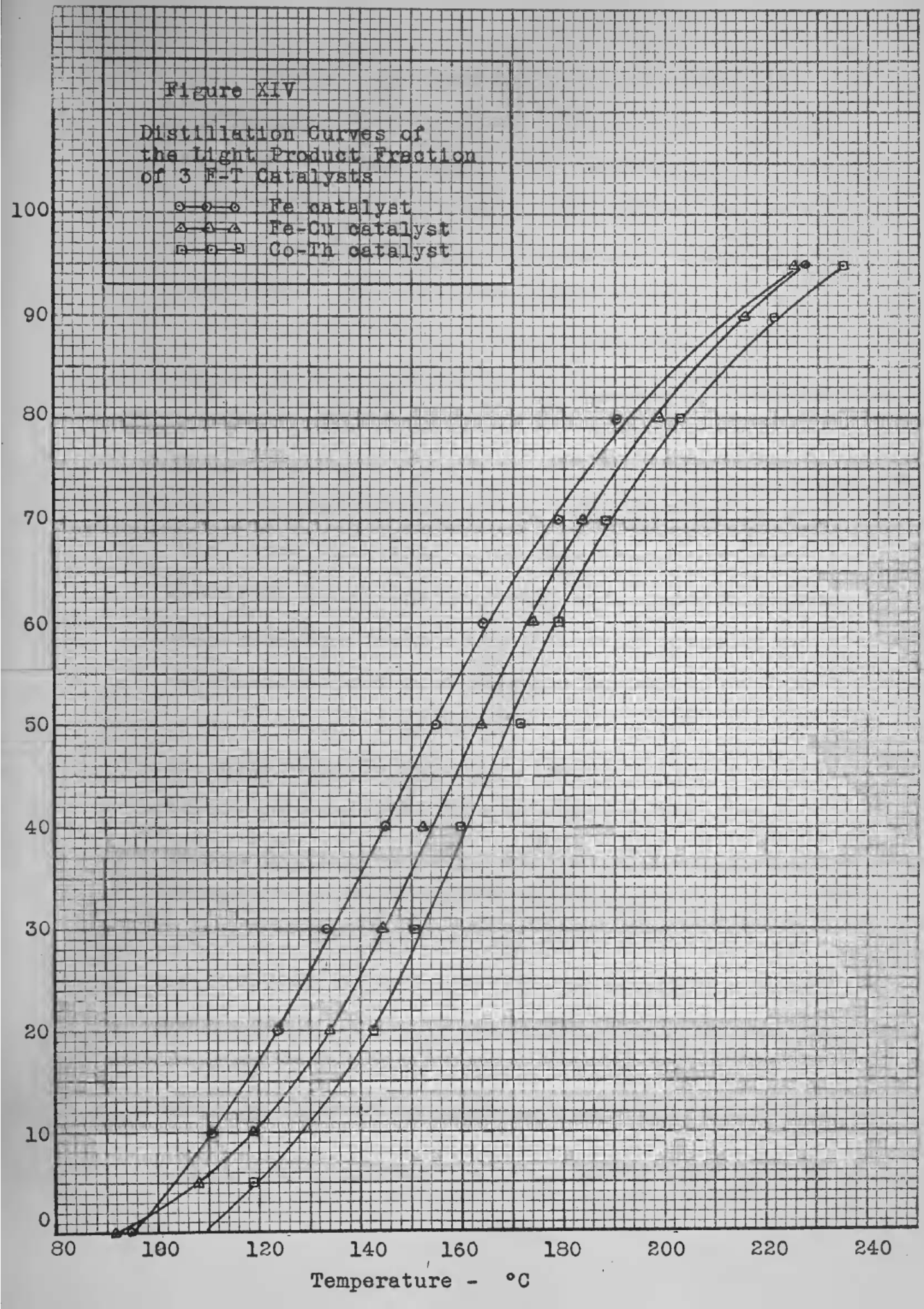


Figure XIV
Distillation Curves of the Light Product Fraction of 3 F-T Catalysts
Fe catalyst
Fe-Cu catalyst
Co-Th catalyst
100
90
80
70
60
50
40
30
20
10
0
80
100
120
140
160
180
200
220
240
Temperature - °C

gas indicated any sign of hydrocarbon synthesis.
Discussion: This catalyst, reduced and conditioned as described above, has proven to be an inert Fischer-Tropsch catalyst. Possibly the temperatures were not high enough to reduce sufficiently the fused iron oxide mass. When this catalyst is used for the synthesis of ammonia, reduction is carried out at temperatures approximating 500°C. With the present equipment, this temperature would be very difficult to obtain.

This catalyst is of the type used in the "iso"-synthesis which involves a relatively inert catalyst, low yields per pass, high space velocities, and recycling. Such a catalyst would probably be difficult to test in a one-pass system.

4. Cobalt-Thoria Catalyst

Source of catalyst - Harshaw Chemical Co., Ltd.
Weight of catalyst - 51.4 grams.
Volume of chamber occupied by catalyst - 58 cc.
Reduction: The catalyst was reduced with hydrogen as described above by raising the temperature slowly over a period of 20 hours to 360 - 380°C and held for 4 hours. A stream of methane through the jacket acted as the heat transfer medium.

Conditioning: Synthesis gas was admitted at atmospheric pressure and space velocity of 100/hr. to the catalyst maintained at 161°C. No perceptible contraction was obtained. The catalyst temperature was raised slowly over a period of 175 hours to 190°C and the first contraction of 5% was obtained. Over a period of six days, the temperature was raised to 199, 206, 210 and 215°C with corresponding increases in contraction of 8 - 9, 10, 16 and 17% respectively. No further increases in temperature were made in view of reports that temperatures above 215°C favor carbon formation and catalyst deactivation. The desired 60% contraction was not obtained at atmospheric pressure.

Operation: Operation was begun at 216°C, a space velocity of 100/hr. and a pressure of 100 psi. gauge. A high initial contraction of over 60% was attained which decreased quite sharply over a period of 40 hours to approximately 32% (Figure XVa). Subsequent operation at temperatures of 209°C and 200°C show the same effect of deactivation, the contraction being lower throughout the operation for lower temperatures.

Low Temperature Reactivation: At the completion of each run, usually at the end of each week, the catalyst was reactivated by passing hydrogen through

the bed at temperatures fifteen degrees above operating temperatures. The catalyst activity was revived.

High Temperature Reactivation: At the end of the eighth week, the catalyst was given a high temperature treatment i.e. hydrogen was passed through it at 350 - 370°C for four hours. This treatment increased the contraction even above that obtained initially. This effect may be observed in Figure XV b.

Yields:

Table VIII

Yields of Products from Co-Th Catalyst - gms.

Wk. No.	Oper. Temp. °C	Vol. of Feed Gas Cu.M *	Liquid Product		Off-Gas			
			Heavy	Light	CH_4	C_2H_6	CO_2	H_2O
1	Activation						2.3	11.3
2	Activation						5.2	19.0
3	215	0.89	20.2	7.2	19	13	4.9	78.8
4	210	0.85	21.5	7.2	14	5	4.7	25
5	200	0.85	6.6	2.3	13	3	0.5	30
6	213	0.67	11.0	3.3	21	14		27
7	213	0.47	13.2	2.8	25	5	8.9	46
8	213	0.92	14.5	4.0	41	23	14.6	42
	High Temperature Reactivation.							
9	200	0.62	17	3.6	15	11	9.1	71
10	200	0.75	17	2.0	23	6	12.1	63

* Measured at N.T.P.

Yields shown above are those actually obtained during each week's operation. Yields computed upon a unit volume of gas serve no useful purpose because of rapidly changing yields other than to show that greater yields per unit volume are obtained during the initial stages of each run when conversion is high.

Analysis of Products

(a) There were no significant trends in the composition of the residue gas during the course of the test. A typical analysis is shown below (Sample #6R23):

Component	Volume %
CO_2	0.5
H_2	57.9
CO	29.4
CH_4	6.5
C_2H_6	1.9
N_2	3.8

The results of the analysis of the light and heavy products and the water revealed:

(b) Light Fraction:

1) Density @ 25°C - 0.7207 gms./cc.
2) Refractive index - 1.4093
3) Aniline point - 74.0°C
4) Distillation - see Figure XIV
5) Odour - suggestive of oxygenated organic compounds
6) Average molecular weight - 85.

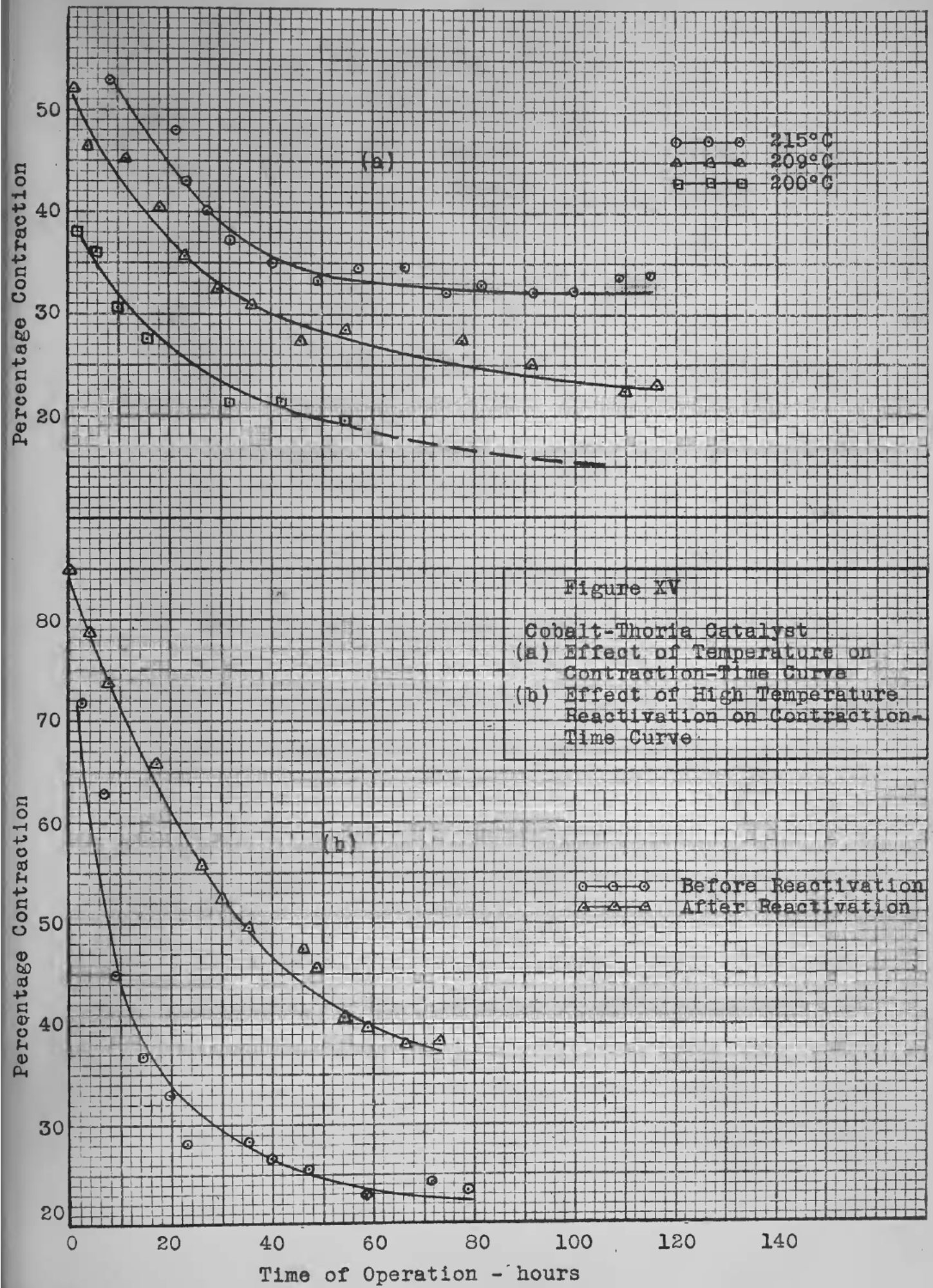


Figure XV

Cobalt-Thoria Catalyst
(a) Effect of Temperature on Contraction-Time Curve
(b) Effect of High Temperature Reactivation on Contraction-Time Curve

(c) Heavy Fraction:

1) Density @ 25°C - 0.7668 gms./cc.

2) This fraction was a thick suspension of wax in oil.

(d) Water:

1) Density - same as pure water.

2) Acidity - 0.004 N.

3) Distillation - very similar to that of pure water.

Discussion: The behavior of this Co-Th catalyst different in several respects from that of proven cobalt catalysts.

1) In the conditioning at atmospheric pressure, the desired contraction could not be obtained even with a temperature as high as 214°C.

2) Operation indicated a very short life catalyst. The initially high contraction dropped very rapidly - 20% in 20 hours. A drop of 10% in four days is normally expected from a good catalyst.

3) The yields of liquid hydrocarbons are about a quarter to a fifth of that reported in the literature. These low values may be explained partly by operation for considerable lengths of time at low contractions. Normally the catalyst is reactivated when the contraction drops from 70 to 60 per cent. During these tests contractions as low as 20 - 30 per cent were allowed.

Low liquid yields account for the high gaseous - liquid hydrocarbon ratio in the products.

4) A high gaseous - liquid hydrocarbon ratio was obtained. This may be due to the method of conditioning. The desired 60% contraction would not be obtained at atmospheric pressure even with a temperature as high as 214°C. Pressure operation at 216°C gave an immediate 60% contraction. This sudden increase in the rate of reaction, as exhibited by the increase from 17 - 60% contraction, may have favored, to some extent, the production of gaseous in preference to liquid hydrocarbons. This is the "methane reaction" reported by Herington and Woodward (21).

Low temperature reactivation restored the catalyst to approximately its original activity. High temperature treatment did not increase the activity much above that obtained by low temperature reactivation. The relative contractions were much higher but the liquid yield increase only slightly. The yield of liquid hydrocarbons dropped sharply during the fourth and fifth weeks suggesting that the catalyst had been poisoned possibly by oxidation. Reactivations restored the catalyst's activity as the yields in the succeeding weeks showed a gradual increase in both liquid and gaseous hydrocarbons.

A definite increase in carbon dioxide production indicated a change in the catalyst favoring the water gas shift reaction. The high temperature reactivation did not improve the catalyst in this respect.

This catalyst produced an oil with a much lower average molecular weight than that from the two iron catalysts but at the same time produced a considerable quantity of solid waxes. The aniline point and refractive index indicate that the oil is highly paraffinic in character. The distillation curve, the average molecular weight and the denisty show that the oil from the cobalt catalyst was more highly saturated than that from the two iron catalysts. This agrees with reports in the literature.

The short life of the catalyst may be due to the presence of only a few highly active centres upon the catalytic surface. The condition may be due to improper reduction or improper activation. During operation a few centres may become deactivated by waxing, this effect being accentuated because of the small number. On the other hand, the short life may be an intrinsic property of this particular catalyst.

5. The Nickel-Manganese Catalyst

Source of catalyst - Harshaw Chemical Co.

Weight of catalyst - 67.6 grams

Volume of chamber occupied by catalyst - 70cc.

Reduction: The catalyst was reduced with hydrogen at a temperature of 358°C. A gas oil heating medium was used.

Conditioning: The catalyst temperature was lowered to 160°C and synthesis gas was admitted at a space velocity of 100/hr. and at atmospheric pressure. A very small contraction was detected. Temperatures were raised slowly and corresponding increases in the contraction were obtained.

Temperature °C	% Contraction	Total hrs. Operation
172	5	5
183	8	24
198	15	35
205	23	38
211	31	42
218	41	48
230	57	54

Operation: Pressure was raised to 100 psi. and operation commenced at 230°C with a 73% contraction. This dropped to 59% over a period of 10 hours. A low

temperature reactivation was then carried out at 240°C. Hydrogen was passed through the catalyst during the shutdown over the week end. Operation was recommenced under the same pressure conditions but only 47% contraction was obtained. This decreased to zero over a period of 16 hours.

The catalyst was given another low temperature reactivation and operated at atmospheric pressure at 231°C. A contraction of 11% was obtained and it decreased in time. Increasing temperatures to 239, 254 and 262°C increased the contraction to 13, 20 and 22% respectively. These contractions however, decreased with continued operation. This concluded tests upon the Ni-Mn catalyst.

Yields: No yield of liquid hydrocarbons, except one and a half cubic centimetres of light oil, produced during conditioning, was obtained. The residue gas analysis revealed high ethane and methane formation. Water and some carbon dioxide was produced.

Discussion: This catalyst was activated according to the method prescribed by the U.S. Bureau of Mines for cobalt catalysts. Although the desired initial contractions were obtained, the decrease in contraction with time and the extremely low yield of liquid hydrocarbons indicated that, operating under these conditions, this Ni-Mn catalyst was ineffective in promoting the Fischer-Tropsch synthesis.

Low temperature reactivations failed to restore the activity of the catalyst for either pressure or atmospheric operation. The loss of activity may be due to one or more reasons:

1) Poisoning by oxygen or sulphur. Delicate tests fail to indicate either in quantities large enough to be detrimental.

2) Too high a temperature employed. To obtain the desired contraction, the temperature had to be raised to 230°C. This is considerably higher than the optimum reported by Fischer (15) (190° - 210°C). The high yield of gaseous products, methane and ethane, with little or no liquid products also supports this view.

3) Loss of active centres by carbonyl formation. Komarewsky and Riesz (23) report that nickel catalysts soon lose their activity at medium pressures due to the loss of active centres in the formation of nickel carbonyl. Nickel carbonyl is very volatile and thus removes the active centres irreversibly.

VII SUMMARY AND CONCLUSIONS

Five catalysts have been tested for their ability to promote the Fischer-Tropsch synthesis. Their performance and characteristics have been studied and discussed. Under the conditions of the tests, none of them has proven to be an effective Fischer-Tropsch catalyst. Poisoning is a possible explanation of their poor behavior. However, sensitive tests have failed to detect the presence of either oxygen or sulphur in the synthesis gas. The catalysts exhibit some signs of poisoning but the evidence is confusing and inconclusive.

In the preparation of the Bureau of Mines' catalysts, the digestion and washing stages extended over several days with possible temperature fluctuations. This deviation in procedure may have affected the activity of the catalysts.

The percentage contraction of the synthesis gas in passing over a catalyst is not a positive criterion of catalyst preformance. In practically all

cases, although the normal contraction was reached, the liquid hydrocarbon yields were much lower than expected. With comparatively inactive catalysts, the methane reaction and the water gas shift reaction appeared to predominate, giving high yields of gaseous products.

Some difference has been found in the products from the two types of catalysts. The cobalt catalyst yielded a more paraffinic product than the iron. The former yielded a high percentage of wax as might have been expected. The pure iron catalyst yielded only oil, while the iron-copper gave some waxes.

The testing of Fischer-Tropsch catalysts in a dynamic system requires special operational techniques. These catalysts are characterized by temperature sensitivity, low space velocities, pressure operation, and high sensitivity to poisoning. No difficulty has been found in maintaining and controlling the operating temperature. Initial difficulties were experienced in maintaining the pressure in the units constant. However, this was remedied by modifying the Cash-type back pressure regulator, replacing the composition seats with a hard vulcanized fibre. The special feature of the experimental equipment was the use of automatic control on these extremely low rates of gas flow. This has on the whole performed quite satisfactorily.

A P P E N D I X

A Preparation of Synthesis Gas

B Design and Calibration of Flowmeters

C Short-Time Catalyst Testing in a Static System.

A - PREPARATION OF SYNTHESIS GAS

The Fischer-Tropsch process, unlike the Bergius process, is an indirect conversion of carbonaceous material to hydrocarbons. This gives the former process a distinct advantage in enabling the use of a wide variety of raw material. All types of coal, or coke, can be used in preparing the synthesis gas, a mixture of CO and H_2. The waste gases of the large steel industries have been suggested as a possible source and natural gases have been used on a small scale. Large scale industrial development in both Germany and Britain has been based on the incomplete combustion of coal and coke. However, production from natural gas, the apparent cheapest raw material on this continent, is still in the experimental stage.

The simplest and most convenient method of preparing synthesis gas for laboratory purposes is by the partial oxidation of natural gas with oxygen,

carbon dioxide or steam:

$$CH_4 + 1/2\,O_2 \rightleftharpoons CO + 2H_2 \qquad (1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (2)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (3)$$

These reactions give H_2:CO ratios of 2, 1, and 3 respectively. Since a synthesis gas with a 2:1 ratio was chosen for the present program of catalyst testing, reaction (1) was employed.

The preparation of water gas is a batch operation. Methane (high methane natural gas) and oxygen are fed simultaneously into a water-seal type gasholder, A, of about 10 cu. ft. capacity (Figure XVI). The rates of flow of each gas, measured by glass capillary flowmeters B and C, are carefully controlled to give a 2:1 methane-oxygen ratio. A high pressure storage, maintained by pumping natural gas from a commercial gas line, serves as the methane supply; the usual commercial cylinders were purchased to provide an oxygen supply.

When gasholder A is full, the methane and oxygen supplies are disconnected. The gas mixture is then passed back through flowmeter C to the reaction chamber D. The latter is essentially a 3/4-inch quartz tube, 18 inches long, and heated by a Multiple Unit Electric Furnace, operating on 220-volt supply. A 6-inch catalyst bed is located in the middle of the tube, with 5 inches of porcelain chips at both ends.

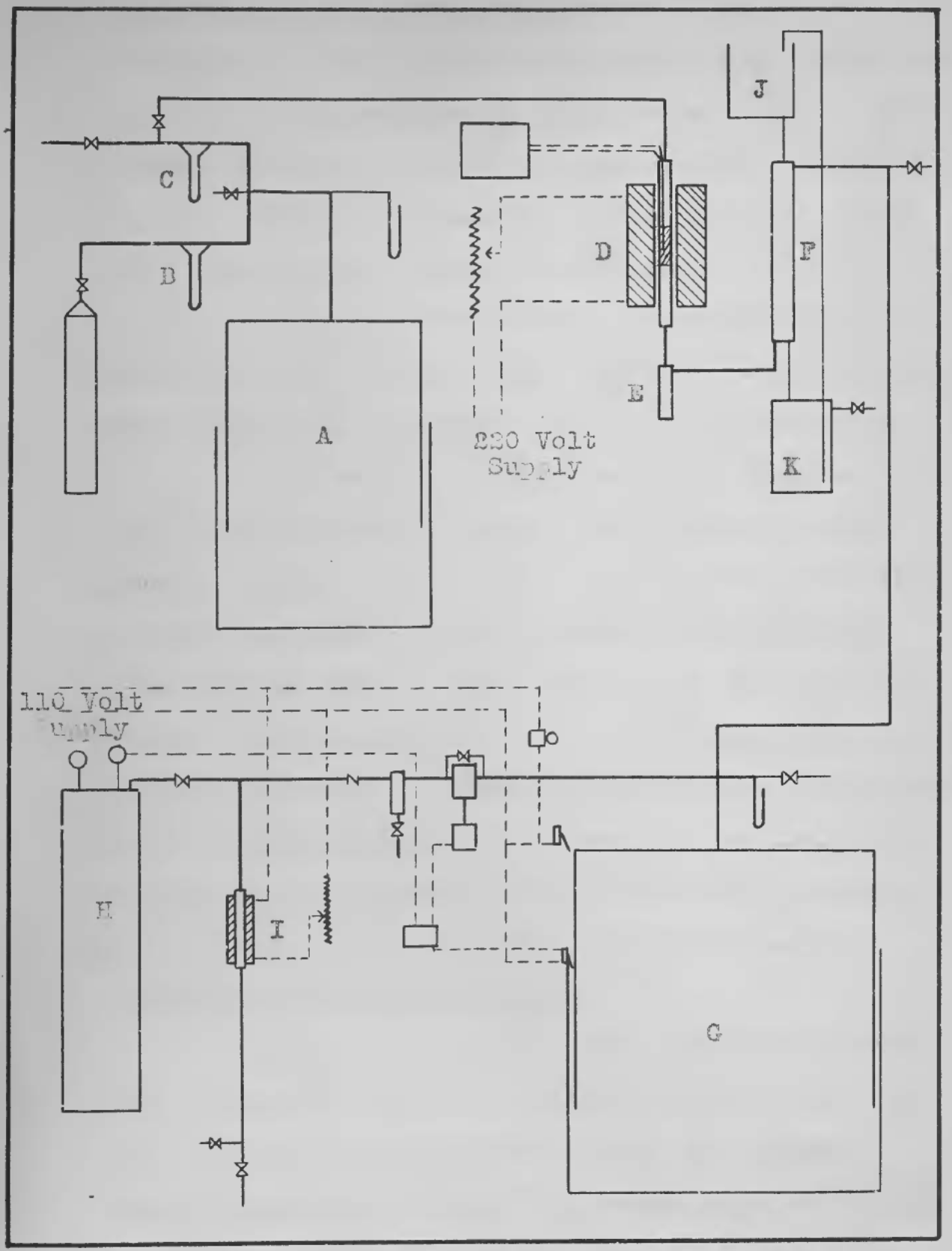


Figure IV - Flow Sheet of Synthesis Gas Preparation

Thus the catalyst, well inside the furnace, is held, in its entirety, at a reasonably uniform temperature. (This precaution is necessary since the water gas reaction reverses over the catalyst at lower temperatures.) The thermocouple well, a 1/4-inch quartz tube, containing a Pt - Pt 10% Rh thermocouple extends to the catalyst bed. Passing over the nickel catalyst at 900° - 1000°C, the CH_4 and O_2 are converted to CO and H_2, with small amounts of CO_2, H_2O, and H_2S. Water is removed in the water trap E; CO_2 and H_2S in the caustic scrubber F.

The caustic scrubber consists of three sections: the absorption column F, and upper and lower storage vessels O and K. The first is a 12-inch length of 1-1/2 inch glass tubing, packed with 6-mm. diam. glass Raschig rings. Glass wool at the top serves to give an even distribution of the scrubbing liquid, preventing channelling. Compressed air is used to elevate the solution (25% NaOH) from K to J. This liquid flows by gravity at a controlled rate through the scrubber. The synthesis gas is purified on passing countercurrently through the scrubber.

The synthesis gas, carbon monoxide, hydrogen, and a little nitrogen, is stored in a water-seal type gasholder, G, of approximately 15 cu. ft. capacity. Flow is maintained through this system by a difference

of pressure of 5 - 6 inches of water between the two gasholders.

The catalyst used is pure nickel on porcelain, as developed at the University of Alberta in 1926 (1a). It is prepared by soaking porcelain chips of 4 - 8 mesh for a period of 24 hours in a saturated solution of nickel nitrate. The chips are removed and heated strongly in a nickel crucible until brown fumes are no longer evolved. The catalyst, now NiO, is placed in the reaction chamber and reduced by heating slowly to 1000°C in an atmosphere of hydrogen.

Oxygen and sulfur, even in very small quantities, are serious poisons to Fischer-Tropsch catalysts. Both attack the active centers, permanently deactivating the catalyst. Oxygen removal presents no serious problems. The reducing atmosphere in the synthesis gas furnace removes any excess oxygen that may be present. The storage and connecting lines are always under a slight positive pressure and any leaks would be outward. Sulfur removal however, presents greater difficulties. Fortunately, in the reducing atmosphere of the furnace, all the sulfur compounds are converted to H_2S, which is later absorbed in the caustic scrubber. Complete removal of the sulfur is essential, as even minute quantities (0.1 grains per 100 cu. ft. of gas is the upper allowable limit) can quickly poison a catalyst.

Little difficulty was experienced in the manufacture of this gas. Though methane and oxygen were mixed in an exact 2:1 ratio, an analysis of the synthesis gas revealed a product slightly high in hydrogen. However, by increasing the proportion of oxygen in the mixture, the proper H_2:CO ratio was obtained. This ratio could be maintained with a deviation of not more than four per cent.

B - DESIGN AND CALIBRATION OF FLOWMETERS

One of the commonest methods of determining the rate of flow of fluids is to measure the pressure drop caused by the insertion of a restricted opening into the line. Thus orifice and venturi meters are popular industrial flow measuring devices. However, for laboratory work where the rate of gas flow is small, capillary flowmeters have proven the most satisfactory. Their behavior is dependable and predictable; the pressure drop easily measurable.

Since the gas flow in the Fischer-Tropsch synthesis is measured under 100 psi. pressure, a flowmeter of sturdy construction must be employed. Two other features are incorporated into the design--a separate capillary holder which may be conveniently removed from the main flowmeter block; and provision for bypassing the gas while this is being done.

A schematic drawing of the whole flowmeter is shown in Figure XVII. The main body, A, is machined

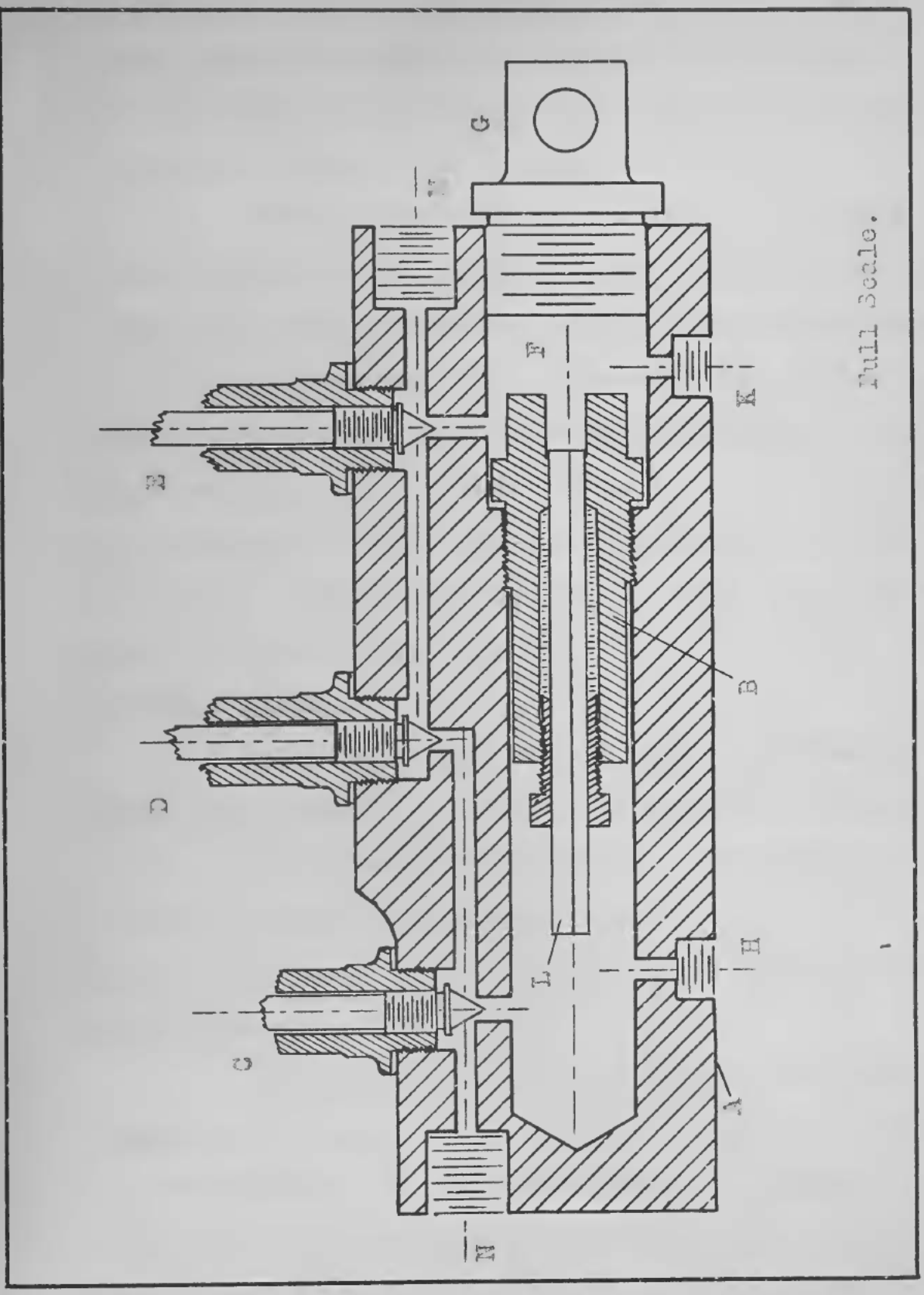


Figure XVII - Capillary Flowmeter -assembled

from a 2-inch hexagonal steel bar and has an overall length of 6 inches. In the interior of the block a brass capillary holder B is threaded and sealed by a garlock gasket. The gas passages and pressure taps are located as shown on the diagram.

Three valve stem assemblies, C, D, and E (from 1/4-inch needle valves) direct the gas flow. The brass needle seats directly onto the steel edged openings in the flowmeter block. The capillary holder chember F is closed by a threaded steel plug G, which is tightened with a dolly bar. Pressure taps at H and K are connected to a Merriam mercury manometer, which indicates the pressure drop across the capillary. Lead gaskets seal the valve stems and the steel plug to the flowmeter block.

The brass capillary holder B is threaded snugly into chamber F. One end is notched to permit the use of a screwdriver for tightening. The capillary L (a short length of thermometer stem) is held tightly in place by the brass gland and packing consisting of a short piece of rubber tubing.

In normal operation the bypass valve D is closed and the other two (C and E) open. The gas enters at M, passes into the hollowed section F, through the capillary, and discharges through outlet N. On closing valves C and E and opening valve D, the capillary is

taken out of the gas stream and may be removed and cleaned without interruption of gas flow to the reactor, manual flow control being necessary, of course, during this operation.

Capillary tubing of the proper length and diameter had to be chosen to give a suitable pressure drop for normal operational flows. Govier (19) has combined in one equation the various factors which determine the pressure drop across a capillary tube with square ends, through which a fluid is flowing.

$$H = \frac{16}{\pi g D^4} \left(81 \mu Q + \frac{\rho Q^2}{\pi}\right)$$

H = pressure drop across capillary - cms. H_2O

D = diameter of capillary - cms.

l = length of capillary - cms.

μ = viscosity of flowing gas - poises

ρ = density of flowing gas - gm./c.c.

Q = rate of flow (under flowing conditions) c.c.'s/sec.

This equation reveals several interesting features about capillary flowmeters:

1) If the end effects are small, then the relationship between Q and H is linear. With the low space velocities used in the synthesis (of the order 0.4 c.c.'s per sec.), this condition is certainly satisfied. Therefore the second term in the above equation may be neglected.

2) The quantity Q in the equation refers to the volume of gas as measured under flowing conditions, i.e., at the average of the upstream and downstream pressures. Since the viscosity of a gas is almost independent of pressure (up to about 10 atmospheres), then the capacity of the flowmeter is roughly proportional to the pressure of the flowing gas.

The design equation may be expressed in the following form:

$$l = \frac{\pi g D^4 (\Delta H)}{128 \mu Q}$$

In order to determine the proper length of capillary to be used, it was decided that synthesis gas flowing at 100 psi. gauge, with a space velocity of 150/hour (or 0.4 c.c.'s/sec. at 8 atmospheres) should give a pressure drop of approximately 4 inches of mercury. All the variables except l and D (and u in the case of the gas mixture) are now known or readily calculable. Data on the viscosity of CO - H_2 mixtures are very scanty and the relationship between viscosity and composition is obscure. It was finally necessary to estimate the value of u, knowing the behavior of CO - H_2 and N_2 - H_2 mixtures over limited ranges.

Convenience with regard to the size of the flowmeter block limited the length of the capillary to a maximum of 12 cms. Preliminary calculations

indicated that only thermometer capillaries had sufficiently small diameters to permit this requirement to be satisfied. By sucking up and weighing a measured length of mercury in the capillaries, it was possible to determine the average diameters. Knowing these data, the proper length of capillary in each case was determined and the cut capillaries inserted into flowmeters.

These capillaries were designed approximately and calibrated absolutely under normal operating conditions. The calibrations were carried out for hydrogen and synthesis gas at atmospheric pressure, and for the latter at 100 psi. gauge.

It is obvious from the design equation that a capillary designed for a space velocity of 150/hour for synthesis gas at 8 atmospheres would only permit a space velocity of 20 - 30/hour for synthesis gas or hydrogen at atmospheric pressure. The latter rate is satisfactory for hydrogen, since it is used only in reducing, conditioning, and reactivating the catalysts, where low space velocities are permissible. These capillaries are, however, not suitable for operating with water gas at 1 atmosphere--the allowable space velocity being too low for effective catalyst testing. Nevertheless, a calibration for this last case was carried out in order to determine whether or not the

effect of pressure on the behavior of the flowmeter is predictable from theoretical considerations.

The calibrations proved to be a rather formidable task because of the small flows involved. Any small leaks in the system were sufficient to change the flow by several hundred per cent. It was found necessary to check for tightness before every set of experimental runs. After passing through the flowmeter, the rate of gas flow was measured accurately in a Precision Wet Test Meter. A stopwatch was used to note the time required for the passage of a 1/10 of a cubic foot of gas (corresponding to one complete revolution of the meter). This was done in duplicate for three or four different rates of flow for each capillary and for each set of conditions. Since some single runs took as long as two hours, the calibrations were tedious and time consuming.

The rates of flow (measured at atmospheric pressure) were then plotted against the pressure differentials. A typical set of curves for one capillary is shown in Figure XVIII.

Since the rate of flow Q' is in this case measured under discharge conditions, the graphs show a slight curvature. In order to test the validity of the design equation, it is necessary to calculate the flow rates as measured under the actual flowing conditions.

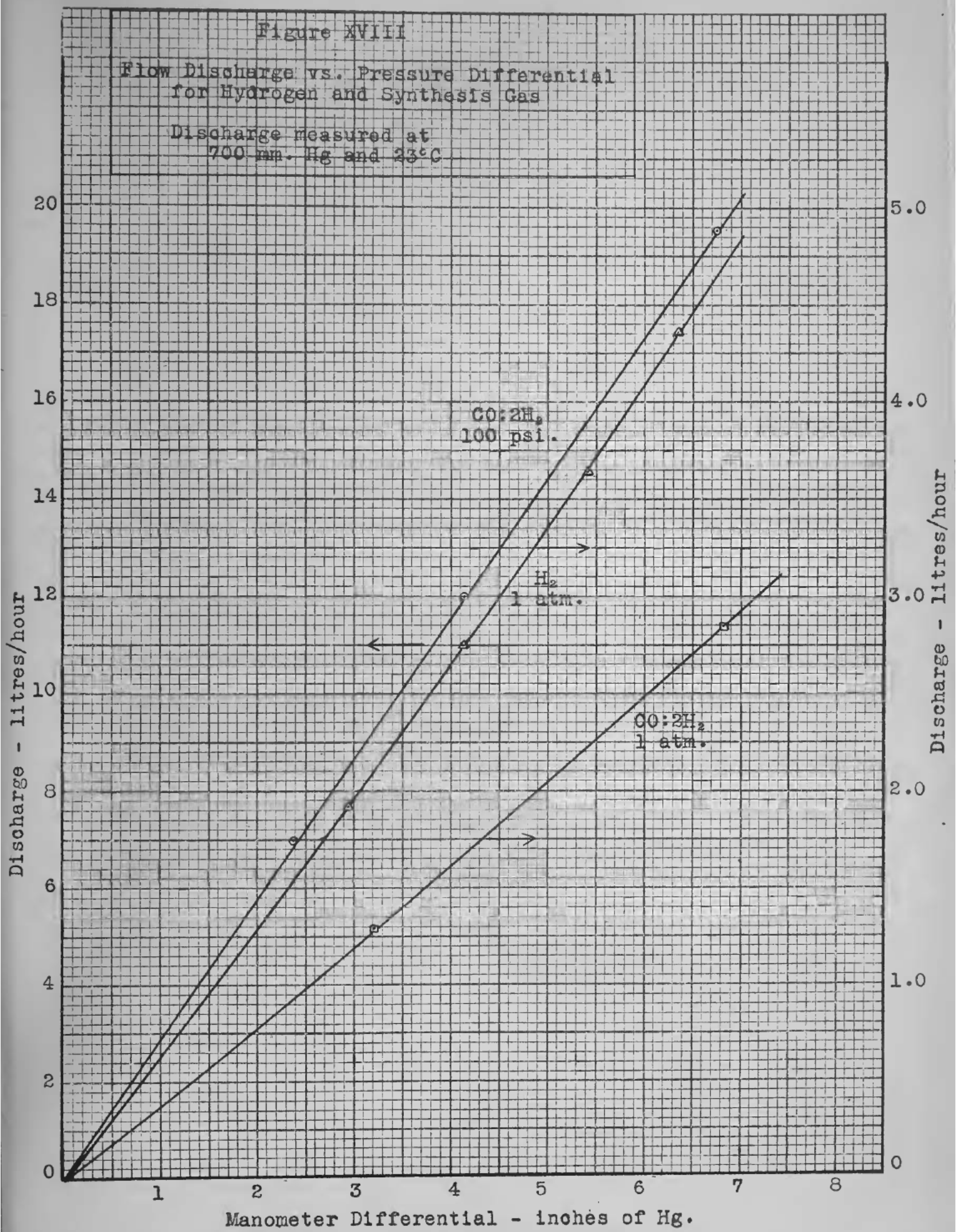


Figure XVIII
Flow Discharge vs. Pressure Differential for Hydrogen and Synthesis Gas
Discharge measured at 700 mm. Hg and 23°C
CO:2H2 100 psi.
H2 1 atm.
CO:2H2 1 atm.
Discharge - litres/hour
Discharge - litres/hour
Manometer Differential - inches of Hg.
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
0
1.0
2.0
3.0
4.0
5.0

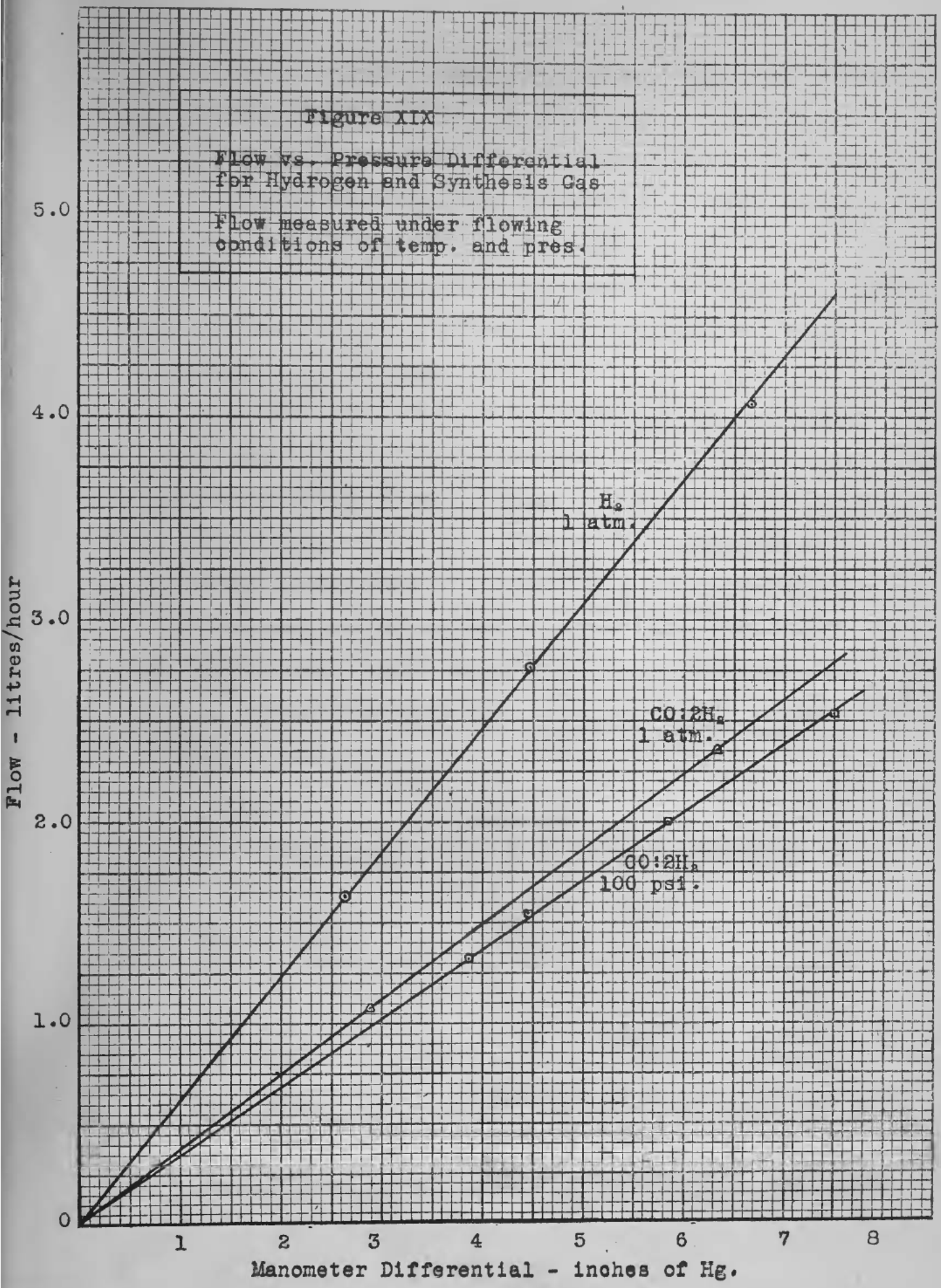


Figure XIX
Flow vs. Pressure Differential for Hydrogen and Synthesis Gas
Flow measured under flowing conditions of temp. and pres.
H₂ 1 atm.
CO:2H₂ 1 atm.
CO:2H₂ 100 psi.
Flow - litres/hour
0
1.0
2.0
3.0
4.0
5.0
1
2
3
4
5
6
7
8
Manometer Differential - inches of Hg.

These results were then plotted--rate versus pressure differential. A typical set of graphs is shown in Figure XIX. Six capillaries were calibrated and 18 curves drawn. An examination of these curves led to the following conclusions:

1. In all cases the linear relationship between the rate of flow Q (under flowing conditions) and the pressure drop ΔH was confirmed.

2. The ratios of the slopes of the curves for hydrogen (1 atmosphere):synthesis gas (1 atmosphere): synthesis gas (8 atmospheres) for all of the six capillaries were consistent. This is to be expected since these ratios depend only upon the flow characteristics (viscosity and density) of the gas being measured. The following table shows this clearly--the ratio of the slopes being based on a value of unity for the hydrogen curve.

TABLE IX

Correlation of Slopes of Calibration Curves

Capillary No.	Ratio of Slopes of Curves H_2 1 atm.	$CO:2H_2$ 1 atm.	$CO:2H_2$ 100 psi.
5	1.0	0.59	0.57
6A	1.0	0.59	0.57
6B	1.0	0.61	0.55
10	1.0	0.60	0.57
11A	1.0	0.60	0.56
11B	1.0	0.60	0.56

The average deviation is less than 1%. This indicates the correctness of the calibrations.

3. The slope of the curves $Q = f(\Delta H)$ for synthesis gas changed only slightly with an increase in pressure from 1 atmosphere to 8 atmospheres--there being a decrease in slope of only about 7%. It is therefore possible to interpolate and obtain curves for any intermediate pressures without incurring any appreciable error.

4. The effect of gas leaks on the calibration curves was clearly demonstrated. A leak in the discharge system causes the graph to shift to the right. A by-pass leak through the capillary holder or through the by-pass valve changes the slope of the graph. These two effects are illustrated in Figure XX.

5. The results did not agree with the calculated values of the basic equation. Deviations were found as high as 25%. Therefore, while the equation is of much value in the design of capillary flowmeters, with flows of this order, the latter should always be calibrated absolutely.

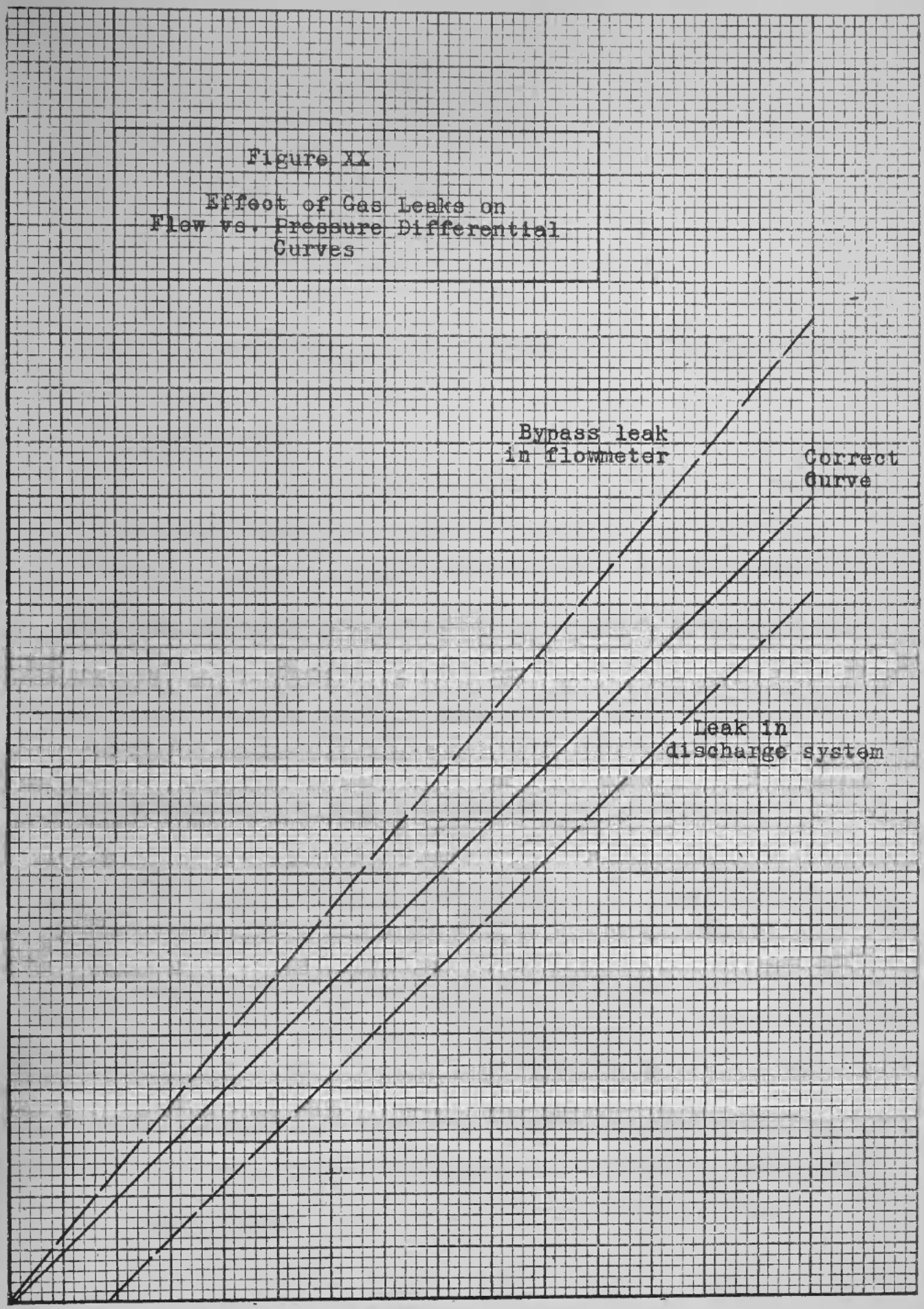


Figure XX
Effect of Gas Leaks on
Flow vs. Pressure Differential
Curves
Bypass leak
in flowmeter
Correct
Curve
Leak in
discharge system
Flow (measured under flowing conditions) - litres/hour
Manometer Differential - inches of Hg.

C - SHORT-TIME CATALYST TESTING IN A STATIC SYSTEM

Introduction

The proper evaluation of a Fischer-Tropsch catalyst requires weeks of testing under conditions approximating commercial operation. This is time consuming and it is desirable to devise a short-time test which can be used to predict the catalyst behavior. Specifically, what is sought is a correlation between the results of these short-time tests and those obtained from long term dynamic tests.

An investigation of this type was started but is still only in the preliminary stages and no conclusive results are as yet available. The method used involves the reaction of synthesis gas in a static system at 1 atmosphere over a reduced but not conditioned catalyst. As the adsorption and reaction proceeds, giving hydrocarbon products (mainly methane but possibly some liquids), the pressure in the system drops. Pressure-time readings are recorded and plotted.

Assuming the initial reaction to be only

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$\text{or } 2CO + 2H_2 \longrightarrow CH_4 + CO_2$$

the slope of the curve gives the initial rate of methane synthesis. Ultimately, a correlation between these rates and catalyst behavior in liquid production will be sought, the absence of any such correlation vitiating this method of evaluation.

Apparatus

The individual pieces of equipment listed below are represented in their proper places in Figure XXI.

A - Storage chamber for the synthesis gas.

B - P_2O_5 drier for drying the synthesis gas.

C - Mercury manometer (vacuum on its right arm) to measure the absolute pressure in A.

D - Activated charcoal to purify the hydrogen.

E - Reaction chamber.

F - Copper wire basket, containing the catalyst pellets.

G - Mercury manometer.

H - Paraffin wax constant temperature bath, heated by a hot plate and two knife heaters (controlled through a rheostat).

K, L, M - Three-way stopcocks.

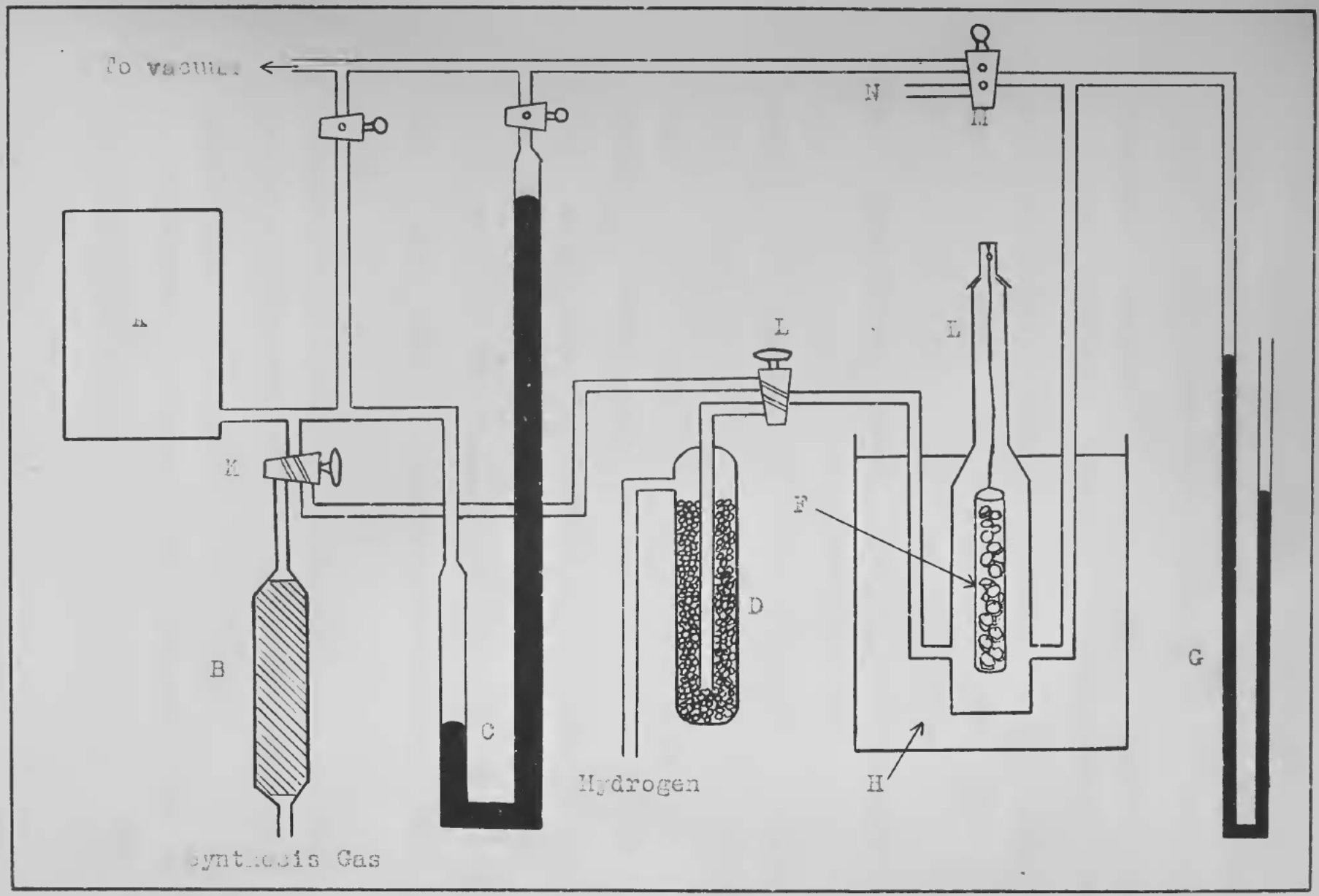


Fig. XXI - Apparatus for Short-Time Testing of Catalysts in a Static System

Procedure

The copper wire basket F was filled with catalyst pellets, weighed, and placed in the reaction chamber E. The latter was surrounded by an air bath. The whole system, including the storage chamber A, was evacuated. Purified hydrogen was admitted into E and a slight but positive flow of hydrogen was maintained, the latter leaving at N. The catalyst was heated to 360° - 370° C and held at this temperature for 4 hours. The storage chamber A was filled with synthesis gas and the pressure measured on manometer C. After the catalyst had been reduced, the air bath was replaced by a paraffin wax bath H and the temperature reduced to 185°C. The reaction chamber E was evacuated free of hydrogen, and synthesis gas from A admitted. The final pressure in A was recorded. On admission of the synthesis gas into E, the pressure was read on the manometer G and the stopwatch started. Pressure-time readings were taken, at 1-minute intervals at first, and at longer time intervals when the pressure readings became steadier. The temperature was maintained constant by adjusting the rheostat which was connected in series with the knife heaters. Each run took from 30 to 60 minutes, depending upon the catalyst. Duplicate runs were made at 185°C, 190°C, and 195°C.

Results

Three catalysts were given preliminary test, namely:

(1) Fe-Cu - Bureau of Mines #24.

(2) Co-Th - Harshaw Chemical Co. Ltd.

(3) Ni-Mn - Harshaw Chemical Co. Ltd.

A comparison of the activity of each may be seen in Figure XXII. The effect of temperature upon the reactivity of the cobalt catalyst is shown in Figure XXIII.

Discussion

With respect to the Co-Th catalyst in particular, successive runs at the same temperature gave duplicate results. Similar performance was obtained after reactivation for four hours with hydrogen. Whether this catalyst could be reactivated after cooling to room temperature was not investigated. Tests upon the Fe-Cu catalyst were inconclusive.

At the temperatures tested the Fe-Cu was much less active than the other catalysts. This is probably not a fair comparison since iron catalysts operate normally at a temperature of 250°C. The nickel catalyst revealed a higher activity than the cobalt but the per cent contraction was less. Since the contraction in the case of the nickel catalyst was approximately one half, the methane reaction is indicated. The contraction in the case of the cobalt

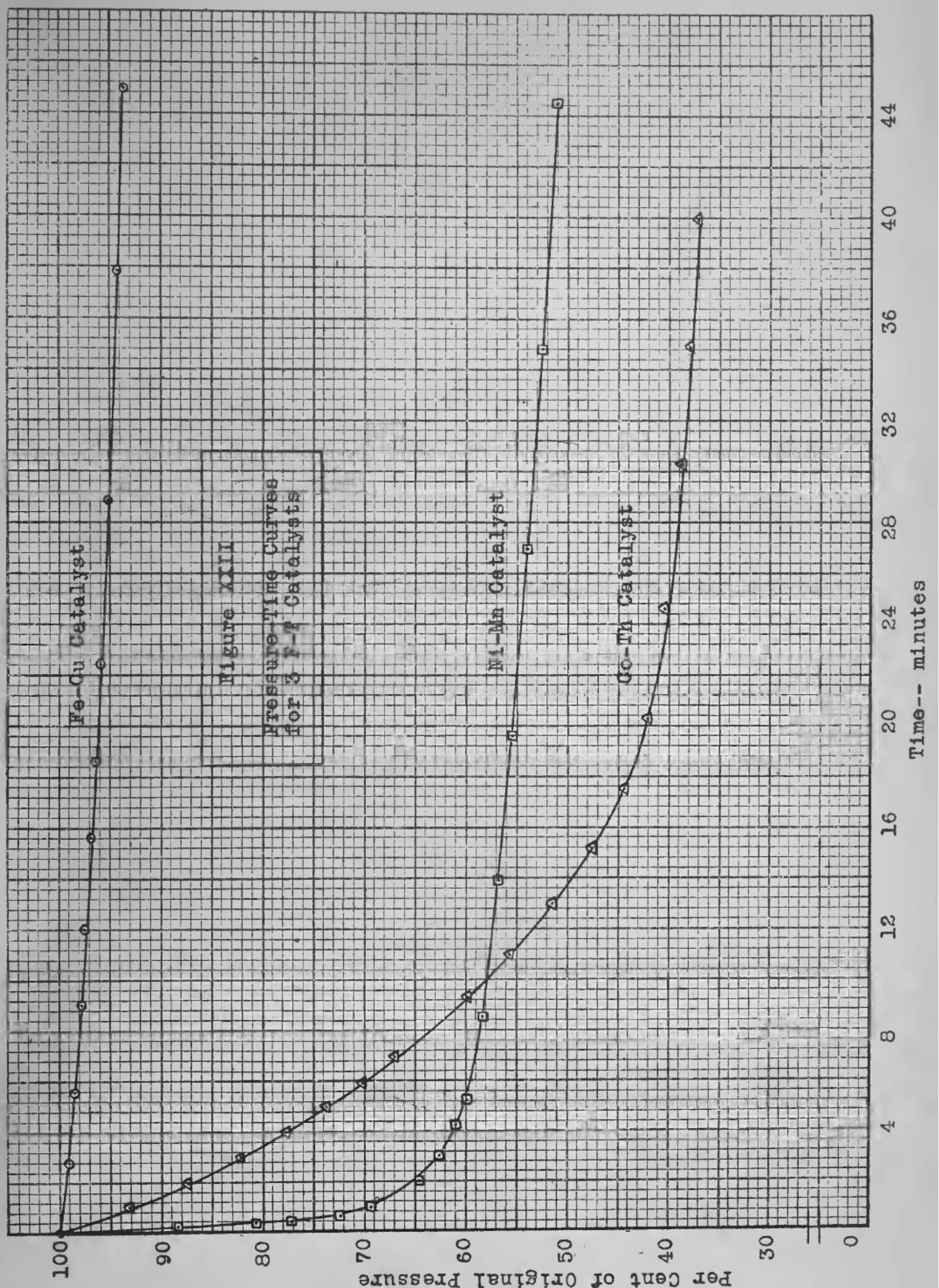


Figure XXII
Pressure-Time Curves
for 3 F-T Catalysts

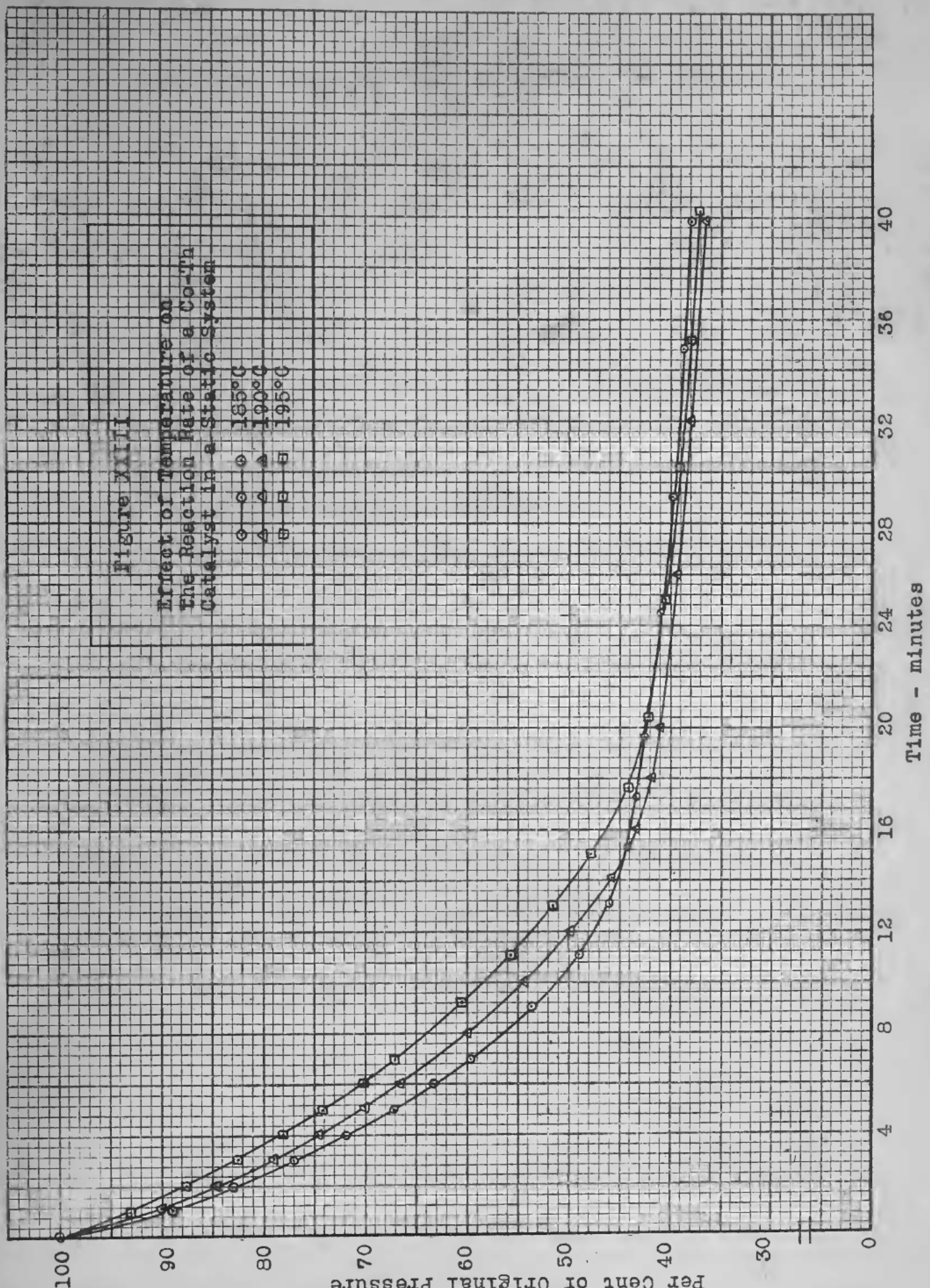


Figure XIII
Effect of Temperature on
The Reaction Rate of a Co-Th
Catalyst in a Static System
185°C
190°C
195°C
Per Cent of Original Pressure
Time - minutes
100
90
80
70
60
50
40
30
0
4
8
12
16
20
24
28
32
36
40

catalyst is 65 per cent, and therefore cannot be explained wholly by this reaction. Adsorption or the formation of higher hydrocarbons are the only two alternatives. Figure XXIII indicates that the temperature coefficient of reaction is comparatively low. This would be the case if, as has been suggested by some authors, diffusion were the rate controlling factor.

Insufficient data have been obtained to determine the order of reaction. The same is true at this stage of the work with respect to the value of these rate measurements as indicative of catalyst performance in the Fischer-Tropsch synthesis.

BIBLIOGRAPHY

(1a) Boomer, E.H., Can. Pat. 289,830, (1926).

(1) Craxford, S.R., Trans. Far. Soc., 35, 946-958 (1939).

(2) Craxford, S.R. and Rideal, E.K., Jour. Chem. Soc., Part II, 1604-1614 (1939).

(3) Domai, S., Bull. Chem. Soc. Japan, 16, 213 (1941), C.A. 36, 739 (1942).

(4) D.R.P. (German patent) 293, 787 (1913).

(5) D.R.P., 293, 797 (1913).

(6) D.R.P., 705, 528 (1938).

(7) Egloff, G., Nelson, E.F., and Morrell, J.C., Ind. Eng. Chem., 29, 555-559 (1937).

(8) Elwin, O.E. and Nash, A.W., Nature, 118, 154 (1926).

(9) Fischer, F., Brennstoff-Chem., 16, 2 (1936).

(10) Fischer, F., J. Inst. of Fuel, 10, 10 (1936).

(11) Fischer, F., Ber., 71, 56-67 (1938).

(12) Fischer, F. and Pichler, H., Brennstoff-Chem., 20, 41-61 (1939).

(13) Fischer, F. and Pichler, H., Brenn. Chemie, 21, 285-8 (1940).

(14) Fischer, F., Roelen, O., and Feist, W., Brenn. Chemie, 13, 461-8 (1932).

(15) Fischer, F., Roelen, O., and Feist, W., Refiner, 22, 429-35 (1943).

(16) Fischer, F. and Tropsch, H., Brenn. Chemie., 4, 276-85 (1923).

(17) Fischer, F. and Tropsch, H., Brenn. Chemie, 7, 97-104 (1926).

(18) Foster, H.L., Oil and Gas Journal, 43, No. 15, 99-101; No. 17, 46-49; No. 18, 66-69; (1944).

(19) Govier, G.W., "The production of formaldehyde by low pressure oxidation of high-methane natural gas", Thesis, Part I, Appendix A, University of Alberta (1945).

(20) Hamon, F., Mayer, A., and Plantefol, L., Ann. physio. physicochim. biol., 6, 452-63 (1930). C.A. 25, 4292 (1931).

(21) Herington, E.F.G. and Woodward, L.A., Trans. Far. Soc., 35, 958-67 (1939).

(22) Hofer, L.J.E., "The preparation and properties of metal carbides", Bureau of Mines (U.S. Department of the Interior) Booklet, July (1944), p. 1, 39.

(23) Komarewsky, V.I. and Riesz, C.H., Refiner, 23, 415-22 (1944).

(24) Myddleton, W.W., J. Inst. of Fuel, 11, 477-92 (1937).

(25) Myddleton, W.W., J. Inst. Petroleum, 30, 211 (1944).

(26) Napthali, M., Refiner, 17, 47-51 (1938).

(27) Russell, R.P., Hearings before a Subcommittee of the Committee on Public Lands and Surveys, United States Senate on Synthetic Liquid Fuels, p. 39 (1944).

(28) Sabatier and Sendereus, Compt. rend., 134, 514 (1902).

(29) Shaw, A.C., "Preparation and Testing of Fischer-Tropsch Catalysts", Unpublished report, Dept. of Chemistry, University of Alberta, (1945).

(30) Storch, H.H., "The Chemistry of Coal Utilization", edited by H.H. Lowry, John Wiley & Sons, New York, N.Y., 1945, Vol. II, pp. 1797-1845.

(31) Underwood, A.J.V., Ind. Eng. Chem., 32, 449-53 (1940).

(32) U.S. Bureau of Mines (Department of the Interior), Pittsburgh, Penn., Private Communication (1944).

(33) U.S. Steel Corporation, "Methods of the Chemists of the U.S. Steel Corporation for the Sampling and Analysis of Gases", Booklet, Third Edition, p. 106 (1927).