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PATENT SPECIFICATION

Application Date: Aug. 2, 1938. *No. 22865/38.* **516,403**

Complete Specification Left: May 19, 1939.

Complete Specification Accepted: Jan. 1, 1940.

PROVISIONAL SPECIFICATION

Improvements in the Manufacture and Production of Hydrocarbons from Carbon Monoxide and Hydrogen

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

In the reaction of carbon monoxide with hydrogen to form hydrocarbons having more than one carbon atom in the molecule it has already been proposed to lead away the heat formed by working in a liquid medium. As such it is advantageous to use a proper oil (i.e. a liquid medium consisting of the oils obtained by the conversion of an amount of the same initial materials previously treated under the same or similar conditions) which contains considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions used; these constituents are in particular those boiling in the boiling range of the benzines or even lower, as for example down to 30° or 40° Centigrade.

The liquid may be led in the same direction as or in counter-current to the gases to be reacted. In carrying out the process on a large industrial scale, working in counter-current offers the difficulty, however, than when using proper oil having low-boiling constituents the large amount of hot gases flowing through readily carries these constituents therewith from the reaction vessel so that they are not available for the reaction in the desired amount; the reaction proceeds much more slowly in the higher-boiling fractions which remain liquid so that the yields per unit of space and time of the desired products is considerably diminished.

If the liquid be led in the same direction as the gases to be reacted, the said carrying away of the low-boiling constituents of the liquid by the gases takes place to a considerably smaller extent. The maintenance of a uniform temperature over the whole of the reaction chamber is rendered difficult, however, because by reason of the exothermic nature of the reaction the products become increasingly hotter during their passage through the catalyst chamber and thus towards the end of the reaction vessel the lower-boiling constituents are vaporised to an undesirably great extent without it being possible to bring them back again into the reaction vessel for example by reflux cooling against the strong current of gas.

My foreign correspondents have now found that the said reaction in the presence of a liquid medium, in particular the proper oil, which contains considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions used can be carried out in a very advantageous manner by first leading the liquid medium past the catalyst chamber in heat-exchange relation to the same and then leading it through the catalyst chamber in the same direction as the gases to be reacted. The catalyst is arranged stationarily in the said chamber. By the liquid medium led in heat-exchange relation to the catalyst chamber, an excessive rise in temperature at the end of the catalyst chamber is avoided and consequently when using a proper oil having considerable amounts of low-boiling hydrocarbons therein the above-mentioned drawback of too strong vaporisation towards the end of the catalyst chamber is considerably reduced or entirely avoided. During the said heat-exchange it is specially advantageous to lead the liquid medium in counter-current to the substances being subjected to reaction. In this way the liquid medium, while it is at its lowest temperature, comes into indirect contact with the hottest part of the catalyst chamber and thus keeps the temperature of this chamber much more uniform.

In order to be able to lead the liquid medium first past the catalyst in the reaction chamber, the catalyst is arranged in one or more separate chambers, so-called cells. These catalyst cells may be of different shapes, as for example tubular, annular or pocket-shaped. The catalyst is introduced into the cells in a suitable

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form, as for example in pieces, the cells being washed round by the liquid medium, preferably preheated to a suitable temperature, before it enters the cells. The temperature of the liquid medium supplied to the reaction chamber is generally speaking regulated so that after heat-exchange with the catalyst cells it is at about the temperature at which the reaction takes place, i.e. so that the last heating up to the said temperature is effected by the said heat-exchange. The medium or a part thereof may, however, also be branched off after the heat-exchange and subjected to a preheating before introduction into the catalyst cells.

The nature of the invention will be further described with reference to the accompanying drawings in which are shewn diagrammatically a number of apparatus in which the process according to this invention may be carried out, but the invention is not restricted to the particular apparatus shewn.

Figures 1 and 1*a* are a longitudinal and cross section of a reaction vessel in which the catalyst cell is constructed as a single cylinder K through which the gas mixture to be reacted which is introduced from below at N is passed together with oil passed along by the catalyst cell through the intermediate space M. Fresh oil is supplied at L. The reaction products together with the accompanying oil are withdrawn at O.

Figures 2 and 2*a* shew an apparatus in which the catalyst is situated in an annular cell K and the heat-exchange oil flows through the centre of the vessel. As regards the supply of gas and withdrawal of the products, the arrangement is similar to that in Figures 1 and 1*a*.

The same is true of the apparatus shewn in Figures 3 and 3*a* in which the catalyst is situated in a number of separate tubular cells past which the heat-exchange oil flows.

Figure 4 shews a complete plant for carrying out the said process and is described in greater detail in the following Example.

The gas mixture may also be brought together with the liquid medium before introduction into the catalyst chamber and thereby preheated at the same time. In the case of direct introduction into the catalyst chamber, the gas is preheated in another way.

The temperature and pressure conditions are those usual for the said reaction; it is preferable to work at temperatures between 200° and 420° Centigrade and at pressures of more than 20 atmospheres, as for example 50 to 700 atmospheres. Lower pressures may, however, also be used. The relative proportions of the initial gases may be varied within wide limits; the ratio of the amounts of carbon monoxide to hydrogen usually lies between 4:1 and 1:4 (measured volumetrically) and it is advantageous to work with an excess of carbon monoxide. Accompanying gases, such as carbon dioxide, nitrogen and/or methane may also be present. The liquid medium is usually added in an amount of 0.5 to 5 parts by volume to 100 parts by volume of initial gases (measured at ordinary pressure and room temperature).

As the final products of the reaction there are obtained mainly liquid hydrocarbons, in addition to gaseous and solid hydrocarbons. The fraction of the single products (benzine, middle oil, lubricating oil, paraffin wax) in the total product varies according to the reaction conditions used.

The said process, especially when working under high pressure, allows of preparing hydrocarbons from carbon monoxide and hydrogen with yields per unit of space and time such as could not be obtained hitherto because even with high loading of the reaction vessel no undesirable rises in temperature can occur and therefore injurious side reactions resulting in reduction in yield are impossible.

The following Example, given with reference to Figure 4, will further illustrate the nature of this invention, but the invention is not restricted to this Example.

EXAMPLE.

A is a high pressure chamber 5.8 metres high and 200 millimetres in internal diameter in which is arranged an inserted tube of 150 millimetres internal diameter which is open at the bottom, the arrrangement being such that between the outer tube and the inserted tube there is an annular space M.

The initial gas, preheated in a gas preheater T to about 240° Centigrade, is led in under a pressure of 120 atmospheres through a supply pipe N which projects into the interior of the inserted tube. The circulating oil formed by the reaction is pumped by a circulatory pump P from a separator B into a preheater H and after being heated therein to 260° Centigrade enters at L into the annular space M, in which it flows downwards until at the bottom it enters the catalyst chamber K.

During each hour there are supplied 83.3 cubic metres of gas having the composition:—

5.8 per cent of CO_2
0.7 ,, ,, ,, C_nH_{2n}
42.6 ,, ,, ,, CO
42.0 ,, ,, ,, H_2
3.9 ,, ,, ,, C_nH_{2n+2}
5.0 ,, ,, ,, N_2

and about 0.75 cubic metre of oil.

After the heating of the chamber with warm oil, a fairly uniform temperature of from 275° to 285° Centigrade occurs over almost the whole length of the catalyst chamber by working in the said manner; this temperature may be maintained by suitable regulation of the amount of oil circulated and the strength of the preheating of the gas and oil. The inner space of the inserted tube is filled with pieces of from 8 to 10 millimetres in size of a catalyst obtained by melting together iron powder with small additions of titanium oxide, manganous oxide and potassium hydroxide in a current of oxygen and treatment for 48 hours with hydrogen at 650° Centigrade.

By one passage through the catalyst chamber, about 56 per cent of the carbon monoxide and hydrogen introduced are reacted.

The circulating oil, the residual gas and the products formed leave the chamber at O, pass through a cooler S and enter the separator B at a temperature of from 70° to 80° Centigrade. The major portion of the water formed separates with the oil in the separator B. Of the oil separated, the following amounts in per cent by volume boil at the temperatures given:—

up to 150° Centigrade - -	24.0
from 150° to 300° Centigrade	48.0
above 300° Centigrade - -	28.0

The excess of oil formed and the water (which contains a small amount of compounds containing oxygen formed, such as methyl alcohol, ethyl alcohol and higher alcohols, dissolved therein) are removed at D. The remaining oil is withdrawn at E and returned through the oil circulating pump.

The gases not condensed in the cooler S flow through another cooler R and separate further amounts of light benzine formed in a separator C; these are removed at F. A further residue of low-boiling benzine hydrocarbons formed is separated from the gas (at G) by oil washing. The final gas, obtained in an amount of 49.2 cubic metres per hour, has the following composition:—

19.2 per cent of CO_2
2.6 ,, ,, ,, C_nH_{2n}
32.4 ,, ,, ,, CO
30.5 ,, ,, ,, H_2
7.3 ,, ,, ,, C_nH_{2n+2}
8.0 ,, ,, ,, N_2

It is subjected to the reaction again after separating the carbon dioxide and methane and admixture of fresh carbon monoxide and hydrogen.

The yields per hour are as follow:—

3.9 kilograms of benzine and oil,
0.9 ,, ,, paraffin waxes,
0.3 ,, ,, alcohols and
1.2 ,, ,, hydrocarbons having more than one carbon atom in the molecule and boiling below the boiling range of benzine, such as propane, butane, ethylene, propylene and butylene.

Dated this 2nd day of August, 1938.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Hydrocarbons from Carbon Monoxide and Hydrogen

I, George William Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It has already been proposed to lead away the heat evolved in the reaction of carbon monoxide with hydrogen to form hydrocarbons having more than one carbon atom in the molecule by means of a liquid medium in which the reaction is carried out. Advantageously an oil containing considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions prevailing in the reaction is used. These constituents are in particular those boiling in the boiling range of benzine or even lower, as, for example, down to 30° or 40° Centigrade. Such oils may be obtained in a previous run of the reaction itself.

The liquid medium may be led in the

same direction as the synthesis gases or in counter-current thereto. In carrying out the process on a large industrial scale, working in counter-current offers the difficulty that especially when using an oil having low-boiling constituents, for example produced in the synthesis itself, the large amount of hot gases flowing through the liquid medium readily carries these low boiling constituents away from the reaction vessel so that these are not available for the reaction in the desired amount; the reaction proceeds much more slowly in the remaining higher-boiling fractions so that the yield per unit of space and time of the desired products is considerably diminished.

If the liquid medium be led in the same direction as the synthesis gases, the low-boiling constituents are carried away to a considerably smaller extent. In this case the maintenance of a uniform temperature over the whole length of the reaction chamber is, however, rendered difficult, because by reason of the exothermic nature of the reaction the products become increasingly hotter during their passage through the catalyst chamber so that towards the end of the reaction vessel the lower-boiling constituents are vaporised to an undesirably large extent without it being possible to bring them back into the reaction vessel, for example, by reflux cooling, against the strong current of the gases.

My foreign correspondents have now found that the said reaction in the presence of a liquid medium, in particular an oil, which contains considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions prevailing in the reaction, can be carried out in a very advantageous manner by first passing the liquid medium along the catalyst chamber in indirect heat-exchange relation with the reaction participants contained in said catalyst chamber and then passing it through the catalyst chamber in the same direction as the reaction participants. Preferably the liquid medium is passed along the reaction chamber in counter-current to the reaction participants contained in the said chamber so that while the liquid medium is at its lowest temperature, it comes into contact with the hottest part of the catalyst chamber and thus keeps the temperature of this chamber much more uniform. An excessive rise in temperature at the end of the catalyst chamber is thus avoided and consequently the above-mentioned drawback of a too strong vaporisation of part of the liquid medium towards the end of the catalyst chamber is considerably mitigated or entirely avoided.

In order to be able to pass the liquid medium first along the catalyst chamber, the catalyst is arranged in one or more separate spaces, so-called cells. These catalyst cells may be of different shapes, as, for example, tubular, annular or pocket-shaped. The catalyst is introduced into the cells in a suitable form, as, for example, in pieces, the cells being bathed by the liquid medium. The temperature of the liquid medium supplied to the reaction chamber is generally regulated so that after heat-exchange with the catalyst cells it has about the temperature at which the reaction takes place. The liquid medium or a part thereof may, however, also be branched off after the heat-exchange and subjected to a preheating before introduction into the catalyst cells.

The liquid medium is preferably a product of the reaction itself, namely an oil obtained from carbon monoxide and hydrogen in an earlier run of the synthesis.

The nature of the invention will be further described with reference to the drawings accompanying the Provisional Specification in which are shown diagrammatically a number of apparatus in which the process according to this invention may be carried out, but the invention is not restricted to the use of the particular apparatus shown.

In the said drawings K indicates the catalyst cells, M conduits for the introduction of liquid medium in indirect heat-exchange relationship with the content of said cells, N the means for introducing synthesis gas and O means for removing reaction products from the cell.

Figures 1 and 1*a* show a longitudinal and a cross section of a reaction vessel in which the catalyst cell is constructed as a single cylinder K through which the synthesis gas, which is introduced from below at N, is passed together with oil passed along the catalyst cell in indirect heat-exchange relationship therewith through the intermediate space M. Fresh oil is supplied at L. The reaction products together with the accompanying oil are withdrawn at O.

Figures 2 and 2*a* show an apparatus in which the catalyst is situated in an annular cell K. The liquid medium flows through conduit M in the centre of the vessel. As regards the supply of gas and withdrawal of the products, the arrangement is similar to that in Figures 1 and 1*a*.

According to Figures 3 and 3*a* the catalyst is situated in a number of separate tubular cells along which the liquid medium flows.

Figure 4 shows a complete plant for

carrying out the said process and is described in greater detail hereafter in the Example.

The synthesis gas may also be admixed with the liquid medium before this is introduced into the apparatus. In case the gas is directly introduced into the catalyst chamber, it is preferably preheated in some way.

The temperature and pressure conditions as also the catalysts are those usual for the said reaction; it is preferable to work at temperatures between 170° and 420° Centigrade and at pressures of more than 2 atmospheres, as for example up to 700 atmospheres or more, say 5 to 200 or 300 atmospheres. Lower pressures down to atmospheric or sometimes below may, however, also be used. The relative proportions of the initial gases may be varied within wide limits; the ratio of the amounts of carbon monoxide to hydrogen usually lies between about 4:1 and 1:4 (measured volumetrically), say between about 2:1 to 1:3, for example about 1:1 to 1:2. It is often advantageous to work with an excess of carbon monoxide. Diluent gases, such as carbon dioxide, nitrogen and/or methane may also be present. The liquid medium is usually added in an amount of about 0.5 to 5 parts by volume to 100 parts by volume of initial gases (measured at ordinary pressure and room temperature).

As the final products of the reaction there are obtained mainly liquid hydrocarbons, in addition to gaseous and solid hydrocarbons, contingently with some products containing oxygen. The amount of the single products (benzine, middle oil, lubricating oil, paraffin wax) in the total product varies according to the reaction conditions used.

The following Example, given with reference to Figure 4, will further illustrate how the present invention may be carried out in practice, but it should be understood that the invention is not limited to the said Example.

EXAMPLE.

A is a high pressure chamber, 5.8 metres high and 200 millimetres in internal diameter in which is arranged a tube of 150 millimetres internal diameter which is open at the bottom, the arrangement being such that between the outer tube and the inserted tube there is an annular space M.

The initial gas, preheated in a gas preheater T to about 240° Centigrade, is led in under a pressure of 120 atmospheres through a supply pipe N which projects into the interior of the inserted tube. The circulating oil which is a product formed by the reaction in a previous run is pumped by a circulating pump P from a separator B into a preheater H and after being heated therein to 260° Centigrade enters at L into the annular space M, in which it flows downwards until at the bottom it enters the catalyst chamber K.

During each hour there are supplied 83.3 cubic metres of gas having the composition:—

5.8 per cent of CO_2
0.7 ,, ,, ,, C_nH_{2n}
42.6 ,, ,, ,, CO
42.0 ,, ,, ,, H_2
3.9 ,, ,, ,, C_nH_{2n+2}
5.0 ,, ,, ,, N_2

and about 0.75 cubic metre of oil.

A fairly uniform temperature of from 275° to 285° Centigrade is maintained over practically the whole length of the catalyst chamber by working in the said manner; this temperature may be maintained by suitable regulation of the amount of oil circulated and the degree of the preheating of the gas and oil. The inner space of the inserted tube is filled with pieces of from 8 to 10 millimetres in size of a catalyst obtained by fusing or sintering iron powder with small additions of titanium oxide, manganous oxide and potassium hydroxide in a current oxygen and treatment for 48 hours with hydrogen at 650° Centigrade.

By one passage through the catalyst chamber, about 56 per cent of the carbon monoxide and hydrogen introduced enter into reaction.

The circulating oil, the residual gas and the products formed leave the chamber at O, pass through a cooler S and enter the separator B at a temperature of from 70° to 80° Centigrade. The major portion of the water formed separates with the oil in the separator B. Of the oil separated, the following amounts in per cent by volume boil at the temperatures given:—

up to 150° Centigrade - -	24.0
from 150° to 300° Centigrade	48.0
above 300° Centigrade - -	28.0

The excess of oil formed and the water (which contains a small amount of compounds containing oxygen formed, such as methyl alcohol, ethyl alcohol and higher alcohols, dissolved therein) are removed at D. The remaining oil is withdrawn at E and returned through the oil circulating pump.

The gases not condensed in the cooler S flow through another cooler R and separate further amounts of light benzine formed in a separator C; these are removed at F. A further residue of low-boiling benzine hydrocarbons formed is separated from the gas (at G) by oil washing. The final gas, obtained in an amount of 49.2 cubic metres per hour, has the following composition:—

19.2 per cent of CO_2
2.6 ,, ,, ,, C_nH_{2n}
32.4 ,, ,, ,, CO
30.5 ,, ,, ,, H_2
7.3 ,, ,, ,, C_nH_{2n+2}
8.0 ,, ,, ,, N_2.

It is recycled to the reaction chamber after separating the carbon dioxide and methane and admixture of fresh carbon monoxide and hydrogen.

The yields per hour are as follow:—

3.9 kilograms of benzine and oil,
0.9 ,, ,, paraffin waxes,
0.3 ,, ,, alcohols and
1.2 ,, ,, hydrocarbons having more than one carbon atom in the molecule and boiling below the boiling range of benzine, such as propane, butane, ethylene, propylene and butylene.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the catalytic conversion of carbon monoxide and hydrogen into hydrocarbons with more than one carbon atom in the molecule in a liquid medium containing considerable amounts of constituents which are gaseous or vaporous under the reaction conditions, characterized in that the liquid medium is passed along the catalyst chamber in indirect heat exchange relation with the reaction participants contained in said catalyst chamber and thereupon is passed through the catalyst chamber in the same direction as the reaction participants.

2. In the process according to claim 1 passing the liquid medium along the catalyst chamber in counter-current with the reaction participants contained in the said catalyst chamber.

3. A process according to any of claims 1 to 2, characterised in that the liquid medium is a product formed in the reaction in a previous run.

4. A process according to any of claims 1 to 3, which comprises operating at 170° to 420° Centigrade.

5. A process according to any of claims 1 to 4, which comprises operating under pressures of 5 to 300 atmospheres.

6. A process according to any of claims 1 to 5, which comprises working with synthesis gases in which the ratio of carbon monoxide to hydrogen lies between about 2:1 and 1:3.

7. A process for the production of hydrocarbons by catalytic conversion of carbon monoxide and hydrogen substantially as described in the foregoing Example.

8. Hydrocarbons when obtained in processes in accordance with any of the preceding claiming clauses.

Dated this 19th day of May, 1939.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Agents.

[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1

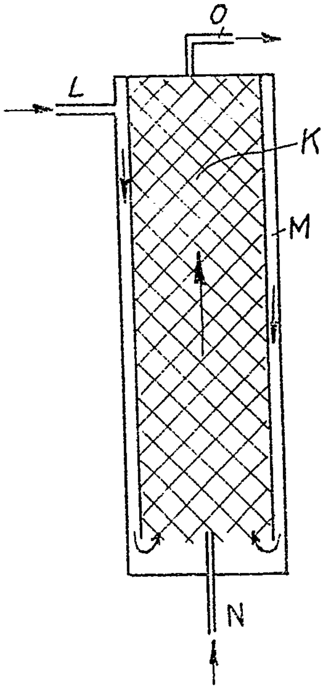


Fig. 2

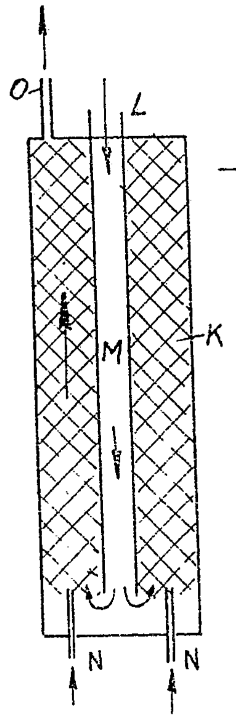


Fig. 3

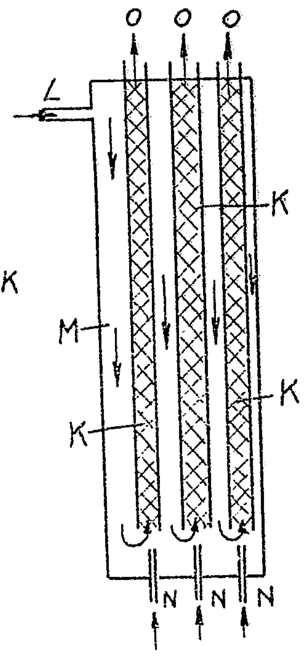


Fig. 1a

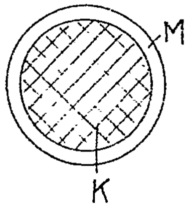


Fig. 2a

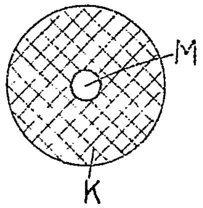
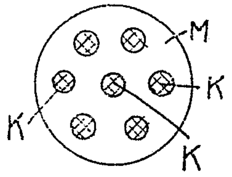
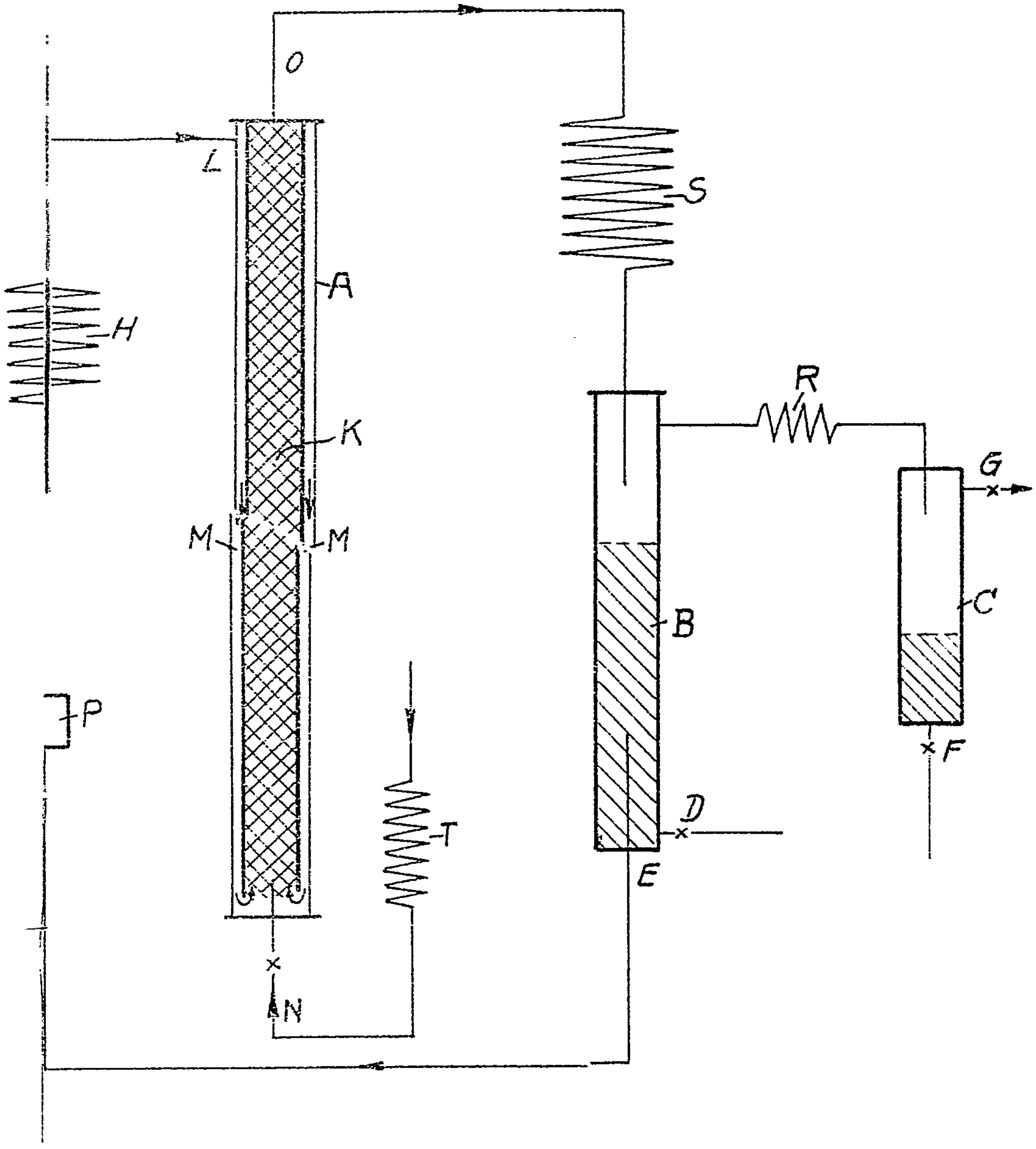


Fig. 3a



2 SHEETS
SHEET 2

Fig. 4



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[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1

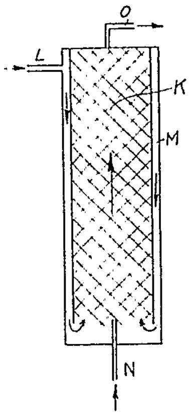

Fig. 2

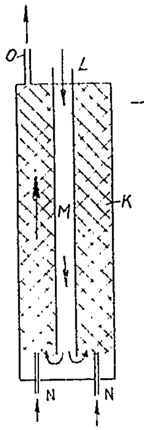

Fig. 3

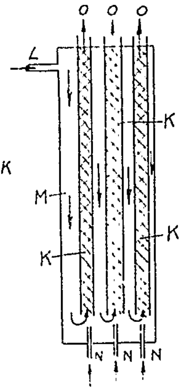

Fig. 1a

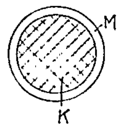

Fig. 2a

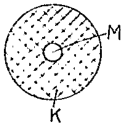

Fig. 3a

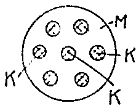

Fig. 4