[Second Edition.]

PATENT SPECIFICATION

Application Date: Nov. 26, 1928. No. 34,831/28.

328,586

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Valuable Hydrocarbons and Oxygen Derivatives of Hydrocarbons, in particular those of Low Boiling Point.

I, James Yate 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 organized under the laws of Germany) to be as follows:—

In the treatment of liquid or gaseous carbonaceous materials such as tars, mineral oils and the like and of oxides of carbon with hydrogen under pressure and at elevated temperatures for the purpose of producing valuable hydrocarbons and hydrocarbon derivatives, in particular those of low boiling point, there is frequently the disadvantage, in particular when employing catalysts, that the reaction subsides or even ceases entirely after a more or less short period of time. This phenomenon appears to be due to the fact that the initial materials form high molecular substances during the reaction and if catalysts be employed these are deposited in the pores of the catalyst and thus impair its activity.

My foreign correspondents have now found that in many cases reactions with carbonaceous gases or liquids, which are converted into vapours under the reaction conditions, can be advantageously carried out at any suitable temperature if desired with the employment of catalysts and in particular under pressure by adding either before or during the reaction so much of a medium which is liquid under the reaction conditions and which does not take part in the reaction of the gaseous or vaporous substances, that the reaction occurs within this liquid medium the injurious appearance of high molecular substances being thus avoided. This manner of working has great practical importance especially in the conversion of middle oils into hydrocarbons of the nature of benzine by treatment with hydrogen under pressure. It can also advantageously be employed for example for the production of methanol from oxides of carbon and hydrogen. It is preferable to choose a liquid medium which is not liable to decompose under the working conditions, for example anthracene oil and the like.

[*Price* 1/-]

It has also been found that in the treatment of the said initial materials in the liquid or gaseous phase the activity of the catalysts is preserved if the deposition of high molecular substances on the catalyst during the reaction be prevented by the presence of high boiling solvents which are not likely to decompose. Suitable solvents are for example anthracene oil or similar oils, namely those of aromatic character.

The process may be carried out for example by adding the catalyst in a state of fine dispersion to the initial material for example mineral oil, or to the solvent or to both. The catalyst can also be arranged in a fixed position for example in tubes or pockets of wire gauze which may be fixed to a stirring device. The solvent can also take part in the reaction. In this case, however, care must be taken that the solvent is always present in the reaction chamber in sufficient quantity to produce the desired action hereinbefore described.

The oil to be treated can also be passed in the form of vapour together with the hydrogenating gas through the liquid solvent which contains the catalyst.

Care should preferably be taken that the liquid, that is the solvent, or the mixture of the same with tar or mineral oil or the like, is vigorously stirred and that there is always a fresh supply of liquid solvent in the reaction chamber. The catalyst is advantageously employed in a state of fine dispersion.

It is advantageous to work in such a manner that the liquid in the reaction chamber is continuously removed therefrom and conducted back again into the same while avoiding cooling, and in this manner, if desired, a greater quantity of reaction gas can also be pumped in with

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it. The sulphur and oxygen content of the circulating liquid is thus very small since these elements are carried away in the form of volatile compounds by the effluent gases. A hot gas cycle, for example as described in the application for Letters Patent No. 27,497/27 (Serial 304343), may also be employed. The quantity of products leaving with the unused hydrogenating gases can be readily regulated by the quantity of gas introduced and thus it is possible to leave the initial materials which are to be treated in the reaction chamber for a very long period of time, and only to remove the products which have been sufficiently treated. This manner of working allows of leaving the participants in the reaction in the reaction chamber for a very long period of time, because any high molecular products formed which would render the catalyst inactive are not precipitated thereon. In addition to the advantage that the products are obtained in a high degree of purity and that the necessity of expensive distillation of the product or return of a portion thereof to the reaction chamber is thus obviated, there is also the advantage that by working according to the present invention a favourable distribution of heat and a great economy in energy are attained. The hydrogen, or gases containing or supplying the same, are suitably introduced into the reaction chamber in a state of fine dispersion, for example through fine nozzles or through solid porous masses.

In order to prevent too strong a concentration of the undesirable high molecular substances in the solvent, the latter can be renewed continuously or at intervals, for example by removing the liquid from the reaction chamber through a filter so that the catalyst remains in the reaction chamber, or by partially or wholly removing the liquid mass from the reaction chamber, separating the catalyst from the liquid and returning the former to the reaction chamber, if desired after a regeneration which can be carried out with or without the employment of pressure for example by grinding in a high speed mill.

The hydrocarbons of low boiling point formed in the reaction chamber, in particular the benzines and also middle oils and the like are drawn off from the reaction chamber in the form of vapour. It is preferable to insert a reflux condenser in the conduit by which the low boiling products leave the reaction chamber in order to return to the reaction chamber any products, which boil at a higher temperature than the desired products. By the process in accordance with the present invention, by which also the material of which the apparatus is constructed is protected, it is possible to convert tars and mineral oils to a great extent into benzines.

In contrast to working in the vaporous phase in the absence of the liquid medium employed according to the present process, for example in the production of benzine from middle oil, there is the advantage that the hydrogen content of the product to be obtained can be varied to a great extent. The reacting materials together with the liquid medium can be removed from and returned to the reaction chamber without appreciable cooling and in this manner very valuable, comparatively pure benzine can be obtained with much less hydrogen. There is also the advantage that the reaction chamber can be much simpler in construction, and that fewer heat exchangers, which on account of the necessary repairs are themselves expensive and which are costly in operation, are necessary and that thus losses of energy are reduced.

The following Examples will further illustrate the nature of the said invention but the invention is not restricted to these Examples.

EXAMPLE 1.

By passing a mixture of about 30 per cent. of carbon monoxide and 70 per cent. of hydrogen at from 390° to 400° Centigrade and at a pressure of 200 atmospheres over a catalyst obtained by fusing together zinc oxide and calcium bichromate, a mixture of higher alcohols is obtained. To a small extent however, high molecular compounds are formed, and these are precipitated on the catalyst and slowly reduce its activity. By carrying out the described reaction in such a manner that the catalyst, during the passage of the gases therethrough, is continuously rinsed by an oil, which is not liable to any substantial decomposition under the reaction conditions and which is as free as possible from asphaltum, for example anthracene oil, flowing in a cycle, the high molecular compounds produced are kept in solution by the rinsing oil and thus cannot be precipitated on the catalyst. The latter therefore retains its activity almost continuously. When the concentration of the high molecular compounds in the circulating rinsing oil become high, the oil is preferably renewed.

EXAMPLE 2.

By splitting a heavy tar from the low temperature carbonisation of brown coal in the liquid phase by employing hydrogen at about 450° Centigrade and at 200 atmospheres and in the presence of a catalyst prepared from a mixture of molybdic acid, chromic acid and manganese carbonate, which is rigidly arranged in the reaction vessel, in consequence of the distilling off of the light splitting products formed, an increase in the concentration of the heavier tar constituents occurs, and these are gradually precipitated on the catalyst and reduce its activity. By introducing anthracene oil in to the reaction vessel, and in such quantity that at least half of the entire liquid in the reaction vessel is anthracene oil, and by passing the said liquid in a cycle, the heavy constituents of the oil subjected to splitting are kept in solution, and the catalyst retains its activity practically continuously.

EXAMPLE 3.

A heavy oil free from asphaltum, obtained by the destructive hydrogenation of coal and of which the greater portion boils about 325° Centigrade is pumped in a high pressure chamber in a cycle, at about 450° Centigrade and 200 atmospheres over a catalyst containing molybdenum and chromium. Then gas oil, which vapourises under the reaction conditions, and hydrogen are introduced, care being taken that by pumping the gases in the hot chamber a brisk movement of the reacting materials occurs. Although by this manner of working the bulk of the heavy oil remains unchanged, the gas oil is completely converted into products boiling below 200° Centigrade. These are carried away from the reaction vessel by the effluent stream of hydrogen. The higher boiling fraction is returned to the furnace by a reflux condenser of the nature of a column, and is pumped in a cycle together with the heavy oil and treated again so that besides benzine and hydrogen no appreciable amounts of other products leave the reaction vessel.

Dated this 26th day of November, 1928.

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

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Valuable Hydrocarbons and Oxygen Derivatives of Hydrocarbons, in particular those of Low Boiling Point.

I, JAMES YATE 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 organized 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:—

In the treatment of liquid or gaseous carbonaceous materials such as tars, mineral oils and the like and of oxides of carbon with hydrogen or gases containing or supplying hydrogen under pressure and at elevated temperatures for the purpose of producing valuable hydrocarbons and oxygen derivatives of hydrocarbons, such as alcohols, ketones and the like, in particular those of low boiling point, there is frequently the disadvantage, when employing catalysts, that the reaction subsides or even ceases entirely after a more or less short period of time. This phenomenon appears to be due to the fact that the initial materials form high molecular substances during the reaction and if catalysts be employed these said substances are deposited in the pores of the catalyst and thus impair its activity.

My foreign correspondents have now found that in many cases the treatment in the gaseous or liquid phase of carbonaceous gases or liquids with hydrogen at elevated temperatures and under pressure and in the presence of catalysts, can be advantageously carried out by adding either before or during the reaction so much of a medium which is liquid under the reaction conditions and which does not take part in the reaction of the gaseous or vaporous substances, that the reaction occurs within this liquid medium the possible injurious formation or deposition on the catalyst of high molecular substances being thus avoided. This manner of working has great practical importance especially in the conversion of middle oils into hydrocarbons of the nature of benzine by treatment with hydrogen under pressure. It can also advantageously be employed for example for the production of methanol from oxides of carbon and hydrogen. It is preferable to choose a liquid medium which is a high boiling organic solvent and which is not liable to decompose under the working conditions, for example anthracene oil and the like. The process of the present invention is not intended to include within its scope processes in which a carbonaceous material is extracted with a solvent and the solvent and extract together are treated with hydrogen at elevated temperature and pressure in the presence of catalysts.

The process may be carried out for example by adding the catalyst in a state of fine dispersion to the initial material for example mineral oil, or to the solvent or to both. The catalyst can also be arranged in a fixed position for example in tubes or pockets of wire gauze which may be fixed to a stirring device.

The oil to be treated can also be passed in the form of vapour together with the hydrogenating gas through the liquid solvent which contains the catalyst.

Care should preferably be taken that the liquid, that is the solvent, or the mixture of the same with tar or mineral oil or the like, is vigorously stirred and that there is always a fresh supply of liquid solvent in the reaction chamber. The catalyst is advantageously employed in a state of fine dispersion.

It is advantageous to work in such a manner that the liquid in the reaction chamber is continuously removed therefrom and conducted back again into the same while avoiding cooling, and in this manner, if desired, a greater quantity of reaction gas can also be pumped in with it. The sulphur and oxygen content of the circulating liquid is thus very small since these elements are carried away in the form of volatile compounds by the effluent gases. A hot gas cycle, for example as described in the application for Letters Patent No. 27,497 A.D. 1927. Serial 304343), may also be employed. The quantity of products leaving with the unused hydrogenating gases can be readily regulated by the quantity of gas introduced and thus it is possible to leave the initial materials which are to be treated in the reaction chamber for a very long period of time, and only to remove the products which have been sufficiently treated. This manner of working allows of leaving the participants in the reaction in the reaction chamber for a very long period of time, because any high molecular products formed which would render the catalyst inactive are not precipitated thereon. In addition to the advantage that the products are obtained in a high degree of purity and that the necessity of expensive distillation of the product or return of a portion thereof to the reaction chamber is thus obviated, there is also the advantage that by working according to the present invention a favourable distribution of heat and a great economy in energy are attained. The hydrogen, or gases containing or supplying the same, are suitably introduced into the reaction chamber in a state of fine dispersion, for example through fine nozzles or through solid porous masses.

In order to prevent too strong a concentration of the undesirable high molecular substances in the solvent, the latter can be renewed continuously or at intervals, for example by removing the liquid from the reaction chamber through a filter so that the catalyst remains in the reaction chamber, or by partially or wholly removing the liquid mass from the reaction chamber, separating the catalyst from the liquid and returning the former to the reaction chamber, if desired after a regeneration which can be carried out with or without the employment of pressure for example by grinding in a high speed mill.

The hydrocarbons of low boiling point formed in the reaction chamber, in particular the benzines and also middle oils and the like are drawn off from the reaction chamber in the form of vapour. It is preferabe to insert a reflux condenser in the conduit by which the low boiling products leave the reaction chamber in order to return to the reaction chamber any products, which boil at a higher temperature than the desired products. By the process in accordance with the present invention, by which also the material of which the apparatus is constructed is protected, it is possible to convert tars and mineral oils to a great extent into benzines.

In contrast to working in the vaporous phase in the absence of the liquid medium employed according to the present process, for example in the production of benzine from middle oil, there is the advantage that the hydrogen content of the product to be obtained can be varied to a great extent, since by suitably regulating the addition of the initial materials the period during which the latter are treated may be varied within a wide range, The reacting materials together with the liquid medium can be removed from and returned to the reaction chamber without appreciable cooling and in this manner very valuable, comparatively pure benzine can be obtained with much less hydrogen, on account of the fact that by suitably regulating the ratio of the supplies of hydrogen and, for example, of middle oil, so that the middle oil is not completely converted in the first stage and is then returned to the reaction chamber and exposed to a further amount of hydrogen, no such great excess of hydrogen as is usually employed, is necessary in this process. There is also the advantage that the reaction chamber can be much simpler in construction, and that fewer heat exchangers, which on account of the necessary repairs are themselves expensive and which are costly in operation, are necessary and that thus losses of energy are reduced.

The catalysts preferably employed according to the present invention are those immune from poisoning by sulphur and in particular those comprising metals of the 6th group of the periodic system in a free or combined state, as for example, molybdenum, tungsten, chromium or uranium. Pressures of above 20 atmospheres, for example 50, 100, 150, 200, 300, 500, or even 1000 or 3000 atmospheres may be employed for the process according to the present invention. In order to make the working at these high pressures possible it is necessary to employ vessels having very thick walls which are carefully tested with regard to resistance to pressure. As examples of elevated temperatures may be mentioned those between about 300° and 700° Centigrade but preferably between about 360° and 500° Centigrade. Temperatures ranging between about 390° and 450° Centigrade are particularly suitable.

The following Examples and the accompanying drawings will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples nor to the specific apparatus shewn in the drawings. Figure 1 has reference to Example 1, Figure 2 to Example 3.

Example 1.

Figure 1 of the drawing shews diagrammatically a vertical section of an apparatus for the production of higher alcohols from carbon monoxide and hydrogen.

a_1 and a_2 are pipes for introducing the initial gases. b_1 and b_2 are valves, c is a heating coil for preheating the initial gas mixture. d is a reaction vessel fitted with a perforated plate f, which supports a catalyst e, m and n are pipes, which lead from a pump o to the reaction vessel d. g is a pipe for drawing off the products obtained. h is a condenser, i a collecting vessel, l a cock for drawing off the condensed liquor and k a pipe for discharging the uncondensed gases and vapours, r is a pipe for supplying fresh material which is liquid under the conditions of working and which does not take part in the reaction, s is a pipe for taking off used liquid solvent. The rate of flow in pipes r and s is controlled by cocks q and p respectively.

Hydrogen and carbon monoxide are passed through the pipes a_1, and a_2, the rate of flow of these gases being controlled by the valves b_1 and b_2, so as to produce a mixture of 70 per cent. of hydrogen and 30 per cent. of carbon monoxide. The said gases are heated in the coil c to a temperature of between 390° and 400° Centigrade and are passed over the catalyst e which is continuously rinsed by an oil, for example, anthracene oil, forced by pump o through pipe m into the reaction vessel. This oil takes off high molecular compounds possibly formed, which drop down to the bottom of the vessel and are drawn off by pump o through pipe n. Fresh liquid solvent may be continuously supplied by the pipe r and used liquid solvent may be drawn off through the pipe s. The aforesaid catalyst e is prepared by fusing together zinc oxide and calcium bichromate. The reaction products pass by pipe g into the condenser h where they are condensed. They are collected into the collecting vessel i and may be drawn off at the cock l. The uncondensed parts of the reaction products are discharged through pipe k. A mixture of higher alcohols is thus obtained. The high molecular compounds produced are kept in solution by the rinsing oil and thus cannot be precipitated on the catalyst. The latter therefore retains its activity almost continuously. When the concentration of the high molecular compounds in the circulating rinsing oil becomes high, the oil is preferably renewed.

Example 2.

In converting a heavy tar from the low temperature carbonisation of brown coal in the liquid phase by employing hydrogen at about 450° Centigrade and at 200 atmospheres and in the presence of a catalyst prepared from a mixture of molybdic acid, chromic acid and manganese carbonate, which is rigidly arranged in the reaction vessel, in consequence of the distilling off of the light split products formed, an increase in the concentration of the heavier tar constituents occurs, and these are gradually precipitated on the catalyst and reduce its activity. By introducing anthracene oil in to the reaction vessel and in such quantity that at least half of the entire liquid in the reaction vessel is anthracene oil, and by passing the said liquid in a cycle, the heavy constituents of the oil subjected to splitting are kept in solution, and the catalyst retains its activity practically continuously.

Example 3.

Figure 2 of the drawing shews diagrammatically a vertical section of an apparatus wherein the conversion of the carbonaceous matter may be carried out in the presence of so much of a liquid medium not taking part in the reaction that the reaction occurs in the liquid phase.

a_1 and a_2 are pipes for introducing hydrogen and a carbonaceous material respectively, b_1 and b_2 are valves, *d* is a pipe for introducing the initial materials provided with an addition of the said liquid medium into the reaction vessel *e* which is fitted with a perforated plate *l* which supports catalyst *f*, *m* is a pipe leading from the reaction vessel to the pump *k*, *g* is a pipe leading from the reaction vessel *e* to the reflux condenser *h*, and *i* is a pipe for drawing off the reaction products. *p* is a pipe for supplying fresh liquid solvent and *q* is a pipe for withdrawing used liquid solvent. The rate of flow in the pipes *p* and *q* is controlled by cocks *n* and *o* respectively.

Hydrogen and gas oil are introduced through pipes a_1 and a_2, the rate of flow being controlled by the valves b_1 and b_2. At *c* the said initial materials are joined with a flow of heavy oil free from asphaltum, obtained by the destructive hydrogenation of coal, and of which the greater portions boils above 325° Centigrade, and are introduced by pipe *d* into the reaction vessel *e* which is filled with the catalyst *f*, which contains chromium and molybdenum and which rests on the perforated plate *l*. Heavy oil is continuously pumped through the reaction vessel by means of the pump *k* being introduced by pipe *d* and removed from the reaction vessel by the pipe *m*. Fresh used liquid solvent may be continuously supplied by the pipe *p* and liquid solvent may be drawn off through the pipe *q*. A temperature of about 450° Centigrade and a pressure of about 200 atmospheres is maintained in the reaction vessel. The gas oil vaporises under the conditions of working. The mixture of gas oil and hydrogen is pumped vigorously into the vessel, so that a brisk movement of the oils contained therein occurs. Although by this manner of working the bulk of the heavy oil remains unchanged, the gas oil is completely converted into products boiling below 200° Centigrade. These are carried away from the reaction vessel through pipe *g* by the effluent stream of hydrogen. The higher boiling fraction is returned to the reaction vessel by the reflux condenser *h* of the nature of a column, and may be pumped in a cycle together with the heavy oil and treated again so that besides benzine and hydrogen no appreciable amounts of other products leave the reaction vessel.

I am aware of my prior Specification No. 317,996 and do not claim anything claimed therein.

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. In the production of valuable liquid hydrocarbons and oxygen derivatives of hydrocarbons by treating carbonaceous liquids or gases in the liquid or gaseous phase with hydrogen or a gas containing or supplying hydrogen at elevated temperatures and under pressures higher than 20 atmospheres in the presence of catalysts the step of adding either before or during the reaction a medium which is liquid under the conditions of working and which does not take part in the reaction of the said carbonaceous materials, for the purpose of preventing the deposition of high molecular substances on the catalysts.

2. In the process as claimed in Claim 1 employing initial materials which are converted into vapours under the reaction conditions, and adding so much of the medium which is liquid under the conditions of working and which does not take part in the conversion of the said fluids that the reaction occurs within the liquid medium.

3. In the process as claimed in Claims 1 and 2, employing high boiling organic solvents which are not likely to decompose and in particular oils of aromatic character as the said medium.

4. In the process as claimed in Claims 1 to 3, carrying out the said conversion in the presence of catalysts immune to poisoning by sulphur.

5. In the process as claimed in Claims 1 to 4, continuously removing the liquid from the reaction chamber and returning it thereto.

6. The process for the production of valuable liquid hydrocarbons and hydrocarbon derivatives by treating carbonaceous materials at elevated temperatures and under pressures higher than 20 atmospheres and in the presence of catalysts substantially as described in each of the foregoing Examples.

7. Valuable liquid hydrocarbons or hydrocarbon derivatives when obtained according to the preceding claiming clauses.

Dated this 8th day of August, 1929.

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

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2nd Edition

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Fig. 1

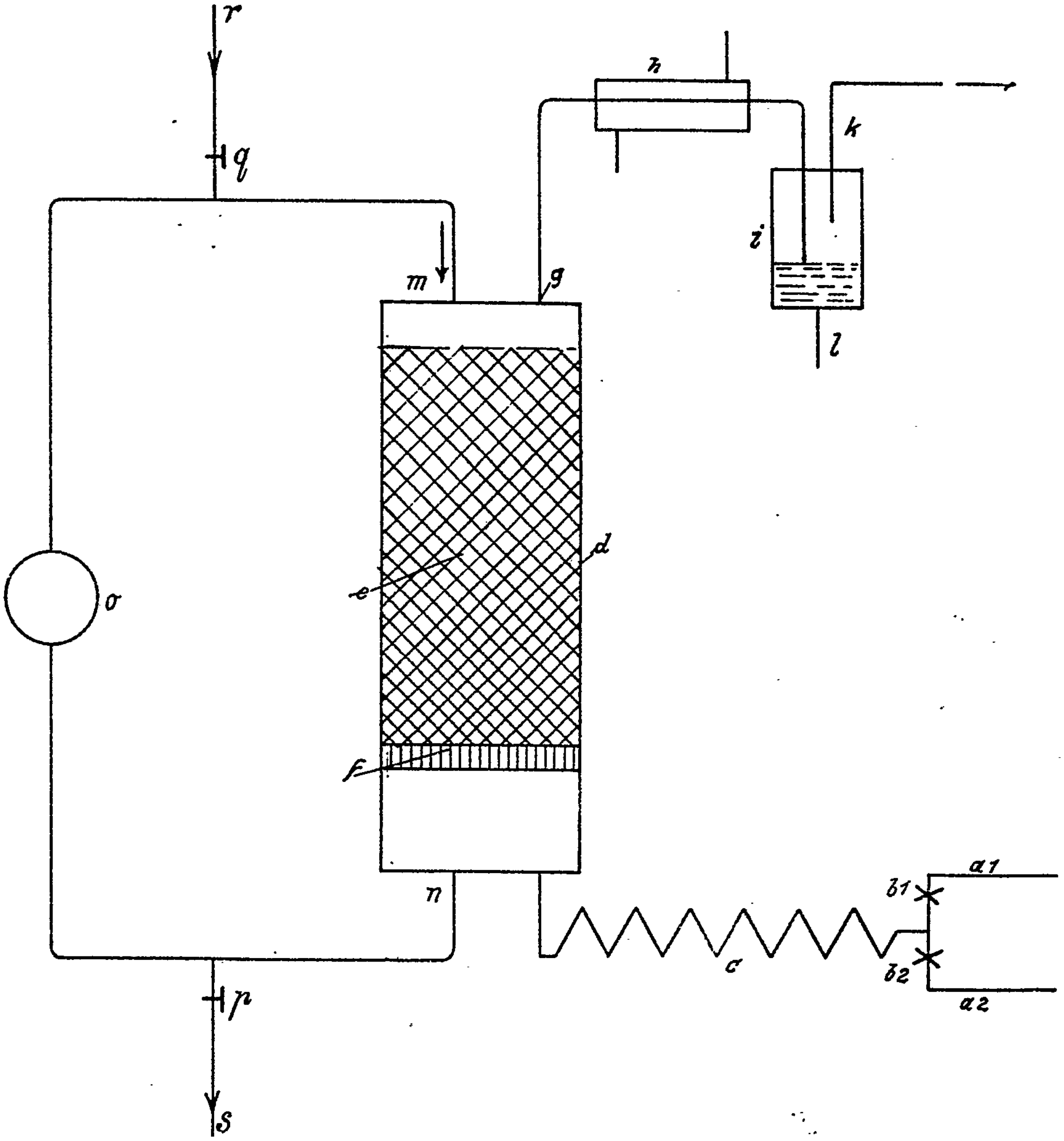

Fig. 2

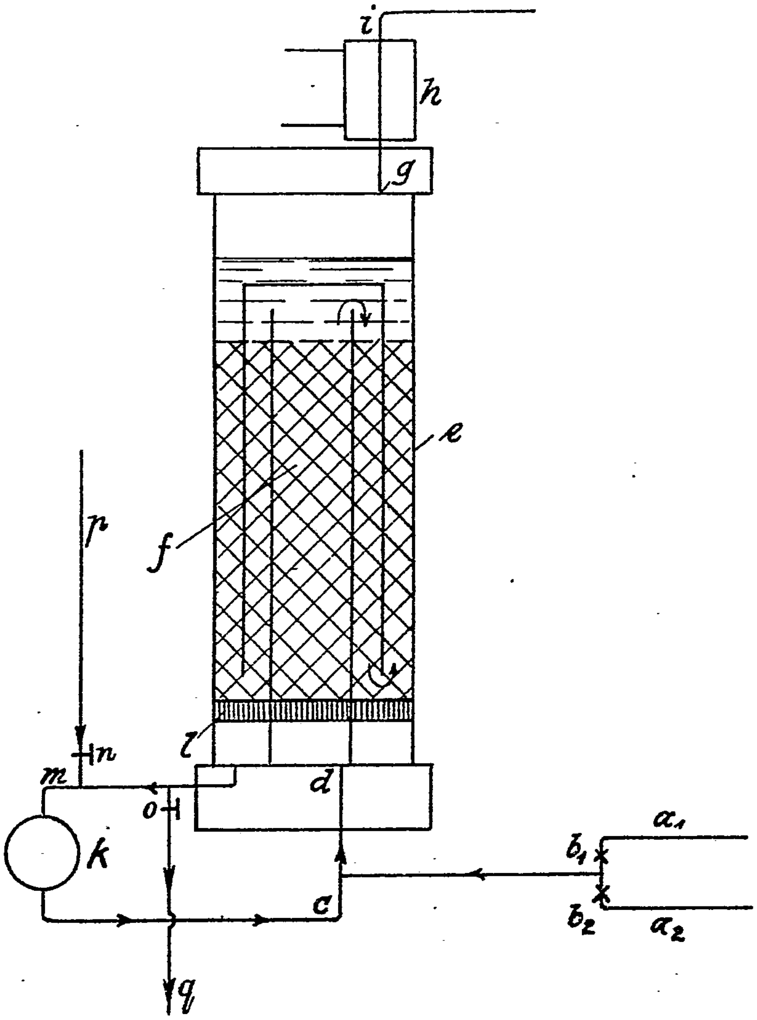

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Fig. 1

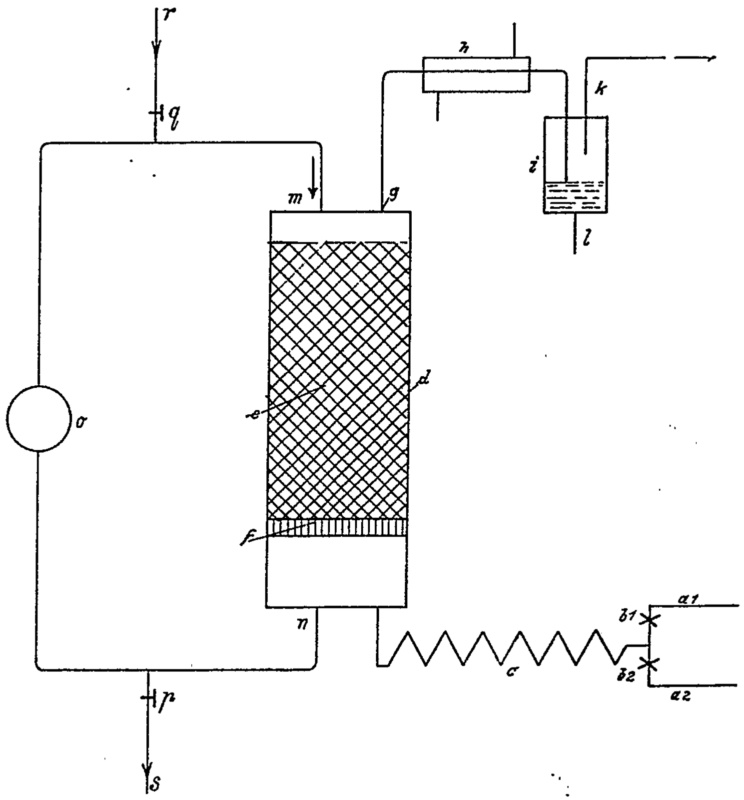
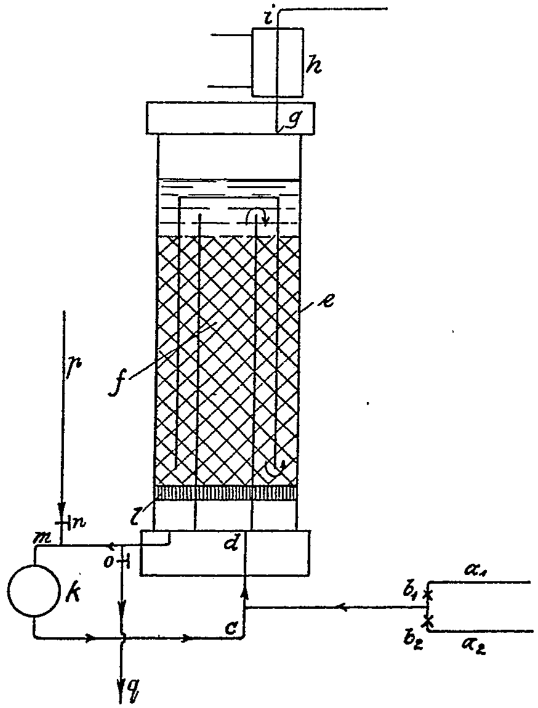


Fig. 2



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