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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Process and Apparatus for the Production of Synthesis Gases mainly consisting of Mixtures of Carbon Monoxide and Hydrogen and of Hydrocarbons therefrom

We, N.V. INTERNATIONALE HYDROGENEERINGS - OCTROOIEN MAATSCHAPPIJ (INTERNATIONAL HYDROGENATION PATENTS COMPANY), of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company (Assignees of PERCIVAL CLEVELAND KEITH, Jr., of Peapack, County of Somerset, New Jersey, United States of America, a Citizen of the United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a process for the production of synthesis gases mainly consisting of mixtures of carbon monoxide and hydrogen and of synthesizing hydrocarbons suitable for use as motor fuel, lubricating oil, Diesel oil, paraffin wax and the like therefrom.

It has already been proposed to produce a gas mixture of carbon monoxide and hydrogen (synthesis gas) from hydrocarbon gases, particularly natural gas, which is predominantly methane. In the production of synthesis gas from hydrocarbon gases it has been found expensive to produce a gas mixture which is free from nitrogen. Natural gas from many producing areas contains considerable amounts of nitrogen, so that synthesis gases produced therefrom also contain this constituent. This production is advantageously effected by converting the hydrocarbons contained in the natural gas by means of steam and carbon dioxide or carbon dioxide alone, in the presence of catalysts at temperatures above 500° Centigrade, generally about 800 to 900° Centigrade. Also gaseous hydrocarbons from other sources such as refinery gases, coke oven gases or fractions thereof may be converted in the said manner.

If the synthesis gas contains inert constituents such as nitrogen or if considerable amounts of methane are formed in the synthesis, it is not possible to recycle without special measures unconverted gases coming from the synthesis back to the reaction, since the inert constituents would accumulate in the cycle. It is therefore necessary to remove such inert constituents from gases to be recycled, at any rate that proportion thereof which it is not desired to have present in the reaction vessel.

We have now found that in the synthesis of hydrocarbons from a synthesis gas mainly consisting of a mixture of carbon monoxide and hydrogen, which mixture is obtained at least in part by conversion of gaseous hydrocarbons with added carbon dioxide, it is advantageous to subject at least part of the gases remaining after the synthesis (tail gases), containing unreacted carbon monoxide, hydrogen, undesired amounts of nitrogen and contingently further constituents to an oxidation, to convert the carbon monoxide to carbon dioxide, to extract the carbon dioxide and to recycle it to the conversion of gaseous hydrocarbons to produce the synthesis gas.

The proportions of carbon monoxide and hydrogen in the synthesis gas may vary within wide limits. The present invention, however, is of particular importance for processes in which the synthesis gas contains more than 30 per cent. by volume and suitably about 50 per cent. or more of carbon monoxide calculated on carbon monoxide and hydrogen.

Any catalysts suitable for the synthesis of hydrocarbons may be employed. Satisfactory results are obtained with mixtures of cobalt-thorium-kieselguhr, nickel-manganese-alumina-kieselguhr, or cobalt-thorium-copper-kieselguhr, prepared by reduction of metallic nitrates with hydrogen. Innumerable combinations of metals precipitated on inert carriers or alloy catalysts have given satisfaction. Good results are also obtained with catalysts in which sintered iron, which if necessary has been further treated, is a prominent component.

The temperature and pressure conditions are those usual for the synthesis reaction. Temperatures between 170° and 420°

[*Price* 1/-]

Centigrade are preferably employed, and the pressures may be more than 2 atmospheres, for example, between 2 and 700 atmospheres, say 70 to 200 or 300 atmospheres. Higher pressures or lower pressures down to atmospheric or therebelow may also be used.

The method of separating carbon monoxide and nitrogen in accordance with the present invention by converting carbon monoxide to carbon dioxide and separating the gases which can be done by a number of well-known and simple methods, is highly desirable since these two gases themselves can be separated direct only by relatively expensive methods.

In certain cases, for example, if the synthesis is only effected to a limited extent, it has been found desirable to recycle tail gases from the synthesis step direct to the synthesis. It may also be desirable to return the tail gases containing gaseous hydrocarbons, which is practically always the case, to the convertor for the production of synthesis gas. In order to prevent the accumulation of inert gases in these cycles a portion of the recycle gases in accordance with the present invention may be withdrawn, the carbon monoxide contained therein oxidized to carbon dioxide, the nitrogen eliminated, and the carbon dioxide returned to the synthesis gas manufacturing step. By this method of operation inert nitrogen is not allowed to build up beyond certain limits in the recycle stream since a portion of the stream is withdrawn and freed of nitrogen.

If desired not all of the synthesis gas need be produced from gaseous hydrocarbons, but a portion thereof by gasification of solid fuels.

The accompanying drawing is a diagrammatic view of one form of apparatus capable of carrying out the process and invention and is given by way of example but it should be understood that the invention is not limited to the process and apparatus illustrated.

Methane from any suitable source, such as a holder 1, passes through line 2 and is forced by pump 3 through line 4 to a convertor 5 containing a catalyst positioned in beds therein, or checker-work brick built of catalytic brick-work built up in the interior of the container. Prior to charging the gas to the system it is preferably desulphurized by any suitable method well known in the art. Organic sulphur compounds may be removed or converted by a catalytic method. A conventional method for removing hydrogen sulphide is that in which the gas is contacted with tri-ethanolamine. Other processes of a similar character use sodium phenolate, diaminoisopropanol, alkali metal salts of amino acids and the like. If desired, sodium hydroxide may be used or combinations of the above method with the use of sodium hydroxide may be employed to reduce the sulphur content of the methane to about 0.2 milligram per cubic metre. The removal of sulphur is desirable in order to avoid poisoning of the catalyst.

Carbon dioxide is added to the methane charge through pipe 6 controlled by valve 7. In the convertor 5 the methane-carbon dioxide mixture is raised to a temperature sufficiently high to convert the mixture to carbon monoxide and hydrogen substantially in the ratio of one to one. The following reaction takes place in the regenerator:—

$$CH_4 + CO_2 + X \text{ cal.} \rightarrow 2CO + 2H_2$$

This reaction will take place within the vicinity of 1100° Centigrade in the presence of a catalyst comprising nickel deposited on clay of high alumina content, such as fire clay or alundum.

The ratio of carbon monoxide to hydrogen may be varied by the addition of steam through line 8.

On being discharged from the convertor 5, the mixture of carbon monoxide and hydrogen is directed through line 9 to a synthesis chamber 10 wherein is maintained a catalyst of the character previously mentioned. Temperatures in the synthesis chamber may be maintained somewhat above 200° Centigrade to obtain a proper reaction. In order to obtain and control the temperatures in the synthesis chamber, a cooler 11 is positioned in the line 9. This cooler is supplied with a cooling medium, either from products of the system or from an outside source. The recirculated carbon dioxide hereinafter described would serve as a proper medium to assist in reduction of the temperature of this synthesis gas mixture. After reaction, the products are discharged from the chamber through pipe 12, thence to condenser 13, through line 14 to a separator 15. The separator is equipped with a liquid draw-off line 16 controlled by valve 17 and an overhead line 18 for removing the unreacted gases.

The unreacted gases are principally carbon monoxide and nitrogen, the latter being inert in the system. Provision is made in the form of a pipe 19 controlled by valve 20 for recirculating desired amounts of this gas back to be reintroduced into the convertor with the methane charge. Gas from the separator that is not recycled is directed by regulation of valve 21 in line 18 to a heater 22 where it is raised to a temperature of the order of

550° to 850° Centigrade. After heating, the gas is passed through line 23 to an oxidizer 24 where carbon monoxide in the gas is converted to carbon dioxide. The oxidizing stage comprises a tank or container partially filled with a porous bed of a metallic oxide, for example, ferrite or iron oxide, diagrammatically shown. Besides carbon monoxide also hydrocarbons, which may be contained in the gas, may be oxidized to give carbon dioxide and water.

This oxidizing stage may be included in the system in the form of alternate chambers so that one can be isolated from the system to be regenerated while the other is used. To regenerate the iron oxide, steam is introduced through line 24*a* under proper temperature and pressure conditions and exhausted through pipe 24*b*. The conversion of the iron oxide to metallic iron or lower oxide takes place in changing carbon monoxide to carbon dioxide, and regeneration with steam converts the metallic iron or lower oxide back to its oxide state, which may be a higher oxide, with accompanying production of hydrogen.

After passing through the oxidizing chamber, the carbon dioxide and nitrogen mixture from the convertor 24 is passed through cooler 38 and introduced through pipe 25 into tower 26. In this tower the gas is passed counterflow with a liquid absorber material selective to and adapted to remove the carbon dioxide from the mixture. This liquid absorber medium is introduced into the tower through pipe 27 and flows downwardly in an opposite direction to the rising gases, to be removed from the bottom thereof with the absorbed carbon dioxide through pipe 28. Its temperature is raised in a heater 29, after which it is charged through pipe 30 to the stripping tower 31. In the stripping tower the carbon dioxide is driven off and passes out through the overhead line 32, through which it is returned by means of a compressor or blower not shown in the drawing to the convertor 5. The absorber liquid is discharged from the bottom of tower 31 through pipe 33 regulated by valve 34, and after having its temperature reduced in cooler 35 it is recirculated through pipe 27 into the top of the absorber 26. The absorption and stripping cycle is one conventional to the art.

In an alternate method of operation the tail gas collected from the synthesis may be burned with air to furnish heat for the production of synthesis gas. Carbon dioxide is recovered from the flue gas by absorption and returned to the synthesis gas manufacturing step.

In a preferred embodiment of the method a major portion of the tail gas from the synthesis step is recycled through line 36 controlled by valve 37 to the synthesis step.

The removal of carbon dioxide in tower 26 is effected by conventional methods well known in the art, such as the use of mono-ethanolamine in a 15 to 30 per cent. aqueous solution.

It is to be understood that our invention is not to be limited to the specific details shown and described.

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

1. A process for the synthesis of hydrocarbons from synthesis gas mixture of carbon monoxide and hydrogen, which mixture is obtained by conversion of gaseous hydrocarbons with added carbon dioxide, characterised in subjecting at least part of the gases remaining after the synthesis (tail gases) containing unreacted carbon monoxide, hydrogen, nitrogen and contingently further constituents, to an oxidation to convert the carbon monoxide to carbon dioxide, extracting the carbon dioxide and recycling it to the conversion of gaseous hydrocarbons for the production of the synthesis gas.

2. A process as claimed in claim 1, characterised in recycling a part of the tail gases to the hydrocarbon synthesis and subjecting another part of the tail gases to an oxidation to convert carbon monoxide to carbon dioxide, extracting the carbon dioxide and recycling it to the conversion of gaseous hydrocarbons for the production of synthesis gas.

3. A process as claimed in claim 1 or 2, characterised in recycling part of the tail gases to the conversion of gaseous hydrocarbons for the production of synthesis gas, subjecting another part of the tail gases to oxidation to convert carbon monoxide to carbon dioxide, extracting the carbon dioxide and recycling it to the said conversion of gaseous hydrocarbons.

4. In the process as claimed in any of claims 1 to 3, effecting the oxidation of carbon monoxide to carbon dioxide by means of a metallic oxide.

5. In the process as claimed in any of claims 1 to 4, effecting the oxidation of carbon monoxide to carbon dioxide by means of an iron oxide.

6. A process as claimed in any of claims 1 to 5, which comprises oxidising to carbon dioxide and water also hydrocarbons contained in the tail gases besides carbon monoxide.

7. Apparatus for the production of mix-

tures of carbon monoxide and hydrogen and of hydrocarbons therefrom, comprising a convertor for the conversion of gaseous hydrocarbons into carbon monoxide and hydrogen with added carbon dioxide, a catalyst chamber for the conversion of the said gas mixture into hydrocarbons, a condenser and separator for the obtained liquid hydrocarbons, means for returning unreacted gases to the convertor and the catalyst chamber, means for oxidizing carbon monoxide contained in the unconverted gases into carbon dioxide, means for extracting such carbon dioxide and means for returning the carbon dioxide to the convertor for the production of synthesis gas.

8. Hydrocarbon products when obtained in a process as claimed in any of claims 1 to 5.

Dated this 15th day of May, 1939.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered Patent Agents.

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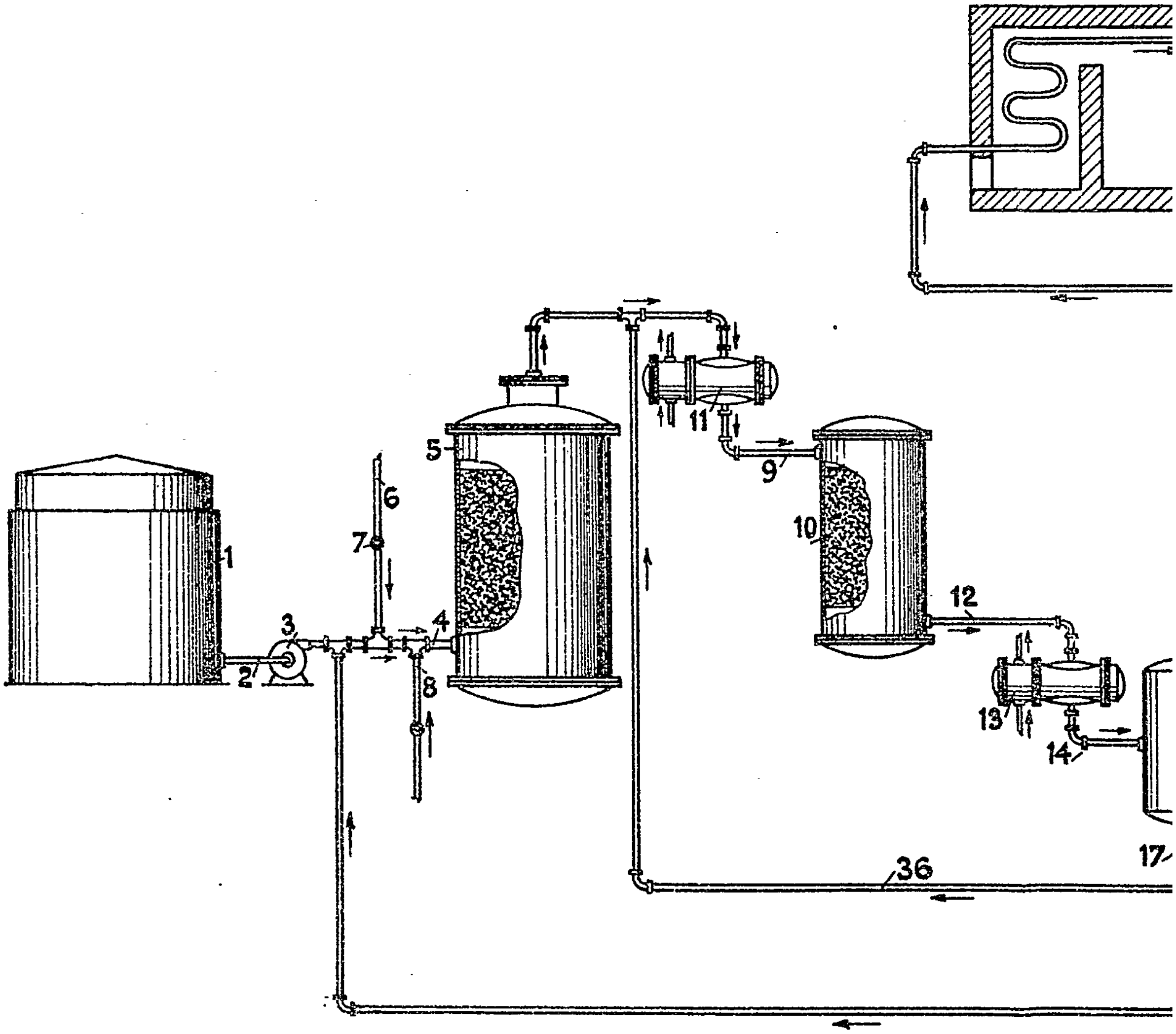

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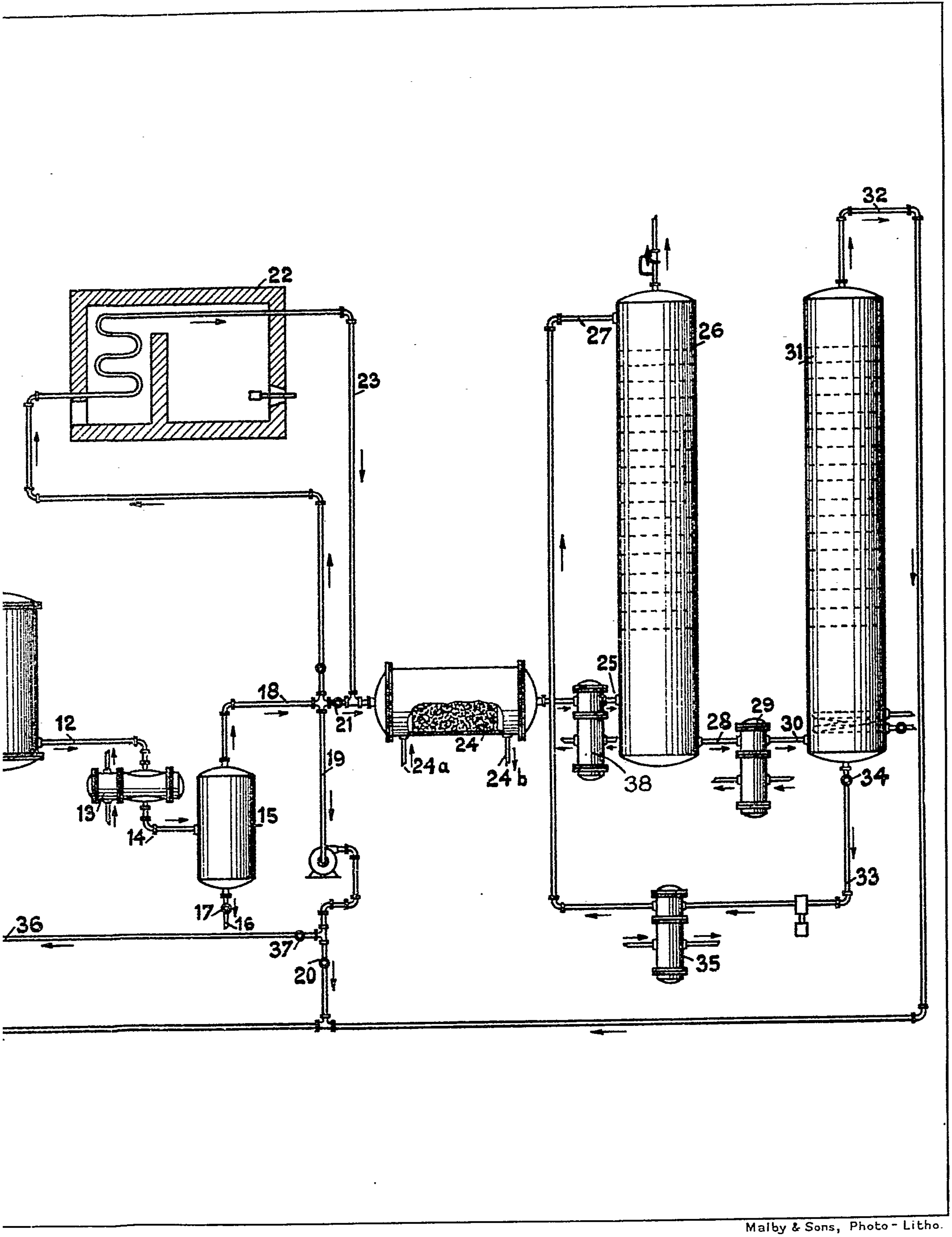

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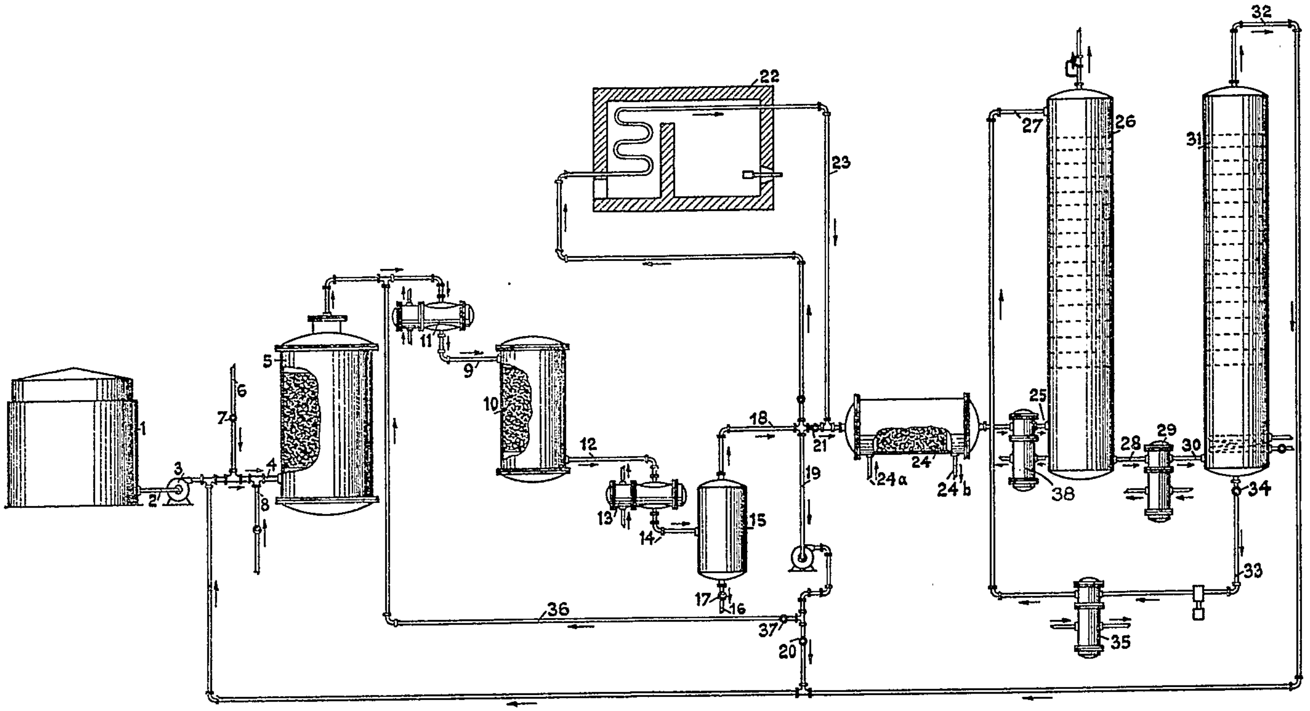

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