

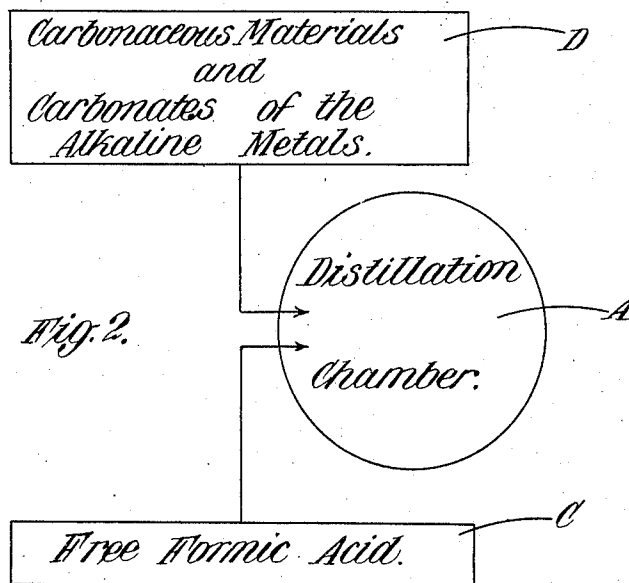
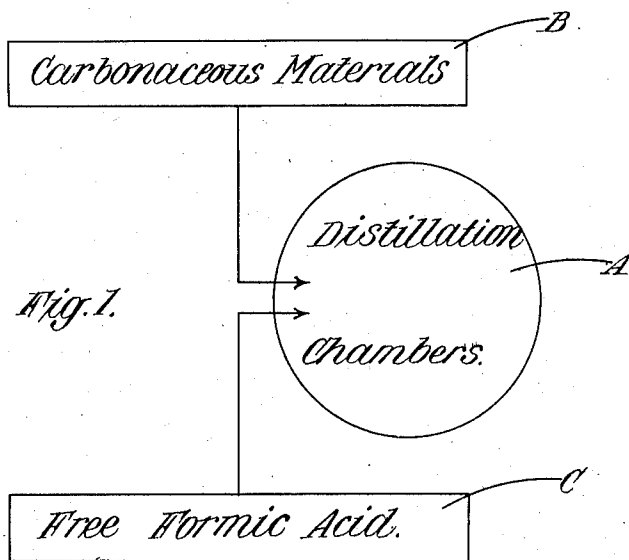
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TREATMENT OF CARBONACEOUS MATERIAL

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UNITED STATES PATENT OFFICE.

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TREATMENT OF CARBONACEOUS MATERIAL.

Original application filed November 27, 1922, Serial No. 603,696, and in Great Britain December 3, 1921.
Divided and this application filed March 7, 1925. Serial No. 13,917.

This invention is a division of my pending application Serial No. 603,696, filed November 27, 1922, and relates to the manufacture and utilization of formic acid more especially for use in connection with the production or conversion of liquid hydrocarbons, the chief object of the invention being to "crack" or transform liquid hydrocarbons or to obtain an increased yield of the more readily liquefiable constituents or condensible hydrocarbons especially during the distillation of carbonaceous materials, such as coal, lignite, peat, shale, wood and the like. A further object of the invention is to cheapen and simplify the manufacture or production of formic acid.

As is well understood, the amount of liquid or condensible hydrocarbons obtained by destructive or other forms of distillation depends primarily upon the amount of volatile matter contained in the material to be distilled and secondly upon the temperature of distillation. In distilling processes as at present carried on, only a percentage of the volatile hydrocarbons contained in the carbonaceous material has been obtained in liquid form, the rest of the volatile hydrocarbons passing off during the process of distillation in the form of a so-called permanent gas, that is to say, a gas which cannot be liquefied unless at an extremely low temperature and under high pressure.

In order to increase the volume of condensible or liquefiable hydrocarbons yielded up during the process of distillation it has been proposed to add to the carbonaceous material before or during the process of distillation certain other materials with the object of exercising a so-called catalytic action thereon, oxidation or hydrogenation being thereby caused to take place in such a way that the relative proportions of the carbon and hydrogen atoms present in the hydrocarbons have been altered so as to produce new combinations which give rise to an increased yield of the more readily liquefiable constituents of the hydrocarbons.

One of the substances which it has been proposed to use for this purpose has been the salts of formic acid, preferably sodium formate, this substance being mixed in various proportions with the carbonaceous material

which is to be distilled and, by its use, a higher proportionate yield of liquid hydrocarbon has been stated to result.

Up to the present time, however, these attempts have been more or less of an experimental character and have not been developed on a commercial scale on account of the fact that the cost of an active catalyzer which would produce oxidization or hydrogenation, or of the sodium formate, was out of all proportion to the value of the increased yield of liquefiable hydrocarbons obtained by its use.

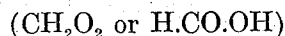
According to one feature of the present invention formic acid is produced directly from methane or a gas containing methane, in the presence of a metallic catalyzer, preferably a metallic oxide catalyzer, or from carbon monoxide in the presence of water vapour and a metallic catalyzer.

A gas also suitable for the catalytic production of formic acid consists for instance of so-called air gas, composed principally of carbon monoxide and nitrogen, or ordinary coal gas, containing methane, or natural gas may be used.

In the case of methane or a gas containing methane the gas is passed over a suitable metallic catalyzer or metallic oxide catalyzer and the following reaction takes place.



In the presence of the catalyzer, the CO combines with the H_2O to produce formic acid.

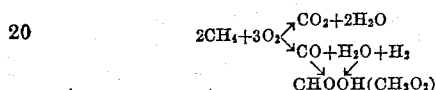


The metallic catalyzer which I have found most suitable may be manufactured as follows:—An activated copper suboxide is produced by precipitating copper from a solution of copper sulphate by means of metallic zinc the copper sulphate being greatly in excess so as to ensure that no metallic zinc is present. The precipitated copper suboxide is thereafter washed and boiled so as to remove as far as possible all traces of zinc and afterwards dried and roasted in the air. Although I have found an activated copper sub-oxide produced in the foregoing manner to be satisfactory, other copper oxides precipitated from copper salts

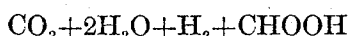
(whether organic or inorganic and by any suitable method including Sabatiers method) or ordinary granulated or powdered copper may also be employed, provided the precipitate is activated by being moistened in a zinc sulphate solution.

In manufacturing free formic acid from methane I have found that satisfactory results can be obtained by proceeding as follows:—

Pure methane, made for example, by the dry distillation of sodium acetate and sodium lime in excess, is carefully cleansed of impurities and conducted over or through the fine spongy granules of an activated copper sub-oxide produced in the foregoing manner. The methane appears to be split up and oxidized in the following manner:—



the resulting products being therefore as follows—



In the foregoing reaction the methane takes its oxygen from the copper sub-oxide, as no free oxygen is required. The reaction is an endothermic one and requires a temperature ranging from 250° to 800° centigrade.

When manufacturing formic acid from carbon monoxide or a gas containing carbon monoxide the reaction is carried on in the presence of water vapour in addition to the metallic catalyzer.

Chemical analysis of the activated copper sub-oxide produced in the foregoing manner shows that it appears to approach very closely the formula Cu_2O before acting on the methane of carbon monoxide. After a comparatively short time however, the copper sub-oxide becomes inactive and appears to have lost a certain amount of its oxygen. At the same time it becomes lighter in colour and analysis gives the formula Cu_4O or $\text{Cu}_2\text{Cu}_2\text{O}$. In order to revivify the copper sub-oxide I may moisten the same with a very weak solution of zinc sulphate. After treatment in this way the copper sub-oxide becomes re-activated and the operation of revivifying the vitiated copper sub-oxide can be repeated over and over again. Precipitated copper sub-oxide produced as aforesaid retains its activity for a prolonged period.

According to a further feature of the present invention free formic acid is admitted in vapour form into the interior of a distillation chamber, retort or the like containing carbonaceous materials which are undergoing distillation, the formic acid being preferably produced as aforesaid from methane, air gas or a gas containing methane or carbon monoxide by the aid of a suit-

able catalyst as a step in the process of distillation. The carbonaceous material may contain a small percentage of admixed carbonates of sodium, potassium or calcium.

The hydrogen liberated during the reaction which results in the production of formic acid, being in the nascent state, is very active in promoting new hydrocarbon products, while at the high temperature prevailing within the distillation chamber or retort, the formic acid is immediately decomposed and further nascent hydrogen is set free.

The catalytic reaction for the production of formic acid being endothermic, that is to say, requiring heat, the heat can conveniently be supplied by utilizing the so-called sensible or mechanical heat of the carbon monoxide or methane itself as it issues from an adjacent producer. After the reaction is completed or carried out to the desired extent, the spent gases, containing free formic acid in the form of vapour, may be injected or admitted to the distillation chamber, retort, or other chamber containing the carbonaceous material or the hydrocarbons which are being distilled or converted. By employing free formic acid vapour in the manner above described, and utilizing the activity of the nascent hydrogen formed in the retort by the decomposition of the formic acid, the proportionate yield of liquid or condensible hydrocarbons is very greatly increased. In cases where the distillation of carbonaceous materials is carried out in a retort which is heated internally by means of the sensible heat of producer gas, such as, for example, air gas as mentioned above or water gas, it is possible to by-pass into a suitable chamber any convenient amount of such gas in the hot state at which it leaves the producer, and, after the conversion of the whole or part of the carbon monoxide into formic acid, this gas may be allowed to mingle, for the purpose described, with the main supply of gases as they enter the retort, or it may be admitted at any other convenient point.

It is to be understood that the present process may also be applied to the conversion of liquid hydrocarbons, the hydrocarbons to this end being heated in a suitable chamber until they volatilize and the free formic acid being admitted to the said chamber, or other gases of the hydrocarbon series may be similarly treated, for example, acetylene gas may be converted into formic acid or, in the presence of hydrogen into formaldehyde. The manufacture of acetic acid or the treatment or conversion of other hydrocarbons, industrial gases, or gases containing hydrocarbons, may also be effected by passing the same over an activated copper sub-oxide prepared as aforesaid, as I have found that the aforesaid copper sub-

oxide converts or produces chemical changes in the said gases.

In order that the said invention may be clearly understood and readily carried into effect the same will now be described more fully with reference to the accompanying drawing, in which,

Figure 1 illustrates diagrammatically the distillation apparatus associated with means for supplying thereto both carbonaceous materials and free formic acid.

Figure 2 is a diagrammatic view illustrating a distillation apparatus associated with a source of supply of carbonaceous materials and carbonates of the alkaline metals, as also a supply of free formic acid.

Referring to the drawings, A is the distillation chamber; B is the source of supply of carbonaceous materials and C is the source of supply of free formic acid. In Figure 2, D is a source of supply of carbonaceous materials mixed with carbonates of the alkaline metals.

What I claim and desire to secure by Letters Patent of the United States is:—

1. A method of increasing the volume of condensible hydrocarbons obtained by destructive or other forms of distillation, which consists in admitting free formic acid in vapour form into the interior of a distillation chamber containing the carbonaceous materials which are undergoing heat treatment.

2. A method of increasing the volume of condensible hydrocarbons obtained by destructive or other forms of distillation which consists in admitting free formic acid in vapour form into the interior of a distillation chamber containing the carbonaceous materials which are undergoing heat treatment, carbonates of the alkaline metals being admixed with the carbonaceous materials prior to the admission of the formic acid thereto.

3. A method of increasing the volume of condensible hydrocarbons obtained by destructive or other forms of distillation which consists in admitting free formic acid in vapour form into the interior of a distillation chamber containing the carbonaceous materials which are undergoing heat treatment, sodium carbonate being admixed with the carbonaceous materials prior to the admission of the formic acid thereto.

4. The process of cracking or converting liquid hydrocarbons which consists in heating the same in a suitable chamber until they volatilize and in admitting free formic acid to the said chamber in order to produce an increased yield of the more readily liquefiable constituents of the hydrocarbons.

HARALD NIELSEN.