[Second Edition.]

NOTICE.
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PATENT SPECIFICATION

Application Date: Oct. 23, 1925. *No. 26,593/25.* 266,410

Complete Accepted: Feb. 23, 1927.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Methanol and other Oxygenated Organic Compounds.

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 the Badische Anilin and Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a corporation organised according to German laws) 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 an economical method for the catalytic production of methanol and other alcohols or oxygenated organic compounds. The synthetic manufacture of these compounds is now carried out with mixtures of carbon monoxide or dioxide with hydrogen, which mixtures are ordinarily obtained by converting coke into water gas and enriching the latter in hydrogen to the desired degree; this may be done either by adding hydrogen or by withdrawing carbon monoxide as such or by decomposing it with steam under the influence of catalysts to produce hydrogen and carbon dioxide. The coke required for the production of such gas mixtures by this method is, however, an expensive raw material.

My foreign correspondents have now found that the catalytic production of methanol and other oxygenated organic compounds can be much more advantageously and economically carried out by employing gas mixtures obtained from gases containing considerable quantities of gaseous hydrocarbons which gases are available at a much cheaper cost. For example, gases obtained by the distillation of bituminous coal, whether in gas works or in coke ovens or in any other plant, or natural gas, or gases obtained in cracking processes and the like, can be used.

According to the present invention the process consists in decomposing the hydrocarbons contained in the said gases by partial oxidation with a restricted quantity of oxygen or a gas rich in oxygen so as to transform part or all of the hydrocarbons into carbon monoxide and hydrogen and passing the resulting gas mixture either directly or after removing the sulphur compounds, if such be present, and/or adjusting the carbon monoxide and hydrogen ratio if necessary, over a methanol forming catalyst. When the initial gases contain any heavy or unsaturated hydrocarbons it is preferable to first separate them in view of their high commercial value, prior to the decomposition with oxygen which decomposition is then effected with the remaining hydrocarbons, particularly methane. The decomposition may as described in my prior Specification No. 231,218, be carried out with pure oxygen or with a gas rich in oxygen and it is effected at a high temperature and preferably in the presence of fireproof contact bodies. Contact bodies containing a metal, for example magnesia on which nickel has been precipitated, or molten iron alloys are specially suitable. The said decomposition of the hydrocarbons or gases containing hydrocarbons may advantageously be effected in the presence of considerable quantities of water vapour or carbon dioxide or both, with which mixtures it may be possible to preheat the gases to a very high temperature by means of heat generated or otherwise, without any decomposition taking place. As most industrial gases contain sulphur in a highly obnoxious form, particularly as difficultly decomposable organic sulphur compounds, profit is in such cases derived by the conversion of such undesirable sulphur compounds into sulphuretted hydrogen or sulphur dioxide simul-

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taneously with the decomposition of the hydrocarbons which newly formed sulphur compounds can be removed with ease in any manner usual or suitable for the removal of sulphuretted hydrogen, for example, by treatment with alkalies or by passing the gases over heated metallic copper, or through active charcoal, or in any other suitable manner.

In some cases, for example when decomposing natural gas in the manner before described, the gas mixture obtained has at once a composition suitable for the synthetic production of organic compounds. In other cases, the percentage of either hydrogen or carbon monoxide must be adjusted which can be done without any difficulty, for example by catalytically decomposing part of the carbon monoxide with steam in the presence of iron oxide or other suitable catalysts when the percentage of carbon monoxide is too high, or by adding gases rich in carbon monoxide when the mixture lacks that gas. Water gas, especially such as is obtained with the aid of oxygen or gases rich in oxygen, as an admixture to the steam and possessing a particularly high percentage of carbon monoxide, may be used for increasing the percentage of carbon monoxide. The percentage of the gas mixture need not, however, necessarily be brought into that required for the reaction. The gases containing one of the components, for example hydrogen in great excess, may also be used even when working in a circulatory system, in which case part of the residual gases having undergone the reaction and being thereby enriched in hydrogen, is continuously withdrawn in such a ratio to the fresh gases introduced as to maintain a constant composition of the gas entering the contact vessel, as described in my co-pending Application No. 26,083 A.D. 1925 (266,405).

The following examples will serve to further explain how the invention may be carried into practical effect but the invention is not restricted to these examples.

Example 1.

Coke oven gas is freed from benzene hydrocarbons and from the bulk of the hydrocarbons of the ethylene series by suitable treatment with active carbon, and the gas so treated having for example a composition of 2 per cent. of carbon dioxide, 2 per cent. of heavy hydrocarbons, 7 per cent. of carbon monoxide, 52.5 per cent. of hydrogen, 29.5 per cent. of methane and 7 per cent. of nitrogen, is mixed with 23 per cent. of oxygen and partially combusted with the latter at about 1000 degrees Centigrade in the presence of nickel-coated magnesia. The resulting gas mixture consists of 1.5 per cent. of carbon dioxide, 26 per cent. of carbon monoxide, 64 per cent. of hydrogen, 3.5 per cent. of methane and 5 per cent. of nitrogen. This mixture is carefully purified from any sulphur compound and other obnoxious admixtures, such as iron carbonyl, for example by treatment with alkali and active charcoal, and passed in a circulatory system over a contact mass suitable to induce the formation of methanol, for example of the kind described in Specification No. 227,147, at 400 degrees Centigrade and at about 400 atmospheres. The gases leaving the contact space are cooled whereby ample quantities of methanol are condensed. Part of the residual gases is continuously withdrawn from the circulating system in the ratio of 1240 cubic metres for each 3500 cubic metres of fresh gases added. In this case the circulating gas reaches the catalyst with a constant composition, possessing 12.3 per cent. of carbon monoxide and 58.9 per cent. of hydrogen.

Example 2.

The gas mixture produced as described in Example 1 by partial combustion of coke oven gas from which benzene and part of the olefines had been removed, is mixed in the proportion of 10 volumes to 1 volume with water gas prepared from coke by means of steam and oxygen in a continuous operation and having the composition of 6.7 per cent. of carbon dioxide, 69.8 per cent. of carbon monoxide, 22.5 per cent. of hydrogen and 1 per cent. of nitrogen. The mixed gas consisting of 2 per cent. of carbon dioxide, 30 per cent. of carbon monoxide, 60.2 per cent. of hydrogen, 3.2 per cent. of methane and 4.6 per cent. of nitrogen, is then used for the production of methanol as described in the foregoing example. Natural gas, or other gases containing hydrocarbons, may be treated in a similar way, and the gases produced thereby employed for the catalytic production of methanol and other alcohols.

Example 3.

100 cubic metres of oil gas containing 3 per cent. of carbon dioxide, 40 per cent. of heavy hydrocarbons, 7 per cent. of carbon monoxide, 15 per cent. of hydrogen, 30 per cent. of saturated hydrocarbons (C_nH_{2n+2}), 5 per cent. of nitrogen are mixed with 150 cubic metres of steam and 40 cubic metres of oxygen and partially combusted at between 900 degrees and 1000 degrees Centigrade in the

presence of a catalyst consisting of 90 per cent. of alumina and 10 per cent. of nickel. The resulting gas, the volume of which is about 300 to 350 cubic metres, has about the following composition: 14 per cent. of carbon dioxide, 28 per cent. of carbon monoxide, 56 per cent. of hydrogen, 1.6 per cent. of nitrogen and 0.4 per cent. of methane. The gas is purified, compressed to a pressure of 200 atmospheres and passed over a catalyst suitable for causing the formation of methanol, for example of the kind described in Specification No. 227,147, at 400 degrees Centigrade. The reaction gases are passed, while maintaining the pressure, through a cooled receiver where ample quantities of methanol are condensed.

I am aware that it has been repeatedly suggested to convert hydrocarbons with a view to produce gas mixtures containing hydrogen and either lamp black or carbon monoxide when steam or air was used for the decomposition, and it is also known to further treat the gas mixture so obtained in order to produce a mixture of hydrogen and nitrogen suitable for the synthesis of ammonia. I do not claim the process of decomposing hydrocarbons for itself nor any further treatment thereof with the intention of connecting it with the synthetic ammonia manufacture, but I claim as my invention the combined process of making a mixture of hydrogen and carbon monoxide by the decomposition of hydrocarbons or an industrial gas containing hydrocarbons and employing the gases so obtained for the synthetic manufacture of methanol or other oxygenated organic compounds, which in this manner can be produced very conveniently.

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 manufacture and production of methanol or other oxygenated organic compounds by catalytically treating mixtures of hydrogen and carbon monoxide at an elevated temperature and pressure consisting in partially oxidising, preferably with the aid of a contact mass containing a metal, a gas consisting of or containing hydrocarbons such as coal gas, coke oven gas, natural gas, cracking gases and the like with a restricted quantity of oxygen or a gas rich in oxygen, with or without an addition of water vapour or carbon dioxide or both to the gas containing hydrocarbons, so as to transform part or all of the hydrocarbons into carbon monoxide and hydrogen, and passing the resulting gas mixture, either directly or after removing the sulphur compounds if such be present and/or adjusting the carbon monoxide and hydrogen ratio if necessary, over a methanol-forming catalyst.

2. The process claimed in the preceding claiming clause in accordance with each of the foregoing examples.

3. Methanol or other oxygenated organic compounds when obtained in accordance with the preceding claiming clauses.

Dated this 23rd day of October, 1925.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London,
W.C. 2,
Agents.

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ERRATUM.

SPECIFICATION No. 266,410.

Page 2, line 122, *for* "($CnH_{2}n \div 2$)," *read* "($CnH_{2}n+2$),"

PATENT OFFICE,
May 18*th*, 1927.