June 3, 1941. P. NASHAN 2,244,210

METHOD FOR PARTIALLY OXIDIZING METHANE

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Fig. 1.

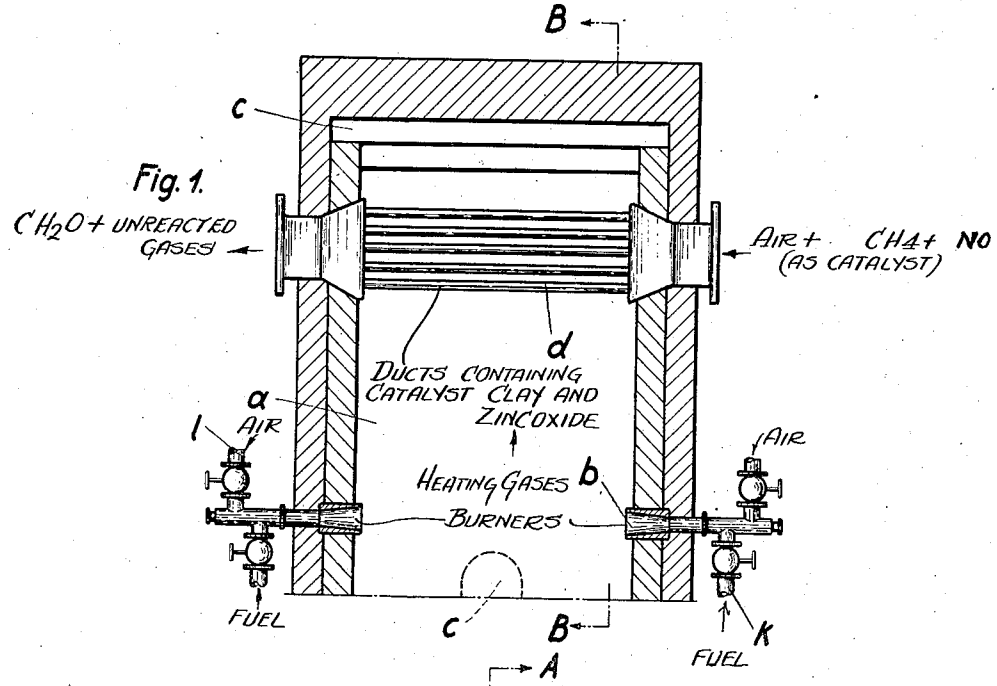

Fig. 2

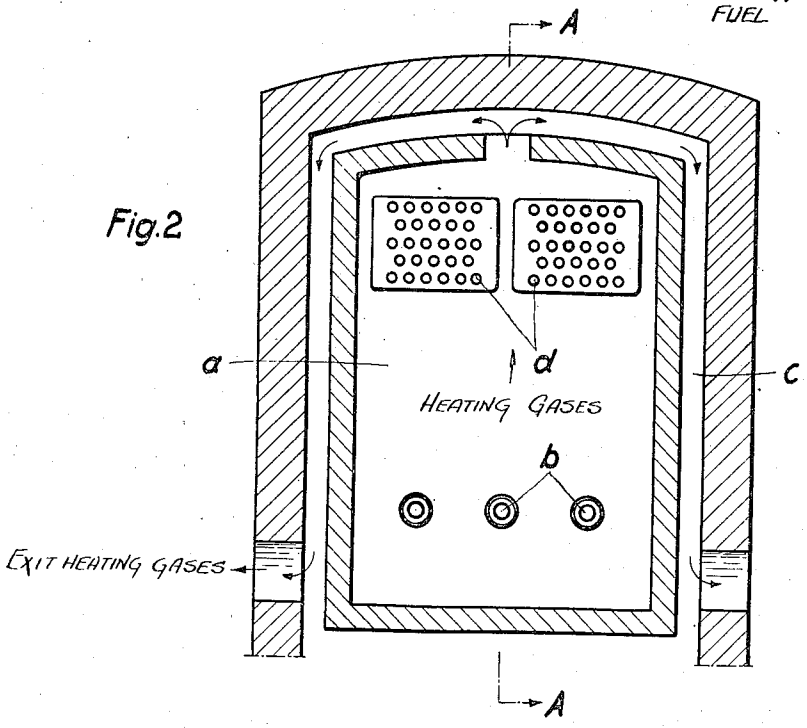

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Fig. 3

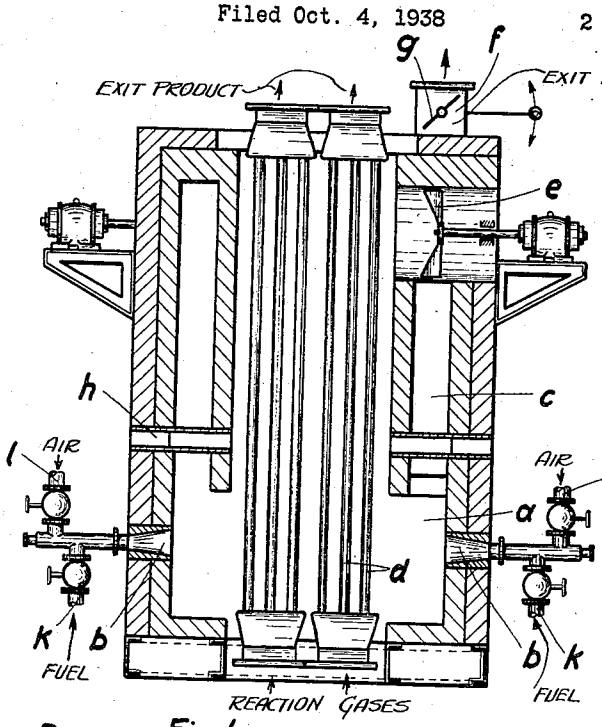


Fig. 4

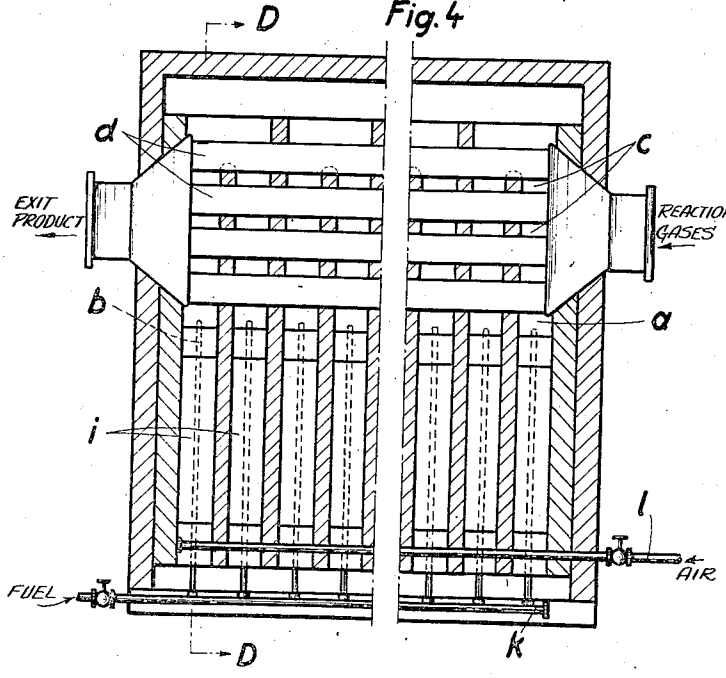
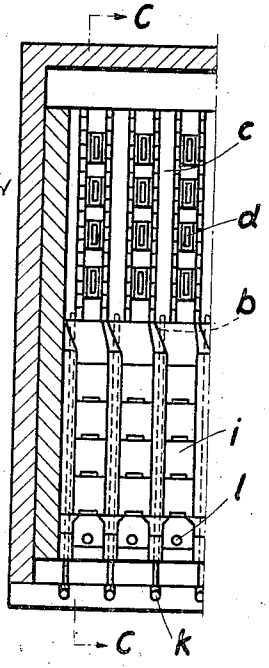


Fig. 5



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UNITED STATES PATENT OFFICE

2,244,210

METHOD FOR PARTIALLY OXIDIZING METHANE

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Application October 4, 1938, Serial No. 233,334
In Germany October 11, 1937

1 Claim. (Cl. 260—604)

It is the object of the present invention to provide a method for obtaining low molecular aliphatic aldehydes on a commercial scale, the aldehydes consisting primarily of acetaldehyde and/or formaldehyde.

Several methods have been suggested for obtaining formaldehyde in particular by partially oxidizing gaseous or vaporous hydrocarbons in the presence of gaseous catalysts in the form of small quantities of nitric oxides and of solid catalysts at temperatures between 500 and 700° C. Gases or vapors of the C_nH_n, C_nH_{2n} and C_nH_{2n+2} types were used as raw materials and organic acids were preferably obtained in addition to the above-mentioned oxidation product. It is not known, however, whether it was possible to develop the proposed methods beyond a certain experimental stage on a laboratory scale, as, when the experiments were carried out on a larger scale, it was found that it was not possible to control the reaction in the desired manner and if the repetition of the experiments on a commercial scale yielded any products at all they were neither economic nor uniform.

It has now been found that desired products, such as low molecular aliphatic aldehydes and acetaldehyde or formaldehyde in particular can be uniformly produced from the gaseous and vaporous hydrocarbons of the C_nH_n, C_nH_{2n} and C_nH_{2n+2} types when they are oxidized on a commercial scale, if in addition to the aforementioned steps the initial mixture is passed through a large number of tubes or ducts which are uniformly heated, possibly by means of a circulating heater. If necessary, the ducts or tubes are lined with the catalysts, further catalysts being possibly arranged in the ducts, or the ducts are themselves made of the catalysts. Oxides which are difficult to reduce, such as those of silicium, zinc, magnesium, titanium, cerium and similar metals, which can be used either alone or in combination, have proved to be particularly suitable catalysts for this purpose. Apart from these artificial materials natural rocks, such as granite, porphyry, mica, quartz and other natural products can with advantage be used as catalysts.

The reaction chamber is heated in a heater in which the individual ducts may be uniformly heated. The favorable effect of the uniform heating of the furnace can be increased by circulating the heating gases, part of the burnt gases being, if necessary, removed and replaced by fresh fuel gas which preferably heats the furnace by means of several burners. The heater is best arranged for regenerative or recuperative heating, which offers the advantage that the residual gas leaving the reaction chamber of the heater can be used for heating the heater, so that the calorific value of the residual gas is utilized.

The method according to the invention is explained by the accompanying drawings—

Fig. 1 being a vertical section through a reaction heater along the line A—A in Fig. 2,

Fig. 2 a vertical section along the line B—B in Fig. 1,

Fig. 3 a longitudinal section through a heater with circulating heating,

Fig. 4 a longitudinal section along the line C—C in Fig. 5 through a heater with regenerative heating, and

Fig. 5 a section along the line D—D in Fig. 4, partially shown.

a is the furnace of the heater with the burners *b* and the flues *c*. The reaction chamber is divided into individual ducts *d* and so arranged in the heating zone that the substances participating in the reaction are uniformly and similarly heated. As far as the ducts *d* are made of metallic materials their inner walls are lined with the catalyst materials. The walls of the ducts *d* can, however, themselves consist of the catalyst materials and catalyst materials may also be arranged inside the ducts.

In the reaction heater according to Figs. 1 and 2 the heating gases coming from the furnace *a* pass round the reaction ducts *d*, through the flues *c* and out of the heater as indicated by the arrows. The air and fuel pipes for the burners *b* are marked *l* and *k* respectively.

According to Fig. 3 fans *e* or blowers for circulating the heating gases are arranged in front of the heating flues. Before the heating gases re-enter the furnace part of them is led off and leaves the heater through the outlet pipe *f*, which is equipped with a control flap *g*. *h* indicates the peep holes.

Figs. 4 and 5 show a heater with regenerative heating. The heating gases are passed alternatively through a part of the regenerative chambers *i* in order to ensure utilization of the waste heat within the heater itself and the preheating of the air and/or gases for combustion in the other part of the regenerative chambers. This makes it possible to burn gases with little heat content in the heater, to which in the present case can be added the residual gases passing out of the reaction ducts. *k* is the gas feed main and *l* the air pipe controlled by means of two-

way flap valves which, though not shown, are sufficiently well known.

Example.—In order to produce formaldehyde from methane a mixture of 49.8% by vol. of a gas separated from coke-oven gas containing 41% by vol. of methane as reaction gas, 50% by vol. of air and 0.2% by vol. of nitric oxides (referred to NO) as catalyst is passed at a rate of more than 75 cm. per second through the reaction ducts *d*, which are heated to a temperature of 620° C. The reaction ducts were lined and charged with solid catalyst material, the catalyst bodies consisting of purified clay mixed with 10% of zinc-oxide. The reaction gases were circulated. The yield was 560 grammes of (100%) formaldehyde per cu. m. of methane introduced into the reaction chamber. The residual gases passing out of the cycle were used for heating the heater.

Besides dividing the reaction chamber into a number of tubes or ducts as explained and passing the substances participating in the reaction through these tubes or ducts it is, of course, also possible if the reaction chamber is arranged accordingly, to pass the heating gases through the tubes or ducts and the reaction mixture round the tubes or ducts. The solid catalysts are then arranged around the outside of the tubes or ducts.

Various changes in the steps of my method may be made by those skilled in the art without departing from the spirit of my invention as claimed.

What I claim is:

A commercial process for preparing a low molecular aliphatic aldehyde consisting in uniformly heating a mixture consisting of 49.8% by volume of a gas separated from coke over gas containing 41% by volume of methane, 50% air and 0.2% nitric oxides to a temperature of from 500° to 700° C., by passing the mixture in the presence of solid catalysts through a closed passage in a uniform heating zone.

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