Dec. 25, 1934. H. HARTER 1,985,875

PROCESS FOR OXIDIZING HYDROCARBONS

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Fig. 2

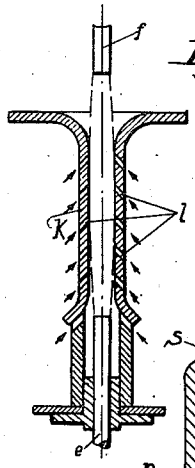


Fig. 1.

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PROCESS FOR OXIDIZING HYDROCARBONS

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3 Claims. (Cl. 260—138)

This invention relates to the process of oxidizing hydrocarbons, more especially methane, to formaldehyde by means of oxygen or air enriched with oxygen or air or other oxidants. It is well known that this reaction has been accomplished in absence of contact substances, however such process requires temperatures of about 1000° C., and the output of formaldehyde is very small for well known reasons.

Now I have found that these reactions can be carried out at considerably lower temperatures, for instance, between 100 and 500° C. by employing, as transferrers of oxygen or catalysts, decomposing nitric oxide which is preferably produced in the apparatus itself in which the hydrocarbon is oxidized, whereby owing to the low temperatures employed far better results may be obtained.

The new process will be more particularly described hereafter in view of an example and with reference to the annexed drawing.

In the latter Fig. 1 is a vertical cross-section of an apparatus for carrying out the invention. Fig. 2 is a cross-section showing a detail.

Air or another mixture of nitrogen and oxygen is introduced into the lower casing *a* through the inlet *b* so that the whole space *c* is filled therewith. Hence the air passes through several slots *d* into a double-walled tube *g* through which a high-tension electric arc is conducted to form nitrogen oxide. The double-walled tube is cooled by water or another cooling medium which is introduced into the hollow space *h* by pipe i_2 and withdrawn by pipe i_1, whereby pipe *g* is cooled and thus protected against the high temperature of the electric arc. The pipe *g* is preferably made of quartz, zirconia, thoria, borium nitride or other substances which influence the formation of nitric oxide by way of catalysis. The tube may readily be exchanged and in some cases replaced by another more simple tube *k* as shown in Fig. 2. This tube is perforated over its whole length by openings *l*, through which cold air is blown into the electric flame, whereby a special cooling device may be dispensed with. Whilst passing through the electric arc the air is activated, i. e. nitric oxide is formed which however is for the most part decomposed when leaving the tube *g*. At this moment the methane or other hydrocarbon to be oxidized is introduced through a great number of small holes *o* formed in the container *n* into which the gas is introduced through the inlet *m*; however, under certain conditions (presence of alkali, rapidity of the gas current) the methane or other hydrocarbons may be introduced conjointly with the oxidant. For assisting the oxidation of the methane, other catalysts *v* suitable for this process may be provided, whereby the formation of formaldehyde is accordingly promoted. The nascent oxygen resulting from the decomposition of the nitric oxide molecule permits of oxidizing the methane to formaldehyde at a temperature at which no decomposition of the product of oxidation is to be feared. The temperatures in the tube *g* or *k* where the nitric oxide is formed, as well as in the space where the methane is oxidized may be regulated or adjusted at will by varying the quantity of air or methane or both simultaneously, or by adjusting the distance of the electrodes. Whereas the lower electrode *e* is stationary, the upper electrode *f* may be adjustable at will and thus the temperature regulated as required. The combustion products are at once withdrawn from the zone of oxidation and, if required, conducted around water-cooled worms of pipes *p* and thereby strongly cooled. By baffle cylinders *q* the gases are well intermixed and brought into intimate contact with the cooling worms. The gases are conducted away by the outlet *r* in the cover *s* of the casing in which all cooling worms and the baffles are arranged, and the products of oxidation are separated in a separator of known construction by washing, liquefying or another known method.

The process may be applied to the oxidation of other hydrocarbons to form the corresponding aldehydes or ketones.

I have further found that for the reactions in question, especially for producing formaldehyde, contact substances are suited which have at the same time an oxidizing and dehydrating effect. The so-called "Bleaching earths" (highly porous aluminum silicates) produced, for instance, by the Pfirschinger Mineral-Works of Kitzingen on the Main (Germany) are well adapted for this purpose.

These bleaching earths in the form of a powder or of granules may be pressed between perforated cylinders or close-meshed net-work, the cylinders as well as the network being formed of inert material or a material by which the reaction is influenced in a catalytic way. On the other hand, the bleaching earth may be formed by means of a binder, such as lime, clay, cement, chamotte, etc. into briquettes or blocks or other suitable bodies. Furthermore the catalytic action of these bleaching earths may be increased by impregnating the same with solutions of any of the well known catalysts used when making formaldehyde synthetically by oxidizing methane.

Good results are also obtained as to the temperature and the output of formaldehyde by simultaneously employing bleaching earths combined with silica-gel of which 5 to 50% may be admixed to the bleaching earths. In the same way the bleaching earths may be employed in combination with activated carbon alone or combined with silica-gel. The proportions of bleaching earths, activated carbon and silica-gel being preferably in the relation of 1:1:1. Of course other relative proportions may be employed. It is understood that all the contact substances just described may also be employed without employing the above described contact apparatus. The above described bleaching earths may be employed either alone or in combination with the above said substances and/or activators.

Excellent catalysts for the above said purpose, especially for the synthesis of formaldehyde are obtained, for instance, by bringing the metals known as catalysts for the synthesis of formaldehyde, such as copper, silver, cobalt, manganese etc. either alone or some or all of them mixed together to a molten condition, with the addition of oxygen if desired, and maintaining the molten condition for some time. The melting is preferably effected in a vessel of quartz, alundum or zirconium. The activity of these molten metals can considerably be increased by admixing to the melt the above-mentioned bleaching earths, or silicic acid of any form, especially, however, in the form of remelted quartz sand, and distributing the same by vigorous stirring. Instead of bleaching earths or silicic acid also zirconium, titanium, thorium oxides, cerite earths etc. may be distributed in the melt. These oxides may be distributed in the melt also alone or some of them together with bleaching earths and silicic acid or only with one of these constituents. Preferably, however, up to 20% of alumina is added to each melt.

I claim:—

1. The process of oxidizing methane by means of oxygen comprising heating the methane with a mixture of oxygen and nitrogen in the presence of decomposing nitric oxide and a bleaching earth.

2. The process of oxidizing methane by means of oxygen comprising heating the methane with a mixture of oxygen and nitrogen in the presence of decomposing nitric oxide and a mixture of a bleaching earth and silica-gel.

3. The process of oxidizing methane by means of oxygen comprising heating the methane with a mixture of oxygen and nitrogen in the presence of decomposing nitric oxide and a mixture of a bleaching earth, silica-gel and activated carbon.

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