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COMPLETE SPECIFICATION

Process for the Pyrolysis of Ketenizable Organic Compounds

We, EASTMAN KODAK COMPANY, a Company organised under the laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, 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:—

This invention relates to a process for the pyrolysis of organic compounds and more particularly to a process for the pyrolysis of ketenizable organic compounds such as acetone, acetic acid and the like to produce ketene and other valuable products.

In the pyrolysis of acetone, acetic acid and other ketenizable compounds to produce ketene and other products, it has heretofore been the practice in carrying out the pyrolysis operation to employ pyrolysis chambers or apparatus constructed of carbon, copper, silver, brass, bronze, clay, silica and various other materials. Such materials have numerous disadvantages which render their use wholly impractical or impossible when carrying out the pyrolysis reaction at temperatures of the order of or in excess of 1000C°., particularly when low vacuum conditions in the apparatus are empolyed. For example, when it has been attempted to pyrolyze acetic acid to ketene in copper coils at temperatures in the vicinity of 1000°C., or higher, it has been found that after only a few days' operation, the copper pyrolysis chamber had become so severely deteriorated as to be completely unuseable for further operation. Silver coils are likewise so easily burned up under high temperature conditions as to be totally unuseable. Coils or pyrolysis chambers constructed of clay and silica, while able under certain circumstaoces to resist the relatively high temperatures employed, are nevertheless wholly unfeasible for use in pyrolysis operation because of the fact that they have such poor heat transfer and because they are so porous.

It will thus be readily understood that the pyrolysis of ketenizable organic compounds, such as the production of ketene by the pyrolysis of acetic acid presents a multiplicity of problems, the solution of which is exceedingly difficult. First, the pyrolysis reaction must be carried out in a reaction vessel constructed of a non-porous material. Second, the material must be able to withstand heat shock and not burn up under the high temperature conditions of the reaction. Third, the material must have sufficient strength to withstand high pressure either from the outside or from the inside of the vessel. Fourth, it must be able to stand up under the severe oxidizing and reducing action of the heating flame at temperatures of the order of 1000° C. or higher. Fifth, the material must be of such a nature that it will have no adverse catalytic effect when in contact with the materials being processed. Finally, the material must not change in composition or physical charactertistics such as by internal grain growth with accompanying development of brittleness after being in use for some time.

Until the advent of the present invention no one has ever provided a process for pyrolyzing ketenizable organic compounds wherein the pyrolysis reaction could be carried out at maximum efficiency and without shutdowns, severe material losses and other undesirable results directly traceable to failure of the material employed in the pyrolysis vessel. In fact, so vital is the matter of carrying out the pyrolysis reaction in contact with a material which will withstand the extremely severe conditions met with, that thereon depends the success or failure, or, in other words, the operability or inoperability, of the process.

It is known that high chromium steel alloys are resistant to carburising and oxidising conditions at high temperatures between about 500° C. and 1100° C. Such alloys may have a chromium content ranging from 15% to 35% with a nitrogen content from 0.15% to 0.65%; in one such alloy the nickel content is not more than 1% with carbon not exceeding 0.15% while another alloy, which has been used for chromium steel tubes, especially articles of this description suitable for use in superheaters, preheaters, soot blowers, hydrocarbon cracking apparatus and analogous structures, may have up to 15% of nickel with 0.05% to 0.5% of carbon.

We have found that the production of ketene by pyrolysis can only be carried out successfully in pyrolysis vessels of high chromium steel having an extremely limited range of chemical constitution.

Accordingly, the present invention provides a process for pyrolyzing ketenizable organic compounds, such as acetone, acetic acid, and other ketenizable compounds, which comprises pyrolyzing the said compound in the vapour phase at a temperature of the order of, or in excess of, 1,000° C. in a heat-resistant and oxidation-resistant pyrolysis vessel composed of a catalytically inactive high chromium steel alloy containing 24 to 27% of chromium, 0.12 to 0.3% of nitrogen, up to 0.6% of manganese, up to 1% of nickel and up to 0.2% of carbon, the balance being iron. Silicon may be present in amounts up to 1.5% and obviously, as known to skilled metallurgists, small fractions of a per cent. of other elements, such as sulphur may be present as impurities.

The term "pyrolysis vessel" as used herein includes a heating coil or a metal still pot.

We have found that the alloy manufactured and sold by the Babcock and Wilcox Tube Company of Beaver Falls, Pa., United States of America, under the trade name "Croloy 27" is a particularly valuable material for the purpose of this invention. This is a high chrome steel alloy containing 27% chromium, a maximum of 0.2% carbon, 1% nickel, about .2% nitrogen (.12 to .25%) and the balance iron. Other alloys having components within the limits designated in the previous paragraph are obtainable upon the open market, such for instance as the alloy manufactured and sold by National Tube Co., Pittsburgh, Pa., United States of America, containing 24—26% chromium, .6% manganese, 1.5% silicon, .2% carbon and .3% nitrogen, each of the last-four-mentioned ingredients being a maximum, and the balance being iron.

The accompanying drawing is a diagrammatic elevational view, in parial section, and in the nature of a flow sheet illustrating a typical method of pyrolizing ketenizable organic compounds in accordance with the instant invention.

Referring to the drawing:

The numeral 1 designates a suitable pipe through which may be led a ketenizable organic compound, such as acetic acid, flow of the compound to the vaporizer 2 being controlled by valve 3.

In the vaporizer 2, which may take the form of a coil, still pot, or other vessel equipped with a suitable source of heat such as a heating jacket, electrical resistance coils or other means, the acetic acid is vaporized and then conducted through conduit 4 to preheating vessel 5, which may likewise take the form of a heating coil, metal still pot or other appropriate device, and is there heated to a temperature of approximately 600 to 800° C.

In order to facilitate the ketene reaction a suitable pyrolysis catalyst, such as a phosphate compound may be admixed in small quantities with the acetic acid vapours passing through conduit 4, the catalyst being conveniently supplied to the acetic vapours passing through conduit 4 through conduit 6 controlled by valve 7.

The numeral 8 designates a pyrolysis vessel which may take the form of a heating coil similar to that of coil 5. This vessel is constructed of the high chrome-nitrogen steel alloy described above. Pyrolysis vessel 8 is connected with the preheating vessel 5 by means of a conduit 9, as shown. The preheated vapours thus pass through conduit 9 into the pyrolysis chamber in which they are heated to a temperature of the order of or in excess of, 1000° C. by means of open flame heater 10 or other equivalent source of heat. As shown, both the preheater and the pyrolysis vessel may be enclosed within a chamber constructed of any appropriate heat-resistant material such as fire brick. Provision is made by means of baffle 14 to cause the flame to travel in a more or less circuitous path before reaching the pyrolysis chamber, or the preheater. Partition 15 divides the preheating chamber from the pyrolysis chamber, but leaves an opening for the passage of the heating medium from the pyrolysis chamber to the preheating chamber. Under the influence of the extremely high temperature prevailing within the pyrolysis vessel the acetic acid or other ketenizable organic compound is cracked to ketene which passes, together with any other products of reaction from the pyrolysis chamber, by means of conduit 11 to condenser 12 where the ketene gas is separated from condensible components, including by-products and unchanged raw materials, which latter are removed by suitable draw-off means as shown. If desired, and as shown, a suitable catalyst neutralizer may be introduced into the vapours passing through conduit 11 before they reach the condenser 12. The ketene gas produced may then be conducted to any other desired reaction zone for conversion to other valuable products such as acetic anhydride by reaction with acetic acid.

In operating the process as above described, the pyrolysis reaction may be conducted at atmospheric or superatmospheric pressure, although in general it is preferable to employ reduced pressure in order to facilitate the reaction. As indicated, the products of the reaction may be disposed of in any desired monner.

Reference has been made to the fact that if the pyrolysis chamber is constructed of copper, it is substantially worthless because of the fact that it burns out almost immediately under the temperatures encountered and the severe oxidizing conditions met with during the reaction. For example, we have found that after a very short period of useage under such conditions a copper vessel loses all its strength and completely disintegrates. In addition even for such short period, it is necessary to protect the outer side of the pyrolysis vessel from attack by the flames ordinarily used to heat such vessels. Even when protected the pyrolysis vessels fail and the process is brought to a standstill.

It might be supposed that other alloys such as Nichrome or other alloys having high chromium and nickel content might be employed. However, we have found that although such alloys will resist fairly well the oxidizing atmosphere encountered, as well as the high temperatures prevailing on the outside of the vessels, these alloys are absolutely worthless when employed in pyrolysis vessels for the production of ketene because their catalytic activities are so great that even at moderate temperatures almost complete carbonization of the ketenizable substances fed through the apparatus takes place.

Other steel alloys have been found to be almost equally deficient for use in the pyrolysis reaction for one reason or another. For example, a well-known stainless steel such as Type—316, when employed in the pyrolysis vessel has approximately ten times the adverse catalytic activity of the high chrome, nitrogen steel described above. This can readily be determined by measuring the amount of carbon formed by passing a known amount of acetic acid over the metal at an elevated temperature and measuring the quantities of the decomposition gases given up when a known amount of the acid is passed over. Furthermore, the heat resistance of stainless steel alloys such as Type—316 or Type—304 is such that they are entirely unsuitable for any continued use above an outside temperature of about 700°C., which is a temperature entirely unsuited for successful large-scale operation.

In addition to deficiences of such alloys from the catalytic standpoint, they present the drawback that, even under the most favourable circumstances, they result in the production of very poor yields. For example, whereas yields of the order of only 20 or 30% are obtainable when Nichrome steels are employed, by the use of the high chrome, nitrogen steels described above, yields of the order of 90—95% can be readily obtained. Thus, we have provided a process and apparatus which will accomplish to an unusual degree of efficiency, a very important chemical reaction with much lower cost of operation than possible with alloys usually employed for such purposes.

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. The process of pyrolyzing ketenizable organic compounds, such as acetone or acetic acid, to produce ketene and other products which comprises pyrolyzing the ketenizable compounds in the vapour phase at a temperature of the order of, or in the excess of, 1,000°C. in a pyrolysis vessel constructed of a non-catalytic high chrome, nitrogen steel alloy containing 24 to 27% of chromium, 0.12 to 0.3% of nitrogen, up to 0.6% of manganese, up to 1% of nickel, and up to 0.2% of carbon, the balance being iron.

2. The process according to claim 1 wherein the said alloy contains up to 1.5% of silicon.

3. The process according to claim 1 wherein the said alloy contains 27% of chromium, up to 0.2% of carbon, 1% of nickel and 0.12 to 0.25% of nitrogen.

4. The process according to claim 1, 2 or 3 wherein the reaction is performed in the presence of a pyrolysis catalyst.

5. The process according to claim 4 wherein the said catalyst is a phosphate compound.

6. The process according to claim 4 or 5 wherein the said catalyst is neutralized after the pyrolysis.

7. The process for producing ketene as described herein.

Dated this 8th day of August, 1947.
L. E. T. BRANCH, B.Sc., F.R.I.C.,
Acting for the Applicants.

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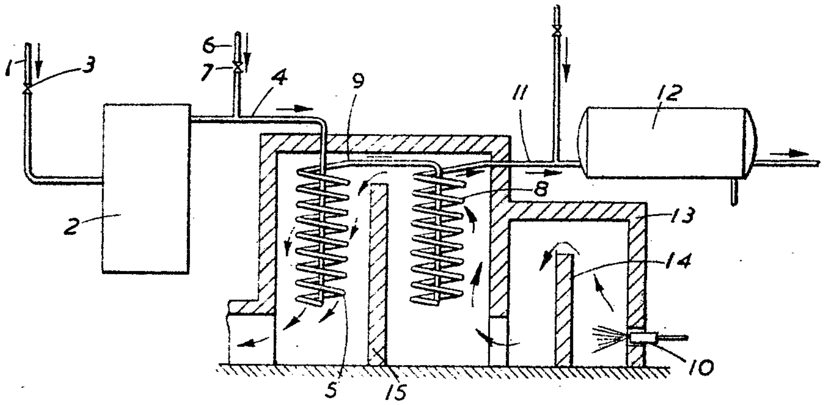
668,268 COMPLETE SPECIFICATION 1 SHEET

This Drawing is a reproduction of the Original on a reduced scale



H.M.S.O. (M.F.P.)