

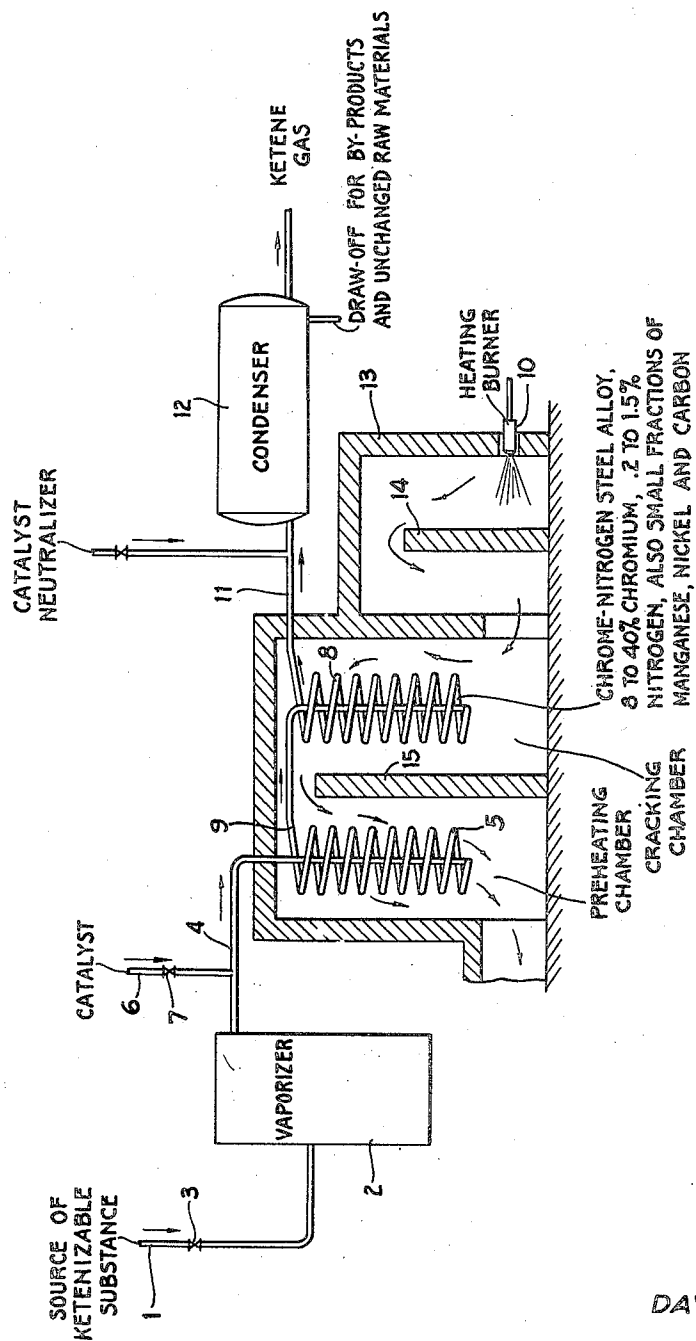
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PROCESS AND APPARATUS FOR THE PYROLYSIS OF ORGANIC COMPOUNDS

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PROCESS AND APPARATUS FOR THE PY-
ROLYSIS OF ORGANIC COMPOUNDS

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

This application is a continuation-in-part of my copending application, Ser. No. 375,051, filed January 18, 1941, which is a division of my application, Ser. No. 186,151, now U. S. Patent 2,232,705.

In the pyrolysis of acetone, acetic acid and other katenizable 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 1000° C., particularly when low vacuum conditions in the apparatus are employed. For example, when it has been attempted, in accordance with the teachings of the prior art, 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 circumstances to resist the relatively high temperatures employed, are nevertheless wholly unfeasible for use in pyrolysis operations 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 katenizable 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 tempera-

tures 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 characteristics such as by internal grain growth with accompanying development of brittleness after being in use for some time.

To the best of my knowledge and belief, in spite of the vast accumulation of knowledge and experience on the part of those skilled in the art and the prophetic statements in the patent and technical literature, no one, until the advent of the present invention, has ever provided a process for pyrolyzing katenizable 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.

This invention has for an object to provide an improved process of and apparatus for the pyrolysis of katenizable organic compounds such as acetone, acetic acid and the like. A further object is to provide a process for the production of ketene by the pyrolysis of katenizable organic compounds under extremely severe temperature and oxidation conditions. A still further object is to provide a process for the pyrolysis of organic compounds at temperatures of the order of, or in excess of, 1000° C. which may be operated continuously for long periods of time without burning out or other deterioration of the equipment and with a minimum decomposition of the reactants through catalytic or other action. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises pyrolyzing katenizable organic compounds such as acetone, acetic acid, and other katenizable compounds at high temperature in a heat-resistant and oxidation-resistant pyrolysis vessel composed of a catalytically inactive high chromium steel alloy containing nitrogen and small fractions of manganese, nickel and carbon, such as an alloy containing 18-40% chromium, about .2% to about 1.5% nitrogen and small amounts, generally not exceeding 1%, of manganese, nickel and carbon, the balance being iron. Obviously, as

known to skilled metallurgists, small fractions of a percent of other elements, such as sulfur and silicon, may be present as impurities.

In extensive research carried out for many years on large scale commercial operations, I have found that pyrolysis of ketenizable organic compounds to produce ketene and other desired products at high temperatures of the order of 1000° C. can be successfully carried out only in pyrolysis vessels of a relatively extremely limited chemical constitution. These materials are steel alloys containing a relatively high chromium content and a relatively low content of other materials, as indicated. I have found that the alloy manufactured and sold by the Babcock and Wilcox Tube Company of Beaver Falls, Pa., under the trade name "Croloy 27" is a particularly valuable material for this purpose. 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., 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.

In the following examples and description I have set forth several of the preferred embodiments of my invention but they are included merely for purposes of illustration and not as a limitation thereof.

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

A clearer understanding of my invention will be obtained from consideration of a typical process and the apparatus employed therein in accordance with my 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 catalyst, such as a phosphate compound may be admixed in small quantities with the acetic acid vapors passing through conduit 4, the catalyst being conveniently supplied to the acetic vapors 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 vapors thus pass through conduit 9 into the pyrolysis chamber in which they are heated to a temperature of 600 to 900° C. with an outside 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 condensable 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 vapors 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 super-atmospheric 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 manner.

In order more fully to set forth the distinguishing features of my invention and to illustrate the very marked and unpredictable increase in efficiency of the process for pyrolyzing ketenizable organic compounds, by carrying out the reaction in a pyrolysis vessel composed of the particular high chrome-nitrogen-steel alloy described above, a further discussion of the wide discrepancy between the results obtained in pyrolysis processes carried out in vessels composed of other alloys and the results to be obtained by carrying out the process in accordance with my invention, is desirable.

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, I 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, I have found that although such alloys will resist fairly well the oxidizing atmosphere en-

countered, 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 deficiencies of such alloys from the catalytic standpoint, they present the drawback that, even under the most favorable 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, I 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.

What I claim is:

1. The process of pyrolyzing ketenizable organic compounds such as acetic acid to produce ketene and other products which comprises pyrolyzing the ketenizable compound in the vapor phase at a temperature of the order of 1000° C. in a pyrolysis vessel constructed of a non-catalytic high chrome, nitrogen steel alloy containing 18-40% chromium, about .2 to about 1.5% nitrogen and, small amounts of manganese, nickel, and carbon, the balance being iron.

2. An apparatus for thermally decomposing ketenizable organic compounds to produce ketene and other products which comprises a pyrolysis vessel constructed essentially of a non-catalytic, high chrome-nitrogen steel alloy containing 18-40% chromium, about .2-1.5% nitrogen and, small amounts of manganese, nickel and carbon, and the balance iron, means for introducing ketenizable organic compounds into the pyrolysis vessel and means for heating the vessel to pyrolysis temperatures.

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