Jan. 1, 1957 | E. S. PAINTER ET AL | 2,776,192

ACETIC ACID CRACKING FURNACE

Filed Dec. 10, 1952 | 2 Sheets-Sheet 1

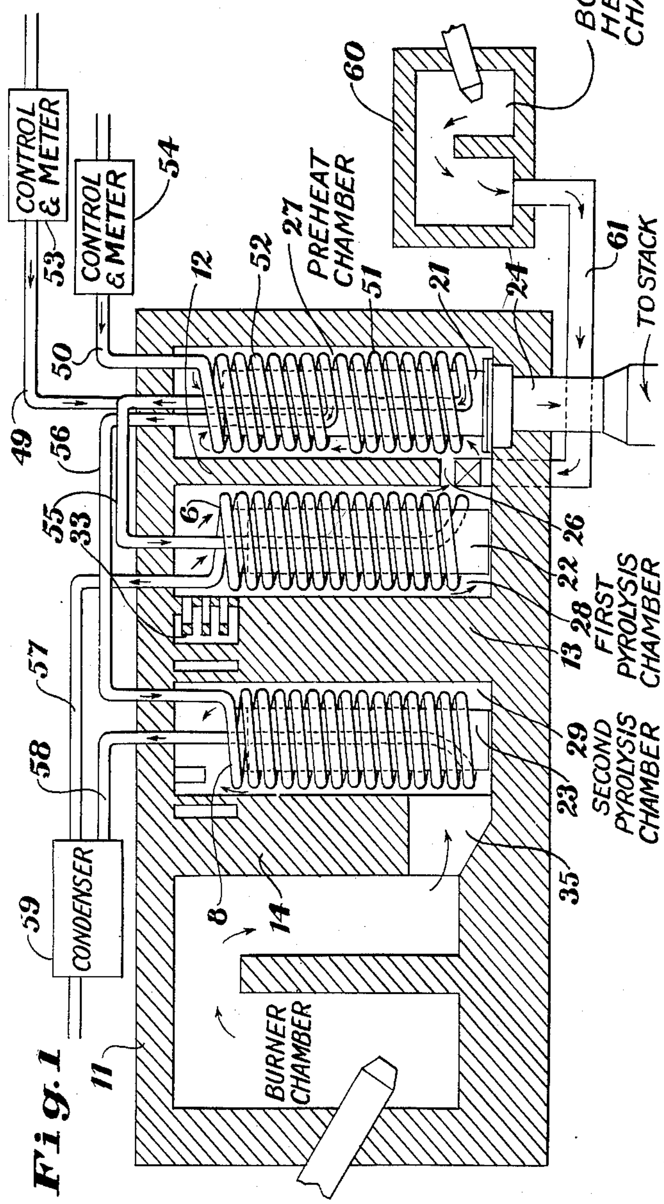

Fig. 1

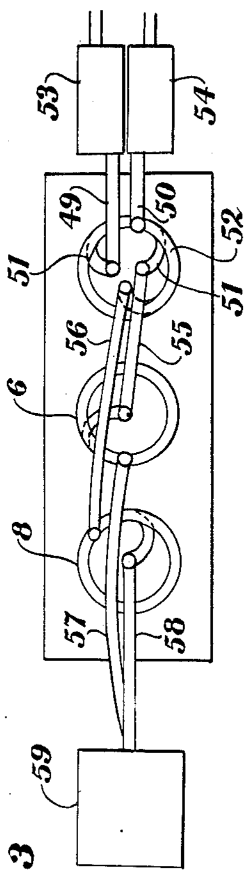

Fig. 3

Edwin S. Painter
Louis G. Haller
INVENTORS

BY Daniel J. Mayne
Harold F. Bennett
ATTY. & AG'T.

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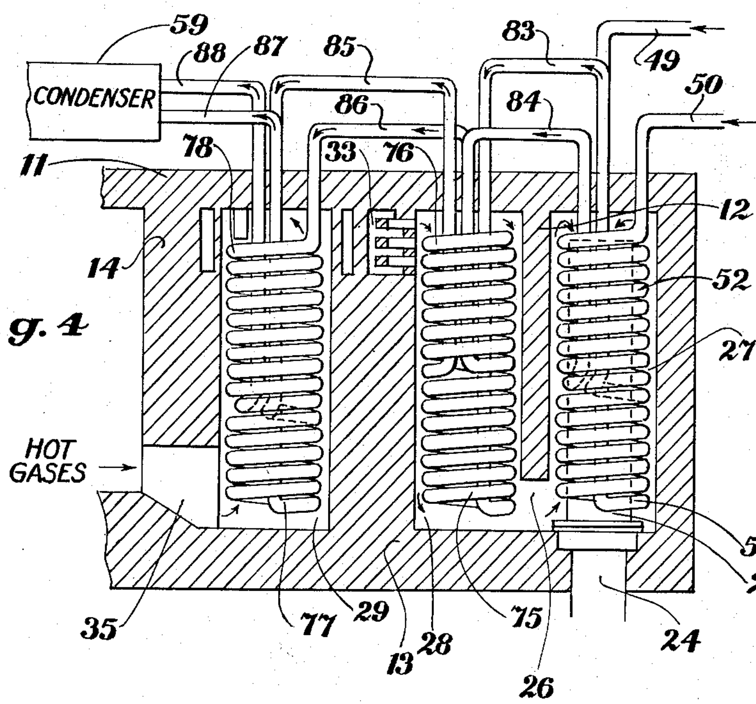

Fig. 4

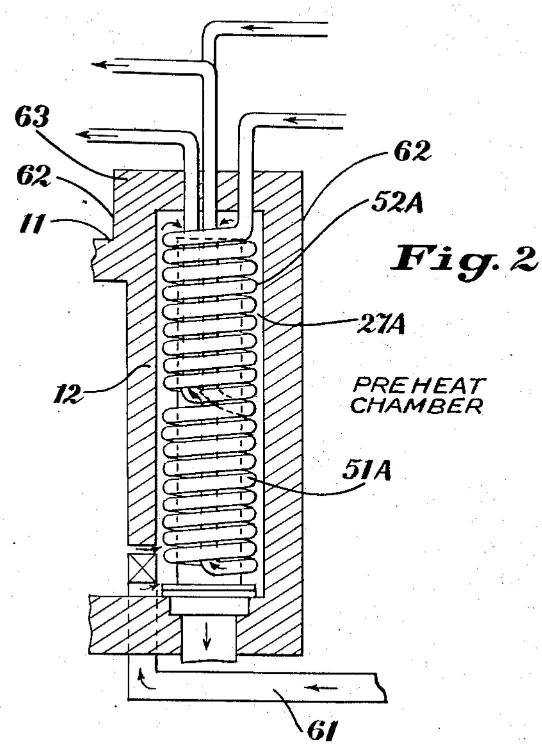

Fig. 2

Edwin S. Painter
Louis G. Haller
INVENTORS

BY Daniel I. Mayne
Harold F. Bennett
ATTY. & AGT.

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ACETIC ACID CRACKING FURNACE

Edwin S. Painter, Kingsport, and Louis G. Haller, Johnson City, Tenn., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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2 Claims. (Cl. 23—277)

This invention relates to apparatus for the pyrolysis of organic compounds and particularly to apparatus having increased capacity for the pyrolysis of ketenizable compounds such as acetone, acetic acid and the like to produce ketene, higher homologs of ketene or other valuable products.

Apparatus for the pyrolysis of ketenizable organic compounds is described in prior Patent 2,541,471 to Hull and Saunders. Other details of the process are described in prior Patent 2,258,985 to Hopkinson and in other publications mentioned therein.

The pyrolysis furnace described by Hull and Saunders comprises three heat-exchange chambers and one burner chamber. The heat-exchange chambers are designated, respectively, as the preheat chamber, the super-heat chamber and pyrolysis chamber. Three coils of metal tubing are connected in series and the organic compounds to be processed are passed through the tubing, first through the coil in the preheat chamber, then through the coil in the super-heat chamber and finally through the coil in the pyrolysis chamber, being heated to a higher degree in each successive chamber, thence out to the coolers and absorbers which are not shown in the Hull and Saunders patent but which are well known in the art and differ in detail according to the final product which is desired. The fuel, which is usually producer gas or natural gas, is burned in a burner chamber from whence the hot combustion gases pass through the pyrolysis chamber from bottom to top, through the super-heat chamber from top to bottom and finally through the pre-heat chamber from bottom to top and down again through a hollow core inside the coil and out to the stack. Thus the combustion gases and the compounds being pyrolyzed flow through the heating chambers in opposite directions. The Hull and Saunders patent describes certain structural features of the heat-exchange chambers whereby the heat exchange is made more efficient. The present invention is an improvement on the Hull and Saunders furnace and preferably retains these details of structure including ceramic cores within the coils which improve the efficiency of the heat exchange.

Recent sudden demands for an immediate and sizable increase in the output of ketene came at the same time that materials for building new furnaces or enlarging the present ones were in very short supply and almost impossible to obtain in sufficient quantities to effect the required increase in production in any reasonable length of time.

Accordingly, it is an object of the invention to convert known pyrolysis apparatus for ketenizable compounds so as to provide a substantially greater production of ketene, while keeping down the expense and use of critical materials.

Another object of the invention is to provide novel pyrolysis furnace constructions giving unusually high production rates compared to known furnaces of similar construction.

A further object of the invention is to provide a novel method of conducting a ketenizable substance through a pyrolysis process so as to obtain unusually high yields.

Previous suggestions along this line, while somewhat similar, were found to be unworkable. One plan was to preheat all the material together and then divide the flow into branches. This failed in the present process because flow meters are not available for use at 600° C., and without regulators the vapor feed would not divide properly. Another suggestion had to do with the form of the divided coils and proposed that the divided coils be interwound in each chamber like multiple threads on a screw. Theoretically, this would be very efficient and should give nicely equalized heating in the separate paths. The practical difficulties of installing and repairing the coils, however, make this scheme impractical.

According to the present invention, the ketene production capacity of a furnace of the Hull and Saunders type is increased by the surprising amount of about 30 percent and also the quality of the ketene and the acetic anhydride manufactured from the ketene produced in the unit is improved, by providing two parallel paths of 1½ coils each in place of a single path of three coils for the compound being pyrolyzed. We have discovered that the capacity of the furnace is limited both by pressure drop in the tubing and by the heat input to the furnace. The pressure drop over a conventional 3-coil furnace is about 700 mm. of mercury from the entrance of the first coil to the discharge of the third coil into the condenser. By arranging the coils in two parallel paths, the pressure drop is considerably decreased and the total flow through the furnace increased.

In one form of the invention, the pre-heater coil is divided into two separate halves connected in parallel with each other, and each half is connected in series with one of the coils in the other two chambers. In this form of the invention there is no essential change in the coils themselves in the other two chambers, but only in the arrangement of the connecting tubing. Preferably also, the half-coil which is in the hottest part of the pre-heat chamber, that is to say the bottom half, is connected with the full coil in the adjacent chamber heretofore known as the super-heat chamber, while the other half-coil in the pre-heat chamber is connected with the coil in the hottest of the three chambers, previously known as the pyrolysis chamber. It will be noted that in accordance with this change, both the chambers that have full coils now operate as pyrolysis chambers.

According to a preferred form of the invention, comprising a variation of the form just described, each of the three coils is divided into two separate halves and each of the two parallel flow paths passes through one half-coil in each furnace chamber. Preferably, in order to equalize the heat transfer in the two paths, one path traverses the half-coil in the hotter end of one chamber (i. e., the end at which the hot gases enter) and through the half-coil in the cooler end of each of the other two chambers. There is but little preference as to which chamber is reversed in this regard with respect to the other two. The most convenient arrangement is to pass one branch of the flow through all the bottom half-coils and the other through all the top half-coils. The two paths of flow are nicely equalized by making the two halves of the coil in at least one chamber unequal in length.

To supply additional heat for the increased capacity, an auxiliary gas-fired combustion chamber is optionally installed at the rear of the furnace—that is, at the end in which the pre-heat chamber is located. The hot combustion gases or flue gases from the auxiliary burner are mixed with the flue gas of the main burner in the furnace at or near the entrance to the pre-heat chamber, that is, at the bottom of the pre-heat chamber. The temperature of the gases in the pre-heat chamber is thus increased, allowing more heat to be transferred to the acid in this zone.

For a better understanding of our invention, reference will be made to the attached drawings forming a part of the present application, in which:

Fig. 1 is a semi-diagrammatic side elevational view largely in section and partly on exaggerated scale for clarity, showing a pyrolysis furnace in accordance with one embodiment of the present invention.

Fig. 2 is a partial similar view of a furnace according to a slightly different form of the invention.

Fig. 3 is a diagrammatic plan view showing the connections to the coils.

Fig. 4 is a view corresponding to Fig. 1 and showing a preferred form of the invention.

In considering the drawings and in particular, Fig. 1, it will be noted that many of the parts are the same as or similar to those described in the Hull and Saunders Patent 2,541,471 over which the present invention constitutes an improvement.

Referring to Fig. 1, the main body of the furnace is substantially as described in the Hull and Saunders patent. Within the furnace housing **11**, there are a plurality of partition walls **12**, **13**, and **14**, separating the furnace into a plurality of chambers **27**, **28**, and **29**, connected to each other and to the burner chamber by passages **26**, **33**, and **35**, all as described in the aforementioned patent. The burner chamber may be the same as in the prior art and so will not be described in detail here. The passageway **33** between chambers **28** and **29** preferably has a special shape described in the aforementioned patent for giving the combustion gases a turbulent flow as they enter the chamber **28**. As in the prior art, the combustion gases flow from the burner chamber through chamber **29**, **28**, and **27** in that order, thence down through the pipe **21** in the center of the chamber **27** and out through the flue **24** to the stack (not shown).

In each chamber is located a coil of tubing preferably of stainless steel, extending substantially the full vertical length of the chamber. The coils **6** and **8** in chambers **28** and **29** may be the same and preferably are the same as in the prior art insofar as the structure of the coils themselves is concerned, and preferably the ceramic cores **22** and **23** extend the length of the coil as described in the aforementioned patent.

In accordance with one form of the present invention, two half-length coils **51** and **52**, are arranged in the bottom half and the upper half, respectively, of pre-heat chamber **27** around the exhaust pipe **21**. The half-coil **51** in the lower part of the chamber is connected by tubing **49** and through a flow control **53** (which is also conveniently a flowmeter) to a source (not shown) of a ketenizable compound, and is connected by tubing **55** to the coil **6** in the second chamber **28**. The half-coil **52** in the upper part of the pre-heat chamber is similarly connected by tubing **50** and through a flow control and meter **54** to the source of the ketenizable compound and is connected at its other end through tubing **56** to the coil **8** in the hottest chamber **29**. The full coils **6** and **8** are connected at their other ends through tubing **57** and **58** respectively to a condenser **59** or other apparatus known in the prior art for utilizing the ketene produced in the furnace.

In order to supply the additional heat needed in reacting a larger quantity of material, a booster heating chamber **60** is optionally provided at or near the back end of the furnace, connected with the bottom of the pre-heat chamber **27** or preferably with the passage **26** between chambers **28** and **27**, through a tunnel or passageway **61**. The hot combustion gases from the booster heating chamber are mixed with the combustion gases from the main burner at this point and increase the heat transfer which takes place in the pre-heat chamber. In furnaces for industrial use, the full coils have 15 to 15¼ turns and the two half-coils conveniently have 7½ turns each.

Fig. 2 is a partial showing of a modified form of the furnace embodying the invention. Only the pre-heat chamber **27*a*** is shown. In this case the top **11** of the furnace has been taken apart, extensions **62** built onto the vertical walls surrounding the pre-heat chamber, and a raised top **63** built over this chamber to take the place of the portion of the top wall **11** which was removed. This higher chamber accommodates two half-coils **51*a*** and **52*a***, of 9½ turns each. Otherwise the furnace shown in Fig. 2 is the same as that shown in Fig. 1.

Fig. 3 is a partial plan view of the coils and their connecting tubes showing one convenient arrangement of the connecting tubes. The flow of the starting material is regulated by the controls **53** and **54**. Tracing the two parallel paths separately (Figs. 1 and 3), the flow through the tube **49** enters the upper end of the lower half-coil **51** and around 7½ turns (Fig. 1) or 9½ turns (Fig. 2) to the bottom, thence up and through the tube **55** to the lower end of the coil **6** in the second chamber, then out the top of that coil and through the tube **57** to the condenser **59**. The other path is through the tube **50** to the top of the upper half-coil **52**, then through 7½ or 9½ turns of this half-coil and out through the connecting tube **56** to the top of the coil **8** in the hottest chamber **29**, then out of the bottom of this coil and through the tube **58** to the condenser. The two outlet tubes **57**, **58** may be joined through a Y-connection or may enter the condenser separately as may be found more convenient. Separate condensers could also be used, of course.

Fig. 4 is a partial view corresponding to Fig. 1 and showing the preferred arrangement of half-coils (separate upper and lower coiled tubes) in the heating chambers. Aside from the omission of the booster heating chamber (**60**) and passageway (**61**), the parts of the furnace itself are the same as in Fig. 1 and are either numbered the same as in Fig. 1 or not shown in Fig. 4. The pre-heat chamber may optionally be oversized as in Fig. 2, with correspondingly longer half-coils. The coils in all three chambers are divided into upper half-coils **52**, **76**, and **78** and lower half-coils **51**, **75**, and **77** in the preheat, super-heat and pyrolysis chambers **27**, **28**, and **29** respectively. The connecting pipes and the outlet pipes are arranged so that one path of flow is through inlet pipe **50**, top coil **52**, connecting pipe **84**, top coil **76**, connecting pipe **86**, top coil **78** and outlet pipe **88** to the condenser **59**, and the other path of flow is through inlet pipe **49**, lower coil **51**, pipe **83**, lower coil **75**, pipe **85**, lower coil **77** and outlet pipe **87** to the condenser.

In order to equalize the flow in the two branches, the top coils (i. e., the coils in the cooler end) in the first and third chambers are made longer and the bottom coils shorter in the ratio of 8½ to 6½ and 9½ to 5½ in the respective chambers. The ceramic cores **22**, **23** are inconvenient to use with divided coils and we prefer to omit them in this form of the invention.

In a furnace for the regular production of acetic anhydride by the cracking of acetic acid and mixing the ketene product in controlled proportions with acetic acid and having three coils of 15 turns each in accordance with Figs. 1 and 3, that is, with the first coil divided into two sections of 7½ turns each, the flow rates were found to approximate 1100 pounds per hour through the bottom of the first coil and the second coil and 900 pounds per hour through the other branch, making a total of 2000 pounds per hour for the unit. The pressure drop across such a furnace is about 350 mm. Hg.

As another example, in an acetic acid cracking furnace in accordance with Fig. 2 with the pre-heat chamber enlarged to accommodate a coil of 20 turns divided into two sections of 9½ turns each, the flow rates achieved were found to approximate 1400 pounds per hour through the bottom section of the first coil and through the second coil and 900 pounds per hour through the other branch, making a total feed of 2,300 pounds per hour. The pressure drop across this furnace is about 400 mm. Hg.

In both cases the differences in the quantity of feed as between the two branches of the tubing corresponds to the difference in the heating conditions of the two branches. The lower half-coil is in a higher temperature zone and has a higher rate of heat transfer than the upper half-coil.

By way of comparison, the maximum feed rate to the conventional 3-coil furnace is 1500 to 1600 pounds per hour and the pressure drop is about 700 mm. Hg across the three coils connected in series.

Thus it will be seen that the embodiments of Figs. 1 and 2 are very successful and represent distict improvements over the prior art, but in operating them there still seemed to be room for further improvement, as the operation was somewhat uneven, left something to be desired in ease of control, and the number of cracking coil failures continued at a high rate. Also, as could be expected, the heat from the booster burner was not efficiently utilized, although it did achieve its aim of an immediate increase in total production from the furnace.

To overcome these difficulities, the preferred arrangement of coils shown in Fig. 4 was conceived and tested without a booster burner. It gave almost as great a rate of production as the furnace of Fig. 1 and ran 165 days without interruption, which was a record run. Thus, with what appears to be only a slight variation of the prior art structure, increased production, far exceeding what could be expected, was obtained, and yet long coil life was obtained, thus providing an operation of extremely high economic desirability.

Furnaces according to the present invention operate in the usual temperature range of 700 to 750° C. The ideal temperature for the reaction in the pressure range from 100 mm. mercury absolute to atmospheric pressure is about 740° C. The invention should operate equally well in furnaces fired by natural gas or other gaseous fuels.

We claim:

1. Apparatus for pyrolysing a ketenizable substance to form ketene, comprising a furnace wall structure defining a plurality of vertically elongated pyrolysis chambers, means for passing hot combustion gases initially into one end chamber, said wall structure having openings connecting the chambers in series for passage of the hot

gasses in zig-zag fashion therethrough, passing last through the other end chamber, separate upper and lower coiled tubes located respectively in the upper and lower ends of each chamber, tubular conduit means connecting each coiled tube in the upper end of each chamber serially with a coiled tube in the upper end of each of the other chambers, tubular conduit means connecting each coiled tube in the lower end of each chamber serially with a coiled tube in the lower end of each of the other chambers, whereby two separate tubular flow paths through said chambers are provided, means for removing ketene from the coiled tubes located in said one end chamber, means for passing a ketenizable substance into each of the coiled tubes located in said other end chamber.

2. Apparatus for pyrolysing a ketenizable substance to form ketene, comprising a furnace wall structure defining a plurality of vertically elongated pyrolysis chambers, means for passing hot gases initially into one end chamber, said wall structure having openings connecting the several chambers for the passage of hot gases through the chambers, seperate upper and lower coiled tubes located, respectively, in the upper and lower ends of each chamber, conduit means connecting one coiled tube in each chamber with one coiled tube in each of the other chambers to provide a flow path for a ketenizable substance, conduit means connecting the other coiled tube in each chamber with the other coiled tube in each of the other chambers to provide a second path for a ketenizable substance, the respective conduit means so connecting the coiled tubes in the upper and lower ends of the chambers that each flow path contains coils which are first swept over by the hot gases entering a chamber and coils which are swept over last by hot gases passing through a chamber, means for removing ketene from the coiled tubes located in said one end chamber, and means for passing a ketenizable substance into each of the coiled tubes located in said other end chamber.

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