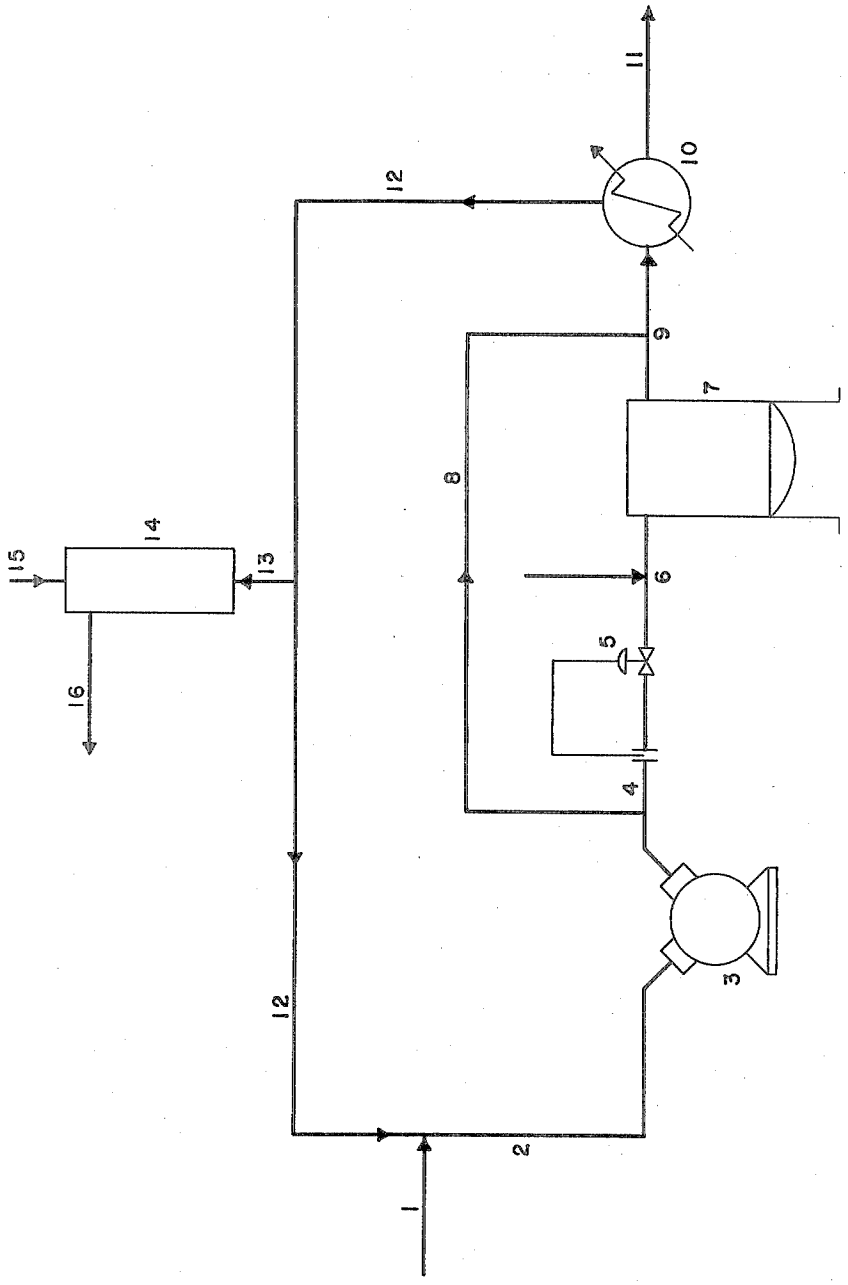
Nov. 13, 1956 W. H. STANTON 2,770,650

PROCESS FOR THE PRODUCTION OF VINYL ESTERS

Filed Jan. 26, 1953



United States Patent Office 2,770,650
Patented Nov. 13, 1956

2,770,650

PROCESS FOR THE PRODUCTION OF VINYL ESTERS

Walter H. Stanton, Texas City, Tex., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

Application January 26, 1953, Serial No. 333,249

4 Claims. (Cl. 260—498)

This invention relates to the production of vinyl esters generally and more particularly to an improved process for the production of vinyl acetate.

The vapor-phase catalytic reaction between acetylene and a carboxylic acid to produce a vinyl ester is a well known reaction. The acetylene and carboxylic acid vapors can be conducted through the reaction zone in stoichiometric proportions. However, advantages are obtained if the rate of supply of the acetylene is greatly in excess of the rate of fixation. Hence, optimum results are achieved when the feed to the reactors consists, for example, of approximately four moles of acetylene per mole of carboxylic acid with the level of conversion maintained at about 30–35% per pass.

Operation under the above conditions leads to a large recycle of acetylene gas: for every mole of acetylene reacted, twelve moles of acetylene are fed. The inert content of the recycle stream is limited to about 10%. Higher percentages, while they serve to reduce the explosive hazards connected with the handling of acetylene, tend to repress the reaction of acetylene and the carboxylic acid. Recycle of the acetylene-rich stream necessitates the use of some form of compressor. The ideal type of compressor in this application from the standpoint of economy in both capital cost and operation is a positive displacement rotary-type compressor. At low production rates, however, a large recycle occurs, and, with the constant output required in the operation of such a rotary compressor, which is normally driven by a constant speed motor, a high temperature rise occurs. The heat of compression is transferred to a small gas stream which becomes hotter and hotter until heat losses to the atmosphere balance the heat of compression. These temperatures in the case of compression of acetylene could readily range between 200–300° F. and cause a real hazard or threat of explosion.

It is an object of this invention, therefore, to provide an improved process for the production of vinyl esters by the vapor-phase reaction of acetylene and a carboxylic acid in the presence of suitable catalysts.

Another object is to provide a process for the production of vinyl esters, such as vinyl acetate from acetylene and a carboxylic acid, whereby hazards attendant upon acetylene handling are materially reduced.

A still further object is to provide a process of optimum efficiency for the production of vinyl esters by the vapor-phase catalytic reaction of acetylene and a carboxylic acid whereby both capital and operating costs are minimized.

It has now been discovered that the recycle stream from such a compressor can be readily cooled by introducing it into the product gas stream downstream of the reactor and then passing this mixed stream into a condenser for cooling and partial condensation. This method of cooling is particularly advantageous since it provides for equally efficient plant operation at various production levels and permits keying production to demand without the usual elaborate storage equipment and

accessory plant equipment required for such changes. The economies thus made possible are obvious. The method is practicable because at times of large recycle, i. e., decreased production rates, the condensers in the system are operating well below rated capacity. Conversely, at high production rates, low recycle rates prevail and the cooling operation is equally feasible. In addition, the hazards inherent in the handling of acetylene are minimized since the acetylene stream is significantly diluted by its injection into the product stream.

According to the invention, an acetylene-containing gas stream made up of recycled gas and fresh feed acetylene is passed through a constant speed compressor. The output from the compressor is controlled so that a predetermined proportion of the flow is admixed with the vaporized carboxylic acid and directed into a catalytic reactor while the remainder of the stream by-passes the reactor and is cooled by introducing it into the product gas stream emerging from the reactor and then passing the mixed stream into a condenser where the vinyl acetate present is condensed. Acetylene and any other non-condensable gases from the condenser are recycled to the compressor and again processed in the same manner. The condensate is then purified by conventional distillation techniques to recover the pure vinyl ester.

The process of the invention is illustrated in the following detailed description of a preferred embodiment of the invention for the production of vinyl acetate from acetylene and acetic acid. References are made to the attached drawing which represents a diagrammatic flowsheet.

Dry, pure acetylene gas is fed via line **1** into the pipe **2** where it is admixed with an acetylene-rich recycle stream. The combined streams contain 90–95 volume percent acetylene. The recycle stream is about 10 times as large as the fresh feed acetylene stream. The combined stream is passed into the compressor **3** and as it comes from the compressor through line **4** it is regulated by means of a flow recording controller **5** so that the flow is divided and a stream of acetylene-containing gas containing approximately 93% C_2H_2 is admixed with vaporized acetic acid entering at point **6** and fed to the reactor **7**. The reactor is packed with a catalyst of zinc acetate impregnated on coke and maintained at a temperature from 200–220° C. The remainder of the flow in line **4** is diverted via line **8** to by-pass the reactor and is cooled by introducing it into line **9** where it blends with the product gases from the reactor. The relative flow in streams **4** and **8** is controlled by process demand. When the product demand is high, the flow via line **8** is small; on the other hand, when the flow of reactants to the process is low, the flow through line **8** is high. The temperature is thus controlled so that the maximum temperature rise is about 50° F. which for 90–95% acetylene in the pressure range of 0–8 p. s. i. g. employed falls within the non-explosive range.

The combined gases are passed to the condenser **10** where they are cooled to 0° F. The condensate is withdrawn via line **11** and sent to a conventional distillation train for recovery of the pure vinyl acetate. Gases from the condenser are recycled via line **12** to the compressor. A portion of the recycle gas stream is vented to prevent the build-up of inert material in the system by passing the gas through line **13** into a vent scrubber **14** where the vented gases are scrubbed with acetic acid which enters through line **15** to remove acetylene. Inert gases after scrubbing are discharged to the atmosphere or to a flare through line **16**. The acetylene may be recovered readily from its acetic acid solution by stripping in one of the columns of the purification system and returned to the system for re-use.

In carrying out the novel improved process of this invention, the specific reactants, quantities of reactants, and reaction conditions set forth in the preferred embodiment are subject to substantial variation. Although the process is particularly advantageous when a constant-speed compressor is employed for compression of the feed and recycle gases, there are obvious advantages in its employment when the equipment includes a variable-speed compressor. Neither is the process limited to the production of vinyl acetate; it is equally applicable to the preparation of vinyl esters generally. Vinyl formates, propionates, butyrates, benzoates, etc., may be produced by the process of the invention by reacting the respective carboxylic acids with acetylene. Lower aliphatic monocarboxylic acids containing from one to seven carbon atoms are to be preferred.

As mentioned previously, the acetylene and carboxylic acid vapor mixture can be passed through the reactor in equimolecular proportions or with either reactant in excess. It is preferred to operate at an acetylene to acid molecular ratio of 4 to 1. At this ratio, about 30–40% of the acid is reacted per pass. These dilute conditions and partial reaction promote increased catalyst life.

Any of the catalysts commonly employed for the vapor-phase reaction of acetylene and carboxylic acids may be employed in the process of the invention. Suitable catalysts include zinc or cadmium salts of the carboxylic acids of which it is desired to prepare the vinyl esters, mercury salts such as mercury acetate, mercuric chloride, etc., free phosphoric acid, zinc and cadmium chromates, and silicates and polysilicates of zinc and cadmium. These compounds may be supported on carriers such as activated carbon, wood charcoal, silica gel, activated alumina, etc.

In general, the process of the invention is operated at temperatures in the range of 180–300° C. The upper temperature limit at which the process is operable depends upon the thermal stability of the compounds involved. The use of temperatures within the range of 180–300° C. is preferred. The actual values selected within the preferred range are dependent upon the properties of the acid and the activity of the catalyst. Optimum temperature is one which is high enough to maintain the acid in a vaporous condition during contact with the catalyst and one at which catalyst efficiency approaches a maximum as indicated by an exothermic effect within the catalyst bed.

Operation at atmospheric pressure is preferred but, if it is necessary in some instances to insure a practical rate of reaction, superatmospheric pressures may be employed.

While the process of the invention has been described with relation to the preparation of vinyl esters, it is equally applicable with the proper adjustment of temperatures, acetylene-to-acid molecular ratios, etc., known to those skilled in the art in the production of ethylidene diesters with all the attendant advantages.

What is claimed is:

1. A process for the production of vinyl esters which comprises the following steps: compressing an acetylene-containing gas stream by means of a constant-output compressor; combining a predetermined portion thereof as it comes from the compressor with a quantity of vaporized aliphatic monocarboxylic acid and passing said combined stream into a catalytic reactor; injecting the remainder of said acetylene-containing stream into the product gas stream emerging from the reactor and passing said mixed gas stream into a condenser where the vinyl ester is condensed; recycling the acetylene and other noncondensable gases to the compression step; venting a portion of said recycled gases through a scrubber where the carboxylic acid is employed as the scrubbing agent to remove acetylene; and purifying the condensed ester by conventional distillation techniques.

2. A process for the production of vinyl acetate which comprises the following steps: compressing an acetylene-containing gas stream by means of a constant-output compressor; combining a predetermined portion thereof as it comes from the compressor with a quantity of vaporized acetic acid and passing said combined stream into a catalytic reactor; injecting the remainder of said acetylene-containing stream into the product gas stream emerging from the reactor and passing said mixed gas stream into a condenser where the vinyl acetate is condensed; recycling the acetylene and other non-condensable gases to the compression step; venting a portion of said recycled gases through a scrubber where the acetic acid is employed as the scrubbing agent to remove acetylene; and purifying the condensed vinyl acetate by conventional distillation techniques.

3. In a process for the production of vinyl esters by the catalytic vapor-phase reaction of acetylene and aliphatic monocarboxylic acids to produce a gaseous product containing the vinyl ester, unreacted acetylene and acid, and other impurities, wherein said product gas is condensed and unreacted acetylene and other non-condensable gases are recycled to the reactor and combined with make-up acetylene, a portion of said recycled gases being vented through a scrubber where the carboxylic acid is employed as the scrubbing agent to remove acetylene, the improvement which comprises injecting any predetermined portion of said combined gas stream after compression in a constant-output compressor into the product gas stream emerging from the reactor.

4. In a process for the production of vinyl acetate by the catalytic vapor-phase reaction of acetylene and acetic acid to produce a gaseous product containing vinyl acetate, unreacted acetylene and acetic acid, and other impurities, wherein said product is condensed and unreacted acetylene and other non-condensable gases are recycled to the reactor and combined with make-up acetylene, a portion of said recycled gases being vented through a scrubber where acetic acid is employed as the scrubbing agent to remove acetylene, the improvement which comprises injecting any predetermined portion of said combined gas stream after compression in a constant-output compressor into the product gas stream emerging from the reactor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,066,075	Reppe et al.	Dec. 29, 1936
2,472,084	Beller et al.	June 7, 1949
2,472,086	Beller et al.	June 7, 1949
2,547,916	Wenner	Apr. 3, 1951
2,552,425	Halbig	May 8, 1951

OTHER REFERENCES

Copenhaver et al.: "Acetylene & Carbon Monoxide Chemistry" (1949), pps. 25–28.