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[54] PROCESS FOR THE RECOVERY OF IODINE

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[51] **Int. Cl.**.....**C07c 5/20**

[58] **Field of Search**.....260/680 D, 681.5 R

[56] **References Cited**

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Primary Examiner—Paul M. Coughlan, Jr.

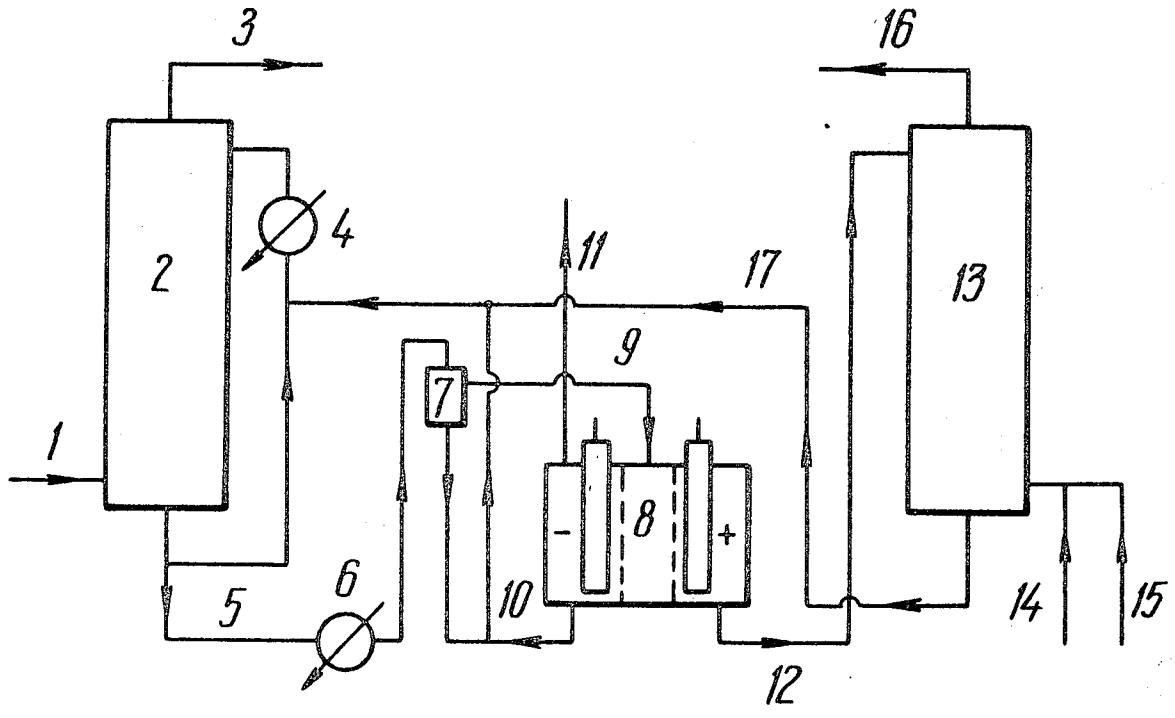
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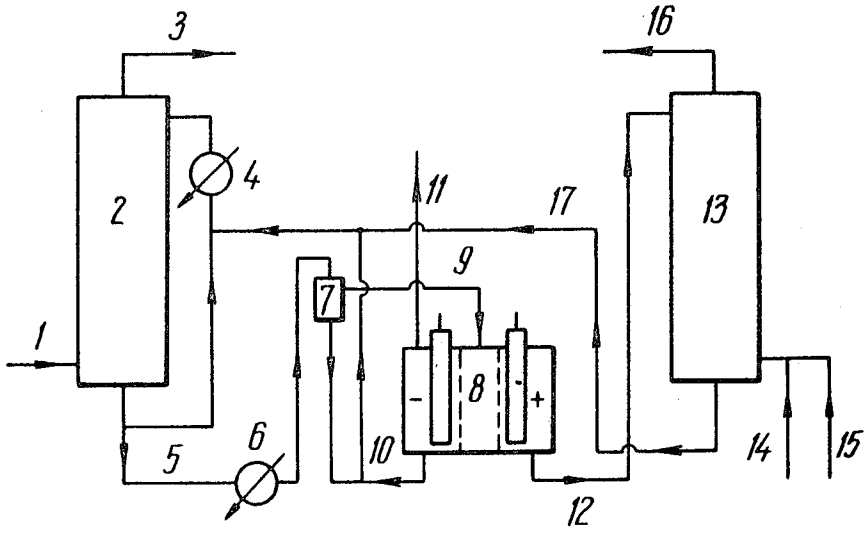
[57] **ABSTRACT**

A process for the recovery of iodine from the products of iodative dehydrogenation of hydrocarbons containing iodine and hydrogen iodide which consists in processing said products of dehydrogenation of hydrocarbons with an aqueous solution of sodium hydroxide, sodium carbonate or a mixture thereof until a weakly alkaline solution of iodine salts (pH = 8 –10), containing iodide and iodate, is obtained. Said solution of iodine salts is electrolyzed to separately obtain the solutions of iodine and alkali, which contain undecomposed salts of iodine as well. The solution of alkali is recycled to the stage for alkali treatment of dehydrogenation products. Iodine is blown off from its solution by oxygen, an oxygen-containing gas or a mixture thereof with steam and recycled to the stage of dehydrogenation of hydrocarbons, and the solution of iodine salts free of iodine is recycled to the stage for alkali treatment of dehydrogenation products.

The process is continuous. It enables complete recovery of iodine (up to 99.7 –99.9 percent), makes it possible to eliminate the formation of waste and crystalline iodine during the process as well as corrosive medium and dangerously explosive compounds.

3 Claims, 1 Drawing Figure




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PROCESS FOR THE RECOVERY OF IODINE

This invention relates to processes for recovery of iodine from the products of iodative dehydrogenation of hydrocarbons.

Several processes for the recovery of iodine from the above mentioned dehydrogenation products are known.

A process based on using metallic copper consists in the recovery of iodine and hydrogen iodide from the dehydrogenation products by the following reactions:

$$2Cu + HI \rightarrow 2CuI + H_2$$

$$2CU + I_2 \rightarrow 2CuI$$

Elemental copper can be used in the form of cuttings, granules, powder, or on an inert carrier. The recovery of metallic copper and elemental iodine from copper iodide is carried out by oxidizing the copper iodide with an oxygen-containing gas to obtain copper oxide and iodine:

$$2CuI + O_2 \rightarrow 2CuO + I_2$$

The copper oxide obtained is reduced by hydrogen or by some other reducing agent to metallic copper and reused in the regeneration process. The recovered iodine is recycled to the reaction zone (see U.S. Pat. No. 3,119,881, 1964).

This process is disadvantageous in that it is a multistage process as a result of the necessity of copper regeneration. It is frequently a batch process and, additionally, it can result in the formation of dangerously explosive copper acetylides.

Another process known in the art is based on mulit-stage, continuous washing of iodine and hydrogen iodide by water or an aqueous solution of hydriodic acid.

Hydrogen iodide is recovered from the first portions of concentrated wash solutions by distillation in a column. The hydrogen iodide obtained is oxidized by oxygen to elemental iodine which is fed into the hydrocarbon dehydrogenation zone. Liquid iodine distilled out in another column is also recirculated into the dehydrogenation zone. Other wash solutions of a lower concentration are passed through columns filled with catalysts to oxidize hydrogen iodide to element iodine, followed by recycling the resulting elemental iodine (see U.S. Pat. No. 2,921,101, 1960).

Still another known process is also based on repeated consecutive removal of iodine and hydrogen iodide by washing with water or an aqueous solution of hydriodic acid. Iodine is removed from the solution in a crystalline state (see U.S. Pat. No. 3,044,862, 1962).

The disadvantages of these process are the presence of a highly corrosive medium, and incomplete recovery of iodine and, in the second case, the difficulties of transportation of iodine crystals.

Processes based on the recovery of elemental iodine and hydrogen iodide by solid acceptors consist in passing the gaseous products of hydrocarbon dehydrogenation through a layer of solid acceptors. The acceptors contain substances which react with hydrogen iodide and iodine to form iodates. The layer of acceptors can be stationary, moving or suspended (fluidized bed). The recovery of the products and regeneration of the acceptor are carried out in up-flow,

down-flow or counter-flow in one or two reactors. After the recovery has been carried out, the solid acceptor is regenerated by oxygen or an oxygen-containing gas. The elemental iodine recovered is returned into the hydrocarbon dehydrogenation zone and the regenerated acceptor is recycled (see Belgium Pat. No. 632082, 1963; British Pat. No. 978181, 1964).

These processes are disadvantageous in that they are either batch processes or, in case of a continuous process, the recovery of iodine is incomplete and the apparatuses employed are complicated in design.

Also known is a process for the recovery of iodine which consists in treating the products of iodative dehydrogenation of hydrocarbons with an aqueous ammonia solution, thereby binding, after cooling said products to dissimilar temperatures, elemental iodine and hydrogen iodide by the following reactions:

$$2NH_3 + I_2 \xrightarrow{\geq 350^\circ C} N_2 + 6HI$$

$$NH_3 + HI \xrightarrow{85^\circ - 110^\circ C} NH_4I$$

Then, the products of dehydrogenation are separated from the solution of ammonium iodide which is decomposed at or somewhat below the temperature of dehydrogenation:

$$NH_4I \rightarrow NH_3 + HI$$

Decomposition is carried out in a separate reservoir. The hydrogen iodide obtained is trapped by a solid acceptor, as iodide, and ammonia is recirculated (see British Pat. No. 978181, 1964).

A disadvantage of this method is the possibility of the formation of dangerously explosive nitrogen triiodide during regeneration.

An object of the present invention is a full and continuous recovery of iodine from the products of iodative dehydrogenation of hydrocarbons.

Another object of the present invention is to prevent the formation of effluents and crystalline iodine during the recovery.

Still another object of the invention is to prevent the formation of corrosive media and dangerously explosive compounds.

With these and other objects in view, the invention consists in processing the products of iodative dehydrogenation of hydrocarbons containing iodine and hydrogen iodide with an aqueous solution of sodium hydroxide, sodium carbonate or a mixture thereof until a weakly alkaline solution of iodine salts (pH $= 8 - 10$), containing iodide and iodate, is obtained.

The solution of iodine salts is electrolyzed to obtain separate solutions of iodine and alkali, which also contain undecomposed salts of iodine. THe alkaline solution is recycled to the stage where the dehydrogenation products are subjected to alkaline treatment. Iodine is blown off from the iodine solution by oxygen, an oxygen-containing gas or a mixture thereof with steam and is recycled as gas to the stage of dehydrogenatation of hydrocarbons. The solution of iodine salts free of iodine is recycled to the stage where the products of dehydrogenation of hydrocarbons are treated with alkali.

To prevent the formation of crystalline iodine and keep the latter in the solution, it is advisable that the electrolysis be carried out until the degree of iodine

decomposition is 10–35 percent, preferably 25 percent, by weight of iodine feed.

The present process enables the complete recovery of iodine (iodine recovery is as high as 99.7–99.9pe rcent).

The present process is carried out as follows and illustrated by the process flow diagram in the single FIGURE of the appended drawing.

The products of iodative dehydrogenation of hydrocarbons containing iodine and hydrogen iodide as well as possible admixtures of organic iodine compounds are fed through a pipeline **1** into a scrubber **2** for alkali treatment. The products of dehydrogenation are processed in said scrubber with the aqueous solution of sodium hydroxide, sodium carbonate or a mixture thereof until a weakly alkaline solution of iodine salts with pH = 8 –10 is obtained, e.g. the solution with the concentration of sodium carbonate 1–2 gm per liter. Iodine and its compounds are recovered from the products of dehydrogenation to form iodide and small amounts of iodate according to the following reactions:

$$NaOH + HI \rightarrow NaI + H_2O$$

$$6NaOH + 3I_2 \rightarrow 5NaI + NaIO_3H_2O$$

$$Na_2CO_3 + 2HI \rightarrow 2NaI + H_2O + CO_2$$

$$3Na_2CO_3\,3I_2 \rightarrow 5NaI + NaIO_3 + 3H_2O$$

After having been treated in the scrubber **2**, the products of dehydrogenation directed via a pipeline **3** to the step of recovering the dienes, e.g. butadiene.

To provide required circulation, the removal of heat and to keep iodide concentration at a desired level in the system, the solution is circulated through the scrubber **2** and a heat exchanger **4**. Concentration of iodide in the system is between 100 and 300 gm per liter, required circulation in the scrubber is from 10 to 20 m^3/m^2. hour.

A part of the weakly alkaline solution of iodine salts containing iodide and small amounts of iodate is continuously supplied from the scrubber **2** by a pipeline **5** through a heat exchanger **6** and a level regulator **7** for electrolysis. Electrolysis is carried out in a diaphragm three-chamber electrolyzer **8** whose anodes are made of materials which essentially do not adsorb iodine: platinum plated titanium, nonporous graphite, magnetite, and cathodes — of low-carbon steel or iron. Depending upon the productivity of the electrolyzer, diaphragms are used which have either a high throughput (50–150 $1/m^2$·hour), such as of asbestos or glass fabric diaphragms, or diaphragms with a low throughout, such as asbestos cardboard diaphragms.

The rate of passage of the solutions of iodine salts through the system of regeneration is determined by the throughput of the diaphragms of the electrolyzer. The increase in the diaphragm throughput and, hence, in the rate of passage of the solutions contributes to a better separation of the electrolysis products (iodine and alkali) and enables the use of less concentrated iodide solutions with the electrolyzer iodine efficiency remaining the same.

The solution of iodine salts is passed through a pipeline **9** into the interdiaphragm space of the electrolyzer **8**. It then passes through the diaphragms into the anode and cathode spaces.

The electrolysis gives the solution of iodine with iodide in the anode space. Additional amounts of iodate are simultaneously obtained in the anode space due to the interaction of iodine with sodium hydroxide or sodium carbonate delivered with the solution and also due to weak overoxidation of iodine.

Anode processes:

$$2I^- - 2e \rightarrow I_2$$

$$I^- - 6e + 3H_2O \rightarrow IO_3^- + 6H^+$$

The iodine obtained is in a soluble state:

$$I_2 + I^- \rightarrow I_3^-$$

A side reaction in the anode space:

$$3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$$

To prevent the formation of crystalline iodine and to keep it in the soluble state, it is advisable to carry out electrolysis with the degree of iodine decomposition from 10 to 35 percent, preferably 25 percent, by weight of the iodide feed.

In the cathode space electrolysis gives alkali and hydrogen, and iodate present in the cathode space is reduced to iodide.

Cathode processes:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$IO_3 + 6e^- + 3H_2O \rightarrow I^- + bOH^-$$

The current density at the cathode is so chosen that practically all the iodate supplied into the cathode space is reduced to iodide. Therefore, the accumulation of iodate in the solution which is circulated through the system of regeneration is eliminated.

The cathode solution comprising a mixture of alkali and undecomposed iodide with small amounts of iodate is fed into the scrubber **2** through a pipeline **10**.

Hydrogen obtained by electrolysis is removed through a pipeline **11** and used for production needs.

The anode solution of iodine with iodide is fed after electrolysis through a pipeline **12** into a desorption column **13** where elementary iodine is blown off from the solution by oxygen or an oxygen-containing gas which is supplied into the bottom portion of the column through a pipeline **14**. These gases, besides, can be used in mixture with steam delivered through a pipeline **15**.

The desorbed iodine is recycled as a steam-and-gas mixture into the dehydrogenation zone through a pipeline **16**.

The solution of iodide, free of iodine, with small amounts of iodate is removed from the bottom portion of the desorption column **13** and is recycled by a pipeline **17** into the scrubber **2**.

Water decomposed by electrolysis and water removed from the desorption column with oxygen are compensated by partial vapor condensation in the desorption column **13** or in the scrubber **2**.

For a better understanding of the present invention, attention is directed to the following Example.

EXAMPLE

Iodine was recovered from the products of iodative dehydrogenation of butane (to obtain 100 kg of butadiene). The products of butane dehydrogenation contained 13.53 percent of iodine by weight of butadiene (7percent of elemental iodine, 93 percent of iodine in hydrogen iodide). These products were fed into the scrubber for alkali treatment with the aqueous solution of sodium hydroxide with sodium carbonate at 80°C. The solution was circulated through the scrubber during the process of washing, whereby iodine and hydrogen iodide were practically completely extracted by the solution from the products of dehydrogenation. Required circulation amounted to 15 m^3/m^2·hour. The obtained solution (450 liters) containing 140 gm per liter of sodium iodide, 6 gm per liter of sodium iodate and 1 gm per liter of sodium carbonate (pH 10) was electrolyzed. Electrolysis was carried out in a diaphragm three-chamber electrolyzer of a filter press type, employing anodes of platinum plated titanium, cathodes of steel and diaphragms of an asbestos fabric.

Basic parameters of electrolysis: current, A 4000

diaphragm current density, A/m^2. 800 voltage across terminals of electrolyzer, v 3.8

temperature of electrolyte, °c 60–L/m

diaphragm throughput(the same for cathode and anode diaphragms) L/m^2 .hour 50

consumption of electric energy for the recovery of iodine to obtain 100 kg of butadiene, kwh 12.4

The degree of anode decomposition of iodide to obtain iodine was 25 percent by weight of the total iodide feed. The anode solution contained 60 g iodine per liter. Passing through the anode space half the total amount of the solution fed into the electrolyzer yielded 13.5 kg iodine (450/2 ×0.06 =13.5) which figure corresponds to the amount of iodine contained in the dehydrogenation products. The anode solution (225 liters) containing 107 gm sodium iodide, 60 gm elemental iodine, and 7 gm sodium iodate per liter was directed desorption with an air-steam mixture, the desorption process being carried out at a temperature of 70°C and providing for practically complete recovery of iodine.

Electrolysis gave alkali and hydrogen in the cathode space, whereas iodate was reduced to iodide. 1.15 m^3 (STP) of hydrogen was removed from the cathode space and used for production needs. 223 liters of the cathode solution containing 20 gm per liter of alkali, 107 gm per liter of sodium iodide and 0.1 gm per liter of sodium iodate was mixed with the anode solution and fed into the scrubber. Thus, all the products of electrolysis were used during iodative dehydrogenation of butane. Loss of iodine during the recovery was mainly of a mechanical character and amounted from 0.1 to 0.3 percent by weight of iodine regenerated. Decomposition and loss of water amounted to 0.5 percent by weight of the solution electrolyzed.

What is claimed is:

1. A process for the recovery of iodine from the products of iodative dehydrogenation of hydrocarbons comprising the steps of:

a. treating said products of dehydrogentation of hydrocarbons with an aqueous solution of an alkali selected from the group consisting of sodium hydroxide, sodium carbonate and mixtures thereof until a weakly alkaline solution of iodine salts with a pH of 8 - 10 containing iodide and iodate is obtained;

b. electrolyzing said solution of iodine salts to separately obtain solutions of iodine and alkali, which also contain undecomposed salts of iodine;

c. recycling said solution of alkali to the alkali treatment of dehydrogenation products step (*a*);

d. blowing off elemental iodine from the solution of iodine by a gas which is inert with respect to iodine, said gas being selected from the group consisting of oxygen, an oxygen-containing gas and mixtures thereof with steam;

e. recovering the iodine from step (d) for reuse in the dehydrogenation of hydrocarbons; and

f. recycling the solution of iodine salts free of iodine to the alkali treatment of dehydrogenation product step (*a*).

2. A process according to claim 1, wherein electrolysis is carried out until the degree of decomposition of iodide of 10–35% by weight of iodide electrolyzed is reached.

3. A process according to claim 2, wherein electrolysis is carried out until the degree of decomposition of iodide of 25 percent by weight of iodide electrolyzed is reached.

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