

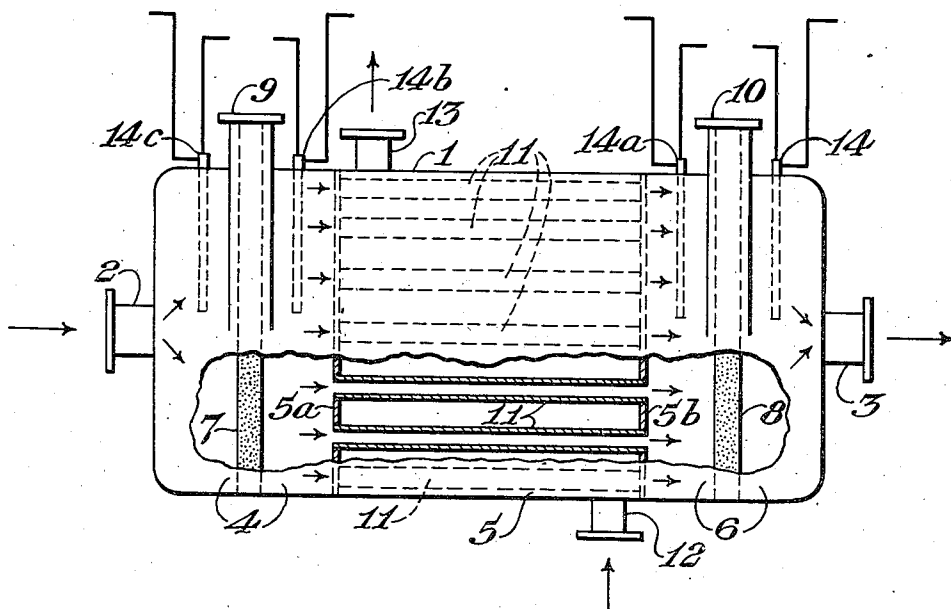
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PURIFICATION AND PRODUCTION OF OLEFINES

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PURIFICATION AND PRODUCTION OF
OLEFINS

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This invention concerns an improved method for purifying olefins which are contaminated with acetylenic compounds. It refers particularly to the conversion of such acetylenic compounds into olefins, whereby the yield and purity of the olefins are simultaneously improved. The present application is a continuation-in-part of our co-pending application Serial No. 174,667, filed November 15, 1937.

One of the usual methods for manufacturing olefins comprises passing a material, such as natural gas, refinery gas, kerosene, or other mineral oil fractions through a zone heated sufficiently to decompose such material with formation of hydrogen and one or more unsaturated compounds. Pyrolyses of the type just mentioned have been carried out at temperatures ranging from about 500° C. to about 1200° C., but the yield of olefinic products per pass of the material through the pyrolyzing zone is usually highest when operating at temperatures above 600° C., e. g., between 600° and 1000° C. The product obtained by the pyrolysis usually comprises not only the desired olefinic products but also hydrogen; saturated hydrocarbons such as methane, ethane, propane, etc.; di-olefins such as butadiene; and acetylenic compounds such as acetylene, methyl-acetylene, etc. The yield of acetylenic by-products becomes appreciable when operating at pyrolysis temperatures above 600° C., i. e., within the temperature range at which the olefins are usually produced in maximum yield.

The acetylenic by-products frequently interfere with subsequent reactions in which the olefinic products are to be employed and various methods for removing such acetylenic by-products from olefin-containing pyrolysis mixtures have been proposed. In general, the methods which have been used for removing acetylenic by-products from such mixtures have comprised extracting the mixtures with various organic solvents such as acetone, ethyl acetate, etc., having the property of selectively absorbing the acetylenic compounds and leaving the olefinic products largely unabsorbed. Such mode of removing the acetylenes from the pyrolysis mixtures involves extra operating steps, utilization of a solvent for the extraction, and usually results in loss of a portion of the olefin product.

As hereinbefore stated, the cracked-gas mixture obtained by pyrolyzing mineral oil fractions or other aliphatic hydrocarbons at temperatures above 600° C. comprises not only gaseous olefins but also hydrogen, acetylenic compounds, saturated hydrocarbons, and other gases. The hydrogen is usually present in an amount sufficient to saturate a substantial proportion of the unsaturated hydrocarbons in the gas and is always in

considerable molecular excess over the acetylenic compounds.

We have discovered that by contacting such cracked-gas mixture with a hydrogenation catalyst under the operating conditions hereinafter described the acetylenic compounds are selectively hydrogenated to form olefins, thereby removing acetylenes from the mixture and increasing the yield of olefins. During such operation the olefins present in the gas are not appreciably hydrogenated and the hydrogenation of the acetylenic compounds stops with the formation of olefins. We have further found that, although any active hydrogenation catalyst may satisfactorily be employed in such operation, certain new catalysts are particularly well adapted to use in the process. The invention, then, consists in the method and new catalysts hereinafter fully described and particularly pointed out in the claims.

The accompanying drawing is a diagrammatic sketch of apparatus suitable for use in practicing the invention. In the drawing, the numeral 1 designates the outer shell of a hydrogenator which is provided at one end with a gas inlet 2 and at the other end with a gas outlet 3. The interior of the hydrogenator is divided into three compartments, viz., a reaction chamber 4 at one end of the same, a cooling compartment 5 in its center, and another reaction chamber 6 at the other end of the hydrogenator beyond said cooling chamber. In the reaction chambers 4 and 6 are located catalyst panels 7 and 8 which may be removed through the well openings 9 and 10, respectively. Each such catalyst panel is usually made by supporting a granular catalyst, or a catalyst deposited on a granular base such as pumice, broken brickware, etc., between two parallel metal screens, the latter, of course, being provided with suitable frame work to hold them and the granular catalytic material in place. On each side of the panels 7 and 8 are located temperature recording means, such as thermometers or thermocouples, which are inserted into the wells 14, 14a, 14b, and 14c, respectively. The cooling chamber 5 is provided with the headers 5a and 5b and has passing through it the tubes 11, which permit the flow of gas from reaction chamber 4 to chamber 6. Cooling chamber 5 is provided with a cooling fluid inlet 12 and outlet 13. Any of the usual cooling fluids, e. g., water, steam, air, etc., may be used in chamber 5. The metal parts of the hydrogenator may be composed of usual structural metals such as iron, steel, nickel, etc. Any solid hydrogenation catalyst, e. g., nickel, cobalt, platinum, etc., may be used in the process, although factors such as the activity of the catalyst and the thickness of each catalyst bed will determine to a considerable extent the rate at which the gas mixture may be

passed through the hydrogenator to obtain the benefits of the invention. Also, the new catalysts described at a point later herein possess good activity and are exceptionally long lived.

In employing apparatus such as that just described for the selective hydrogenation of the acetylenic compounds in a gas mixture containing the same and also olefins and hydrogen in excess over that required to convert the acetylenes into olefins, the operating conditions which require control are the temperature at which the hydrogenation is carried out, the rise in temperature of the gas mixture which occurs during its passage through a given panel or bed of catalyst, and the rate at which the gas mixture is passed through the catalyst. Of these three variable operating conditions, the rise in temperature of the gas during passage through the catalyst is most critical, but fortunately this temperature rise is directly dependent upon the rate of gas passage and may be varied by changing the rate of flow.

When using any solid catalyst for the hydrogenation, the operating conditions to be observed are:

(1) The temperature of the gas mixture during contact with the catalyst should be sufficient to cause reaction but not above 450° C., since at higher temperatures the olefins as well as the acetylenes become hydrogenated and this secondary reaction, once started, usually causes overheating with resultant carbonization and frequent plugging of the apparatus. Temperatures of from 80° to 450° C. have successfully been employed and temperatures between 125° and 225° C. are generally most satisfactory.

(2) The rise in temperature of the gas during passage through a catalyst bed should not exceed 300° C. and preferably does not exceed 275° C. If a greater temperature rise is permitted, over-hydrogenation with formation of paraffins and carbonization are liable to occur.

(3) The rate of gas flow should be controlled so that the difference between the temperature of the gas entering a catalyst bed and that leaving the bed does not exceed 300° C. When necessary, this temperature difference may be decreased by increasing the rate of gas flow.

Since the temperature rise which occurs during passage of the gas mixture through a catalyst bed is due to heat liberated by hydrogenation of the acetylenic compounds, the temperature rise is dependent upon the concentration of acetylenes in the gas treated, upon the heat lost by radiation or conductance, and upon the quantity of acetylenic compound reacted during passage of the gas through the panel. Stated in simpler, though less exact, terms, the rise in temperature of the gas during passage through a catalyst bed is approximately proportional to the decrease in concentration of acetylenic compounds in the gas which occurs during such passage. Usually a 1 per cent by volume reduction of acetylene in such gas, brought about by hydrogenation in a catalyst bed, raises the temperature of the gas by between 48° and 56° C. Accordingly, in order to avoid a temperature rise of more than 300° C., the acetylene concentration of the gas should be reduced by not more than 6 per cent, and preferably not more than 5 per cent, during passage through a given panel or bed of catalyst.

It will thus be seen that in treating a gas mixture containing less than 5 per cent by volume of acetylenic compounds a single bed of catalyst can be used to convert substantially all of such

compounds into olefins, but that when the gas to be treated contains acetylenic compounds in higher concentration a plurality of catalyst panels must be used and not more than about 5 per cent reduction in the acetylenic content of the gas should be permitted to occur in any single panel of catalyst. In practice, it is preferable to employ a hydrogenator containing two or more panels of catalyst, with cooling means located between the panels, in treating any gas mixture containing more than 2 per cent of acetylenic compounds, since the use of a multi-panel reactor permits better temperature control with resultant increase in the life of the catalyst than is obtained when using only a single panel or bed of catalyst.

In manufacturing olefins in accordance with the invention natural gas, refinery gas, kerosene, or other mineral oil fractions or any substance rich in saturated aliphatic hydrocarbons may be employed as the starting material. Also, higher olefins, such as amylene, hexene, octylene, etc., may be used to produce lower olefins, such as ethylene, propylene, etc. Any such starting material, alone or admixed with diluents such as steam, carbon dioxide, etc., is pyrolyzed at temperatures above 600° C. in the presence or absence of dehydrogenation catalysts in accordance with any of the usual modes of pyrolyzing aliphatic hydrocarbons to obtain a vapor mixture comprising one or more olefins, hydrogen, and one or more acetylenic compounds. Other products, such as saturated hydrocarbons, di-olefins, etc., may also be present in the pyrolyzed mixture. The pyrolyzed vapor mixture may be cooled somewhat and passed over the hydrogenation catalyst, as hereinbefore explained, to effect the desired hydrogenation of the acetylenic compounds present.

However, such pyrolysis mixture frequently contains di-olefins, e. g., butadiene, which tend to polymerize or decompose and coat the catalyst during the hydrogenation, thereby shortening the active life of the catalyst. In practice, such di-olefins, are preferably removed before carrying out the hydrogenation. This may be accomplished in any of several ways, e. g., the pyrolysis mixture may be cooled and treated with a condensation catalyst, such as aqueous sulphuric acid, of activity sufficient to polymerize and condense the di-olefins without appreciably affecting the other unsaturated compounds present, or the mixture may be scrubbed with a solvent such as light mineral oil having the property of selectively absorbing di-olefins and other higher hydrocarbons from the olefinic mixture, or the mixture may be cooled under pressure and thereafter distilled to separate the hydrocarbons containing 4 or more carbon atoms, which include all di-olefins, from the more volatile substances such as hydrogen, ethylene, propylene, and acetylene, or the crude pyrolysis mixture may be cooled and treated with sufficient chlorine or bromine to react with the unsaturated hydrocarbons containing 4 or more carbon atoms, but not the ethylene or propylene present, to form liquid polychlorinated hydrocarbons. The vapor mixture remaining after any such treatment contains hydrogen, one or more olefins, and usually acetylene or other acetylenic compounds. Such residual vapor mixture is passed over or through one or more beds of a porous hydrogenation catalyst at a temperature sufficient to cause reaction between the hydrogen and acetylenic compounds in the mixture with formation of addi-

tional olefins. As hereinbefore pointed out, such temperature is usually between 125° and 250° C., and it is essential that neither the catalyst nor the gas in contact therewith be permitted to become heated to temperatures above 450° C. The gas mixture is passed through the catalyst bed at such rate that the temperature of the gas leaving the bed does not exceed that of the gas entering the bed by more than 300° C. When the gas subjected to the hydrogenation initially contains more than 5 per cent by volume of acetylenic compounds, it is, as hereinbefore explained, necessary to contact it with a series of catalyst panels or beds, the gas being cooled during passage from one such panel or bed to the next so that it never becomes heated to a temperature exceeding 450° C.

The hydrogenation is usually carried out at atmospheric pressure or slightly above, but it may be carried out under considerably higher pressures, e. g., 50–200 pounds per square inch gauge. In most instances we prefer to operate at pressures below 50 pounds per square inch gauge since the reaction is most readily controlled at such moderate pressures.

The vapor mixture issuing from the hydrogenation chamber is relatively free of acetylenic compounds and is considerably richer in olefins than before contact with the catalyst. The treated mixture may be employed directly in most reactions for the preparation of olefin derivatives, such as alcohols, alkyl halides, olefin halides, etc.

As hereinbefore stated, any active hydrogenation catalyst, such as platinum, cobalt, reduced nickel, etc., may be employed to promote the reaction between hydrogen and the acetylenic by-products, but certain catalysts possess a greater catalytic life than others and display less tendency to cause overheating when employed in the reaction. In practice, we prefer to use reduced nickel or catalysts comprising reduced nickel in the process and we have found that certain compound catalysts comprising reduced nickel and other metals are more useful than reduced nickel itself for the purpose. Reduced nickel prepared by heating nickel nitrate to a temperature at which it is decomposed with formation of the oxide and subsequently or simultaneously hydrogenating the latter is very active, but tends to cause overheating during use in the hydrogenation. Accordingly, careful control is required in using reduced nickel itself as the catalyst.

We have found that mixed catalysts comprising finely divided nickel and one or more of the metals iron, copper, zinc, and cobalt, also in finely divided form, possess numerous advantages over nickel alone as catalysts. Such mixed catalysts may contain their metal ingredients in widely varying proportions and may frequently be prepared and employed more economically than nickel alone.

For instance, a mixed catalyst comprising between 0.1 and 1.0 gram atom of iron per gram atom of nickel displays less tendency to cause overheating during the hydrogenation and is less susceptible to becoming poisoned, i. e., deactivated, than reduced nickel alone. This catalyst may be prepared by heating a mixture of iron and nickel nitrates to form a mixture of the corresponding oxides and reducing the latter with hydrogen at temperatures between 375° and 425° C. under a hydrogen pressure of between 100 and 200 pounds per square inch gauge. Such operations are preferably carried out consecu-

tively, but they may be carried out in a single step by heating the nitrates in a current of hydrogen to a temperature at which they are decomposed.

A mixture of between 0.05 and 0.25 gram atom of copper per gram atom of nickel is substantially as active in the process as nickel itself, but is less easily poisoned than nickel. Such catalyst is prepared by heating a mixture of the metal nitrates to form the corresponding oxides and reducing the latter at temperatures between 275° and 325° C. under a hydrogen pressure between 100 and 200 pounds per square inch. If desired, this reduction may be carried out at atmospheric pressure and at temperatures between 300° and 325° C.

A mixture of about 0.1 gram atom of copper, 0.25 gram atom of iron, and 1 gram atom of nickel is substantially equivalent in activity to the iron-nickel catalyst mentioned above. Such catalyst is made by heating the necessary metal nitrates to form a mixture of the corresponding oxides and reducing the latter with hydrogen at atmospheric pressure and a temperature between 350° and 375° C.

Mixed catalysts comprising nickel, zinc, and iron, or nickel and cobalt, are also less sensitive than nickel itself toward poisoning during the hydrogenation. Such catalysts are prepared from a mixture of the corresponding metal nitrates by procedure similar to that mentioned above.

The hydrogenation catalyst may be used in pure finely divided form but is preferably used on a support such as pumice, alumina, silica gel, carborundum, coke, etc. In practice, we find coal-coke to be satisfactory and most economical as a support for the catalyst. The supported catalyst is prepared by treating the supporting material, e. g., coal-coke, with a solution or melt of the necessary metal nitrates, heating the resultant mixture to generate the metal oxides on the supporting material and reducing the metal oxides to obtain the metals on and/or in the supporting material. As hereinbefore stated, the operations of decomposing the nitrates to oxides and reducing the latter are preferably carried out consecutively but may be performed simultaneously. The supported catalyst is employed in granular form, preferably of size capable of passing a four mesh, but not a three mesh, screen.

The following examples illustrate certain ways in which the principle of the invention has been applied but are not to be construed as limiting the invention.

Example 1

Fuel oil was pyrolyzed by first vaporizing the same, passing the vapors into admixture with about 3 parts by weight of superheated steam, and passing the mixture through a reaction zone at a temperature of about 850° C. The vapors issuing from the reaction zone were cooled to condense the higher hydrocarbons, e. g., unreacted oil, and most of the water vapor, and the remaining vapors were scrubbed with light mineral oil in accordance with known procedure to remove hydrocarbons containing more than 3 carbon atoms therefrom. The remaining gas contained 39.6 per cent by volume of ethylene, about 20 per cent of hydrogen, 12 per cent of methane, about 7 per cent of propylene, 3 per cent of acetylene and traces of other gases. This gas mixture was passed at approximately atmospheric pressure and at space velocities varying from 6.6

to 47 cubic feet of gas per cubic foot of catalyst per minute through a bed of a granular hydrogenation catalyst maintained at temperatures which increased gradually from 150° to 250° C. during the run. The catalyst employed in this experiment was one prepared by soaking granular pumice in a concentrated nickel nitrate solution, drying the treated pumice at about 100° C., whereby the nickel nitrate was deposited on and in the pumice, and thereafter simultaneously decomposing the nitrate to the oxide and reducing the latter by passing hydrogen over the treated pumice while maintaining the latter at a temperature between 300° and 350° C. The gaseous mixture issuing from the catalyst bed during the above-described employment of the catalyst contained 43.2 per cent by volume of ethylene, 8 per cent of propylene, and only 0.5 per cent of acetylene.

Example 2

A cracked-oil gas fraction containing 42.4 per cent by volume of ethylene, 22 per cent of hydrogen, 16.2 per cent of methane and other saturated hydrocarbons, 9.5 per cent of propylene, 4 per cent of nitrogen and oxygen, 3.7 per cent of acetylene, 1.2 per cent of higher acetylenic compounds (apparently allylene for the most part), and 1 per cent of carbon dioxide and hydrogen sulphide was reacted to convert the acetylenic compounds into olefins, using a reactor similar to that illustrated in the accompanying drawing except that it contained a series of three panels of granular catalyst and had cooling means located between the panels. The catalyst used in the panels was prepared by soaking granular silocel (a diatomaceous earth) of 3 to 4 mesh size in a saturated aqueous nickel nitrate solution, thereafter heating the granular material to 350° C. and maintaining it at temperatures between 350° and 375° C. for about one-half hour, and then heating it at temperatures between 400° and 420° C. in a current of hydrogen for 4 hours. It will be noted that the cracked-oil gas employed in this experiment contained a total of 4.9 per cent of acetylenic compounds. This gas was preheated and passed at a space velocity of 100 through the reactor. By "space velocity" is meant the ratio of the volume of gas per minute (expressed as cubic feet of gas at 0° C. and atmospheric pressure) per cubic foot of granular catalytic material in the reactor. During passage of the gas through the reactor measurements were taken of the temperature of the gas just before entering each catalyst panel and of the temperature in the center of each panel. The gas was, of course, cooled during passage from one panel to the next. Also, samples of the gas leaving each panel were withdrawn and analyzed to determine their content of acetylenic compounds in per cent by volume. The values obtained are given in the following table.

Table

Measurement	1st panel	2d panel	3d panel
Temp. of entering gas.....°C.	154	152	154
Temp. inside of panel.....°C.	280	248	180
Per cent acetylenes in exit gas.....	2.4	0.8	0.2

The gas leaving the reactor was analyzed and found to contain, on a volume basis: ethylene, 48.2 per cent; hydrogen, 18.1 per cent; saturated hydrocarbons, 17.1 per cent; propylene, 11.2 per cent; nitrogen and oxygen, 4.2 per cent; carbon

dioxide and hydrogen sulphide, 1 per cent; acetylene, 0.2 per cent.

The invention may be applied in ways other than those hereinbefore mentioned. For instance, it may be applied to produce one or more olefins from a single saturated aliphatic hydrocarbon such as ethane, propane, or a butane, by pyrolyzing such individual hydrocarbon at a temperature above 600° C. and passing the pyrolysis mixture over a hydrogenation catalyst to effect reaction between the hydrogen and acetylenic compounds present in the mixture. It may also be applied where an aliphatic hydrocarbon is pyrolyzed at very high temperatures, e. g., in an electric arc, to form acetylene as the principal product. The resultant pyrolysis mixture may be scrubbed with a suitable solvent to extract selectively most of the acetylene leaving a vapor mixture comprising hydrogen, olefins and a minor proportion of acetylene. This residual vapor mixture may be contacted with a hydrogenation catalyst under the reaction conditions hereinbefore specified to convert the remaining acetylene into an olefin, e. g., ethylene, thereby increasing the yield of olefin.

Other modes of applying the principle of the invention may be employed instead of those explained, change being made as regards the method or ingredients herein disclosed, provided the steps or ingredients stated in any of the following claims or the equivalent of such stated steps or ingredients be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a durable hydrogenation catalyst at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

2. In a method for producing ethylene, the step of passing a gaseous mixture comprising ethylene as its major ingredient and also containing acetylene, and more than one mole of hydrogen per mole of acetylene, through a bed of a durable hydrogenation catalyst at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form ethylene and the ethylene content of the gas is increased.

3. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene, and more than one mole of hydrogen per mole of the acetylene, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. through a series of beds of durable hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby the acetylene is hydrogenated to form

an olefin and the olefin content of the gas is increased.

4. In a method for producing ethylene, the step of passing a cracked-oil gas fraction comprising ethylene as its major ingredient and also containing acetylene, and more than one mole of hydrogen per mole of the acetylene, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. through a series of beds of durable hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby acetylene is hydrogenated to form ethylene and the ethylene content of the gas is increased.

5. In a method for producing olefins, the steps of pyrolyzing an aliphatic hydrocarbon at a temperature above 600° C. to obtain a gaseous mixture comprising hydrogen, olefins and acetylene, and containing the olefins as the major ingredients of the gaseous mixtures and passing the gas through a bed of a durable hydrogenation catalyst at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form ethylene and the olefin content of the gas is increased.

6. In a method for producing olefins, the steps of pyrolyzing an aliphatic hydrocarbon at a temperature above 600° C. to produce a gaseous mixture comprising hydrogen, olefins, and acetylenes, and containing the olefins as the major ingredients of the gaseous mixtures removing any diolefin present in the gas, and thereafter passing the gas at a reaction temperature sufficient to cause hydrogenation of the acetylenes but below 450° C. through a series of beds of hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

7. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular durable hydrogenation catalyst containing nickel as an essential ingredient at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

8. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst, containing finely divided nickel and a finely divided catalytic metal of the class consisting of iron, copper, zinc, and cobalt, at a reaction temperature sufficient to cause hydro-

genation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

9. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst comprising nickel and iron, each finely divided, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

10. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst containing nickel and copper, each in finely divided form, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

11. In a method for producing olefins, the step of passing a cracked-oil gas mixture comprising as its major ingredient at least one olefin and also containing an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst containing nickel, copper, and iron, each in finely divided form, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

12. In a method for producing olefins, the step of passing a cracked-oil gas mixture, comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of at least one acetylenic hydrocarbon and more than one mole of hydrogen per mole of the acetylene, through a bed of a durable hydrogenation catalyst at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

13. In a method for producing ethylene, the step of passing a gaseous mixture, comprising ethylene as its major ingredient and also containing more than 5 per cent by volume of acetylene and more than one mole of hydrogen per mole of acetylene, through a bed of a durable hydrogenation catalyst at a reaction tempera-

ture sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form ethylene and the ethylene content of the gas is increased.

14. In a method for producing olefins, the step of passing a cracked-oil gas mixture, comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of an acetylene and more than one mole of hydrogen per mole of the acetylene, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. through a series of beds of durable hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

15. In a method for producing ethylene, the step of passing a cracked-oil gas fraction, comprising ethylene as its major ingredient and also containing more than 5 per cent by volume of acetylene and more than one mole of hydrogen per mole of the acetylene, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. through a series of beds of durable hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby acetylene is hydrogenated to form ethylene and the ethylene content of the gas is increased.

16. In a method for producing olefins, the step of pyrolyzing an olefinic hydrocarbon at a temperature above 600° C. to produce a gaseous mixture comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of acetylenic hydrocarbons and hydrogen in amount exceeding the molecular equivalent of the acetylenes, removing any diolefin present in the gas, and thereafter passing the gas at a reaction temperature sufficient to cause hydrogenation of the acetylenes but below 450° C. through a series of beds of hydrogenation catalyst with intermediate cooling of the gas during passage from one catalyst bed to another such bed, the rate of gas flow being

sufficient to prevent a more than 300° C. rise in temperature of the gas during passage through any catalyst bed, whereby the acetylenes are hydrogenated to form olefins and the olefin content of the gas is increased.

17. In a method for producing olefins, the step of passing a cracked-oil gas mixture, comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst, containing finely divided nickel and a finely divided catalytic metal of the class consisting of iron, copper, zinc, and cobalt, at a reaction temperature below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

18. In a method for producing olefins, the step of passing a cracked-oil gas mixture, comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst comprising nickel and iron, each finely divided, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

19. In a method for producing olefins, the step of passing a cracked-oil gas fraction, comprising as its major ingredient at least one olefin and also containing more than 5 per cent by volume of an acetylene and more than one mole of hydrogen per mole of the acetylene, through a bed of a granular supported hydrogenation catalyst containing nickel and copper, each in finely divided form, at a reaction temperature sufficient to cause hydrogenation of the acetylene but below 450° C. and at a rate of gas flow sufficient to prevent a more than 300° C. rise in the temperature of the gas during its passage through the catalyst bed, whereby the acetylene is hydrogenated to form an olefin and the olefin content of the gas is increased.

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