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HYDROCARBON SYNTHESIS

Robert E. Burk, Cleveland, Ohio, assignor to The
Standard Oil Company (Ohio), Cleveland, Ohio,
a corporation of Ohio

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Many suggestions have been made in the direction of synthesis of hydrocarbon compounds from lower molecular materials. Generally, the conditions suggested have involved operation with mixtures of more or less indeterminate character, and dependance upon averages over wide spread ranges, and without compensated temperature and concentration and other relations. In general, insufficient account has been taken of the inherent tendency of such reactions to overrun. In the U. S. Patent to Plauson No. 1,436,819, there is set forth a process particularly for diolefine production from a mixture of gases of the ethylene and acetylene series, depending in important measure upon dilution by presence of diluent gases or the like. I have found that in commercially synthesizing of hydrocarbons it is important to operate with raw materials and conditions of definite and certain character as contradistinguished from averages, and with avoidance of diluents, over-run of reaction being controlled against. By the present invention thus, it becomes possible to operate with production of definitely controllable products and with elimination of excessive wastes and losses which have been customary.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

The materials for the present synthesis are on the one hand acetylene, and on the other hand hydrocarbons of gasiform character, as detailed subsequently. The acetylene is prepared in a suitable manner, for instance by thermolytic action in an electric arc or electric furnace from methane or at least gas which is predominant in methane, or preferably by the cracking of selected hydrocarbons. Thus, yields of acetylene by cracking hydrocarbons at temperature higher than the conventional cracking temperatures have been mentioned in the art, e. g. U. S. Patent No. 1,962,502, and as reported by Tropsch, Parrish and Egloff, Ind. Eng. Chem. 28: 501, yields of acetylene by cracking ethylene at 1400° C., and somewhat poorer yields by cracking propylene at the same temperature. Contrary to the opinion expressed in current literature however, I have found that operating with ethylene, desirable yields of acetylene may be obtained therefrom

at a much lower temperature range than 1400° C., as for instance down to about 600° C., and particularly favorably around 700° C. And, with the acetylene there is obtained an advantageous yield of olefins. Thus, ethylene, or for that matter hydrocarbons higher than methane, or from two carbon atoms up, including those normally in liquid fractions such as kerosene, gas oil etc., may be so treated, heating at the noted moderate temperature range rather than the high temperature range customary heretofore, and desirably with the presence of a diluting gas, for instance steam, and after separating the acetylene from the product mixture, for instance conveniently by solvent extraction with a ketone, as acetone, etc., and separating the hydrogen, as for instance by suitable cooling or fractional condensation of the hydrocarbons whereby the hydrogen may be eliminated, there is thus available acetylene, also ethylene, and some higher molecular weight hydrocarbons. In such cracking, the time of heating is a few seconds, for instance 2-8, depending somewhat upon the particular hydrocarbons. With suitably selected raw gas material, the entire synthesis including the preparation of the acetylene and the reaction between the acetylene and the other hydrocarbons can be carried through from one consistent standpoint. A gas of methane content 25 to above 96 per cent is readily obtainable from natural gas sources, or from certain refinery gases. In fact, in favorable situations, refinery gas sources are able to supply such gas as is desired of high methane content; and on the other hand other gas which is of hydrocarbons from ethane and up, short of the condensible or absorbable hydrocarbons, or in other words a gas comprising hydrocarbons in the range of 2-4 carbon atoms. Furthermore, there is a distinction possible as between saturated and unsaturated hydrocarbon sources in this range. For the process then, a methane-rich gas may be passed through a furnace, and with temperatures higher than 1500° C., acetylene is formed from the methane, together with free hydrogen. The yield of acetylene here is in general, as known, higher, the higher the temperature and the greater the dilution, or the lower the pressure, Ind. Eng. Chem. 26: 56. The detail of suitable furnaces is not important, and it is sufficient to here state that the gas stream may be fed directly through the path of a suitable arc, or the heating zone may be somewhat more extensive in that the electrodes are employed in conjunction with granulated carbon used as a resistance furnace, the methane being

forced therethrough at a rate keeping the passageways clear. Hydrogen may be recycled for the latter purpose. Immediately as the acetylene is formed, and before it has opportunity to drop in temperature sufficiently to polymerize, my procedure provides for its shock-cooling, and while this may be effected more or less mechanically as by molten lead through which and with which the hot stream is contacted, a more efficient action is had by commixing selected hydrocarbons with the hot acetylene stream, and thereby the shock-cooling and prevention of losses of acetylene is accomplished and at the same time there is presented the reaction material for the second stage of the synthesis. Preferably, the proportion of the commixed hydrocarbons on their temperature is so adjusted with respect to the hot acetylene stream as to give a resultant temperature in the total mixture, of the desired reaction level, and the reaction proceeds. In particular cases, I shock-cool the acetylene stream suitably, for instance by molten lead, and separate hydrogen, then pass the acetylene and other hydrocarbons for reaction therewith, through a heating zone controlled to temperature for the particular products in view. Taking a refinery gas source for instance providing propylene and butylene, the butylene tends to combine with the acetylene in order first, and then the propylene, with respect to speed. Propylene plus acetylene forms isoprene, which is available for various syntheses, including rubber and rubber-like products.

By employing such gases or gas fractions as are of saturated character, as ethane, propane, butane, products free from the diolefinic type foregoing, are obtained viz. for instance butene, pentene, hexene, etc. on reaction with acetylene.

In general, the selected hydrocarbons which are to be reacted with the acetylene, or the closely-ranged hydrocarbon gases are brought into reaction with substantial absence of diluents although the contrary may be practiced. Catalysts are not always of advantage. In some instances for certain products, a catalyst is of advantage, and for this I prefer catalysts containing copper or certain halides. Pressure of high order is not necessary, and in fact it is preferable to operate at atmospheric pressure or at least not substantially in excess of 500 pounds per square inch.

Immediately as the reaction between the acetylene and the other hydrocarbon component is accomplished, the formed products are stripped out from the reaction mass, this being accomplished in a suitable way, depending upon the precise character of the end products being made. Thus, normally gaseous unsaturated products

may be taken out by suitably cooling and passing the gaseous mixture through selective oil-absorption columns. Condensable products such as pentene may be taken by passing through a condensation zone. If operating by saturated gas components together with acetylene and forming pentene in mixture with higher hydrocarbons as hexene and heptene, all of the condensable portion may in some instances be desired to be taken out en masse, as available for special usages in lightening or blending motor fuels.

The olefines produced conjointly with the acetylene may be polymerized separately, or be caused to react with acetylene or to react with paraffins.

The olefines formed by reaction of acetylene with paraffins similarly may be handled in these several ways.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. Hydrocarbon synthesis, comprising acetylenizing methane in a furnace zone, shock-cooling the acetylene before polymerization substantially occurs by admixing therewith an aliphatic hydrocarbon of 2-4 carbon atoms and in amount reducing the temperature of the mixture to inter-combining temperature, and separating the formed hydrocarbons.

2. Hydrocarbon synthesis, comprising acetylenizing methane in a furnace zone, shock-cooling the acetylene before polymerization substantially occurs by admixing propylene therewith and in amounts reducing the temperature of the mixture to inter-combining temperature, and separating the so-formed diolefine.

3. Hydrocarbon synthesis, comprising acetylenizing methane in a furnace zone, shock-cooling the acetylene before polymerization substantially occurs by admixing therewith unsaturated hydrocarbons of 2-4 carbon atoms and in amounts reducing the temperature of the mixture to inter-combining temperature, and separating the formed hydrocarbons.

4. Hydrocarbon synthesis, comprising acetylenizing methane in a furnace zone, shock-cooling the acetylene before polymerization substantially occurs by admixing therewith saturated hydrocarbons of 2-4 carbon atoms and in amounts reducing the temperature of the mixture to inter-combining temperature, and condensing out the formed hydrocarbon products.

ROBERT E. BURK.