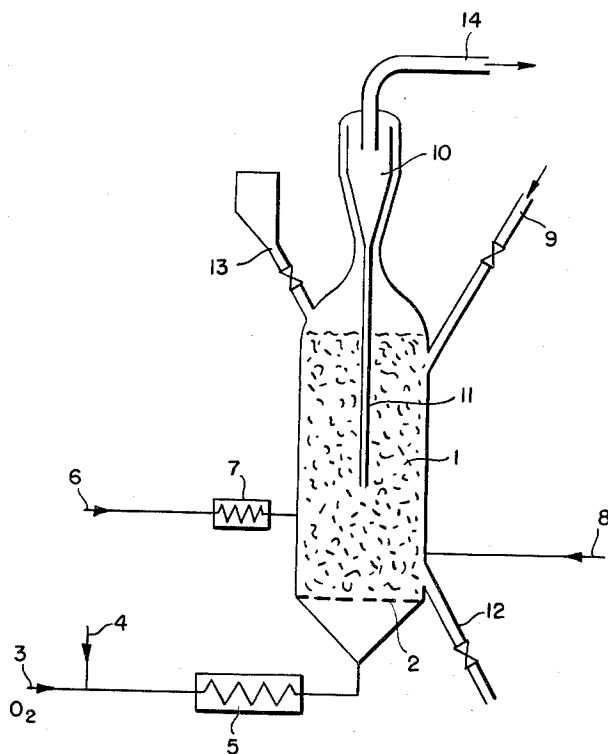


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PRODUCTION OF UNSATURATED HYDROCARBONS
BY CRACKING HYDROCARBONS
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PRODUCTION OF UNSATURATED HYDROCARBONS BY CRACKING HYDROCARBONS

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This invention relates to the production of unsaturated gaseous hydrocarbons. More specifically, this invention relates to the production of unsaturated gaseous hydrocarbons by cracking hydrocarbons.

It is known to produce gaseous olefins by cracking hydrocarbons at high temperatures. The disadvantage of this process consists in the fact that in the cracking more or less large amounts of carbon black are formed and are entrained with the reaction gases and vapors. This carbon black tends to be deposited on the walls of the reaction vessel and outlet pipe, whereby the continuous operation of the process is made exceedingly difficult. If the hydrocarbons to be supplied to the cracking contain sulfur-containing compounds and the cracking occurs with the addition of oxygen to cover the heat requirement of the cracking reaction, then there is added as a further disadvantage of the process the fact that the cracking gas contains, besides hydrogen sulfide, more or less large amounts of sulfur dioxide and sulfur trioxide after leaving the reaction chamber and costly measures are necessary to prevent corrosion.

Cracking has been carried out with the aid of catalysts to avoid this disadvantage. As such there have already been used compounds of group IIa of the periodic system, in lump or granular form. It has been shown, however, that undesirable reactions, for example the reaction of water vapor with hydrocarbons to form carbon monoxide and hydrogen, are accelerated to such a large extent by the catalysts used hitherto that the yield of gaseous olefins is strongly diminished. Furthermore, it is known to carry out the cracking of gaseous or vaporous hydrocarbons with or without catalysts, by adding continuously to the gaseous or vaporous hydrocarbons before introduction into the reaction chamber very small amounts of compounds of groups Ia and IIa of the periodic system in such a form that these exist in mist or vapor form in the reaction chamber. These processes, therefore, require an accurate control of the amounts of compounds of groups Ia and IIa to be added and in many cases do not produce the desired result.

We have now found that the said disadvantages are avoided in a simple manner by carrying out the cracking of the liquid hydrocarbons in a fluidized layer of solid material with the addition of 20 to 200% by weight of water vapor and providing the fluidized layer with a small amount of compounds of groups Ia and IIa of the periodic system.

As initial materials for the process according to this invention there may be used liquid petroleum hydrocarbons, especially sulfur-containing petroleum hydrocarbons, such as for example sulfur-containing fractions from petroleum distillation incorporating a large percentage of non-vaporizable hydrocarbons. The substances of this type include residues of crude oil and residues from petroleum distillation.

The process is carried out at temperatures of 600 to 900° C., preferably at 650 to 850° C. Working is usually at normal pressure. It is also possible however to work at slightly higher pressure, e.g. at 5 to 20 atmospheres.

During the reaction, an endothermic gasifying agent, which may at the same time serve as a fluidization agent,

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is introduced into the fluidized layer, preferably from beneath the grate. It is advantageous to add water vapor in an amount of 20 to 200% by weight, preferably 25 to 100% by weight. In order to cover the heat requirement of the reaction and to maintain the reaction temperature, oxygen may, if required, be added in the necessary amounts and advantageously diluted with water vapor. The oxygen may also be introduced into the fluidized layer in admixture with the hydrocarbons to be reacted.

As solid materials to be used in accordance with this process there are suitable inert substances, especially fire-resistant materials, having a small pore volume and a small inner surface. Such materials include mineral or synthetic compounds containing magnesium, alumina or silicon, e.g. sillimanite, corundum and magnesite. Preferred substances are oil coke or other materials containing carbon, such as high-temperature coke, anthracite or brown-coal low temperature coke. A preferred embodiment of the invention consists in using as the solid material the oil coke formed in the cracking. A constant height of the fluidized layer is maintained by withdrawing from the fluidized layer the excess oil coke formed, either periodically or continuously.

During the process, small amounts of compounds of groups Ia and IIa of the periodic system are supplied to the fluidized layer as catalytically active additions, either directly or indirectly. In the latter case, the solid materials are soaked with a solution of the said compounds. The compounds of groups Ia and IIa may however also be introduced directly into the fluidized layer in solid, e.g. pulverulent, form. This is particularly advantageous when the oil coke formed in the reaction is used as the solid material. In this case the compounds, which are preferably used in powder form, are introduced directly, either in batches or continuously. The quantities should be such that the concentration of the substances remains approximately constant during the process and 0.01 to 1%, preferably 0.01 to 0.5% by weight of the element used, based on the weight of the solid material, is present in the fluidized layer. By the fluidized motion, the pulverulent material introduced is distributed completely uniformly over the surface of the globular particles of the oil coke after a short time. When using inert solid materials, the catalytically active compounds should be applied to the solid materials before these are introduced into the fluidized layer. As catalytically active additions of groups Ia and IIa of the periodic system there are advantageously used the carbonates or nitrates, i.e. compounds which form oxides under the reaction conditions, or the oxides of sodium, potassium, beryllium, calcium and magnesium.

As initial materials there are suitable in particular mineral oils and their fractions, for example fractions of the boiling range of gasoline and mineral oil residues.

The following examples will further illustrate this invention but the invention is not limited to these examples.

Example 1

A fluidized layer 1 (see drawing) of oil coke formed in the cracking is situated in a blast furnace of cross-section 1 m.² on a metal grate 2 provided with fine slits. At the beginning of the operation anthracite having a grain size of about 3 mm. is used and this is introduced through filter neck 13. Beneath the grate a mixture of 400 kg. of steam (through conduit 4) and about 200 normal cubic meters of oxygen (through conduit 3) which has been preheated to 600° C. in the preheater 5, is blown in every hour into the fluidized layer. Above the grate, 600 kg. of a Kuwait crude oil is introduced per hour through conduit 6 and the preheater 7. The hydrocarbons of boiling point above about 25° C. formed in the

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process, are recycled through conduit 8 in an amount of 400 kg. per hour, into the fluidized layer above the grate, together with the carbon black formed in the process and the solid material originating from the fluidized layer and washed out from the cracking gas. At each periodic interval of four hours, 600 grams of anhydrous pulverulent sodium carbonate is introduced dry into the fluidized layer through conduit 9. The proportions of steam and oxygen are so adjusted that a reaction temperature of about 720° C. prevails in the fluidized layer. The solid materials entrained out of the fluidized layer by the cracking gases and vapors formed are separated for the most part in a cyclone 10 situated above the fluidized layer and flow back into the fluidized layer through the cyclone down pipe 11. The cracked gases which are obtained in the process and which contain ethylene and propylene are withdrawn through pipe 14. In an hour, about 15 kg. excess oil coke is formed which is continuously sluiced out from the fluidized layer through conduit 12. In the stationary operating condition the sodium content of the oil coke amounts to 0.4% by weight.

There are formed only very small amounts of carbon black which are taken up by the liquid reaction products boiling above 250° C. used as washing oil and are recycled with these into the fluidized layer. The cracking gas contains no sulfur dioxide and no sulfur trioxide. The process can be carried out continuously for months without obstruction of the supply pipes above the fluidized layer.

For each metric ton of refining oil there are formed about 160 kg. of ethylene and 125 kg. of propylene. Moreover there are formed a residual gas of high calorific value, a gasoline containing large amounts of aromatic, and oil coke.

When working under the same conditions but without supplying sodium carbonate, more than three times the amount of carbon black is formed. The cracking gas contains appreciable amounts of sulfur dioxide and sulfur trioxide. The hot tubes above the fluidized layer are obstructed in the course of time by deposits and the colder tubes corrode.

The sulfur dioxide and sulfur trioxide have to be separated prior to the cracking of the olefin-containing gases. In contrast, in the process according to the present invention the sulfur is present in the end products in the form of hydrogen sulfide and can be obtained as elemental sulfur in a technically simple manner. The hydrogen sulfide content of the cracking gases has no troublesome effect in the working up.

Example 2

In the same manner and in the same apparatus as described in Example 1 800 kg. of Aramco oil are cracked in the fluidized layer. Simultaneously with the oil, there are blown into the fluidized layer per hour 300 kg. of water vapor and about 300 Nm.³ of oxygen. 500 kg. per hour of those hydrocarbons formed in the process which boil above 250° C. are returned to the fluidized layer above the grate, together with the carbon black formed, and the solid materials washed out from the cracking gas. In a modification of the procedure according to Example 1, magnesium oxide in powder form is introduced

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in an amount of 168 g. per hour. A temperature of 740° C. is established in the fluidized layer and 50 kg. per hour of excess oil coke are sluiced out from the fluidized layer in continuous operation. The oil coke thus withdrawn has a magnesium content of 0.2% by weight. 180 kg. of ethylene and 115 kg. of propylene are formed for every ton of oil introduced. Moreover there are formed a residual gas of high calorific value, a gasoline containing large amounts of aromatic, and oil coke.

We claim:

1. In a method of producing unsaturated gaseous hydrocarbons by cracking liquid hydrocarbons at temperatures of about 600° to 900° C. in a fluidized layer of inert solid material with the addition of 20 to 200% by weight of water vapor, the improvement which comprises providing as part of the fluidized solids in said fluidized layer from 0.01 to 1.0% by weight of a compound of a metal of groups Ia and IIa of the periodic system, calculated as elements.

2. In a method as claimed in claim 1 the improvement which comprises using a fluidized layer consisting of oil coke formed in the cracking and adding the metal compound to the fluidized layer in solid form.

3. In a method of producing unsaturated gaseous hydrocarbons selected from the group consisting of ethylene, propylene and butylene by cracking liquid hydrocarbons at temperatures of 650° to 850° C. in a fluidized layer of oil coke formed in the cracking with the addition of 25 to 100% by weight of water vapor, the improvement which comprises adding a compound of a metal selected from the group consisting of sodium, potassium, beryllium, calcium and magnesium in solid form in an amount, calculated as elements such that during the process 0.1 to 0.5% by weight of said compound with reference to the weight of the oil coke are present in the fluidized layer.

4. In a method as claimed in claim 3 the improvement which comprises adding sodium carbonate.

5. In a method as claimed in claim 3 the improvement which comprises adding magnesium oxide.

6. In a method of producing unsaturated gaseous hydrocarbons selected from the group consisting of ethylene, propylene and butylene by cracking liquid hydrocarbons at temperatures of 650° to 850° C. in a fluidized layer of oil coke formed in the cracking with the addition of 25 to 100% by weight of water vapor, the improvement which comprises adding a compound of a metal selected from the group consisting of sodium, potassium, beryllium, calcium and magnesium in solid form in an amount, calculated as elements such that during the process 0.01 to 1% by weight of said compound with reference to the weight of the oil coke are present in the fluidized layer.

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