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AUTOTHERMAL CRACKING OF LIQUID
HYDROCARBONS

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This invention relates to a process for the production of gaseous olefines, especially ethylene, from liquid hydrocarbons, and especially to a process for the autothermal cracking of liquid hydrocarbons, for example crude petroleum, in a fluidized bed of oil coke formed by the cracking.

It is known to crack liquid hydrocarbons for the production of gaseous olefines, especially ethylene, in a fluidized bed of granular solids, by burning part of the hydrocarbon to be cracked with oxygen to produce the necessary cracking heat and cracking the remainder of the hydrocarbon with or without the addition of steam. The continuous cracking of hydrocarbons in a fluidized bed is in general carried out at temperatures of more than 600° C. and it is advantageous to use for the fluidized bed oil coke formed by the cracking. This oil coke usually forms in globular form, is less corrosive than other inert solids and is less liable to attrition.

For uniform cracking it is essential that a constant height of the fluidized bed, and consequently a constant content in the fluidized bed of oil coke formed by the cracking to be maintained. It is therefore necessary to carry out the process in such a way that the losses occurring by attrition and combustion are at least compensated for by fresh formation of oil coke. The fresh formation of oil coke during the cracking and the extent of consumption of oil coke already present are dependent on many factors.

We have now found that the equilibrium between the formation of oil coke during cracking and consumption of oil coke by combustion and attrition can be regulated so much in favor of the fresh formation of oil coke and at the expense of consumption of oil coke that decrease in the amount of fluidized solid is prevented by adding to the fluidized bed small amounts of substances which contain phosphoric and/or boric acid or salts of the same.

The said process is of special importance in processing liquid hydrocarbons with low Conradson carbon, for example with more than 0% up to about 2.5% Conradson carbon, such as crude petroleum having this property, and in the processing of liquid hydrocarbons, especially crude petroleum, which contain water. When using crude petroleum with low Conradson carbon, for example in the said range, the formation of oil coke during cracking is usually insufficient to compensate for the loss by combustion and attrition. In the case of hydrocarbons containing water, for example crude petroleum, a content of salts, especially alkali salts, such as sodium and potassium chloride, often favors the combustion of oil coke. It has therefore always been necessary to separate the water by a special purification method prior to the use of such initial hydrocarbons. By the process according to this invention it is now possible to crack both crude petroleum containing aqueous solutions of salts and also crude petroleum having low Conradson carbon, autothermally to gaseous olefines and to provide the fluidized bed solely from the oil coke formed by the cracking.

Liquid hydrocarbons or certain fractions of petroleum

distillation, gas oils and mineral oil residues, may be used as initial materials for the process. The process is especially suitable for processing crude petroleum. The additions which inhibit burning of the oil coke may be substances which contain phosphoric and/or boric acid or their salts, for example boric acid and phosphoric acid themselves and also the various salts of phosphoric and boric acids, such as sodium, potassium, ammonium, magnesium, calcium, strontium, barium, zinc and aluminum salts. Primary, secondary and also tertiary phosphates, i.e., alkali metal and ammonium salts, may be used as phosphates, and also mixed phosphates, for example sodium ammonium phosphate. Ammonium phosphate $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ is especially suitable. Compounds of boron and phosphorus may be used, as well as mixtures of boric acid and its salts with phosphoric acid and salts of phosphoric acid.

In general, 0.05% by weight up to about 6% by weight, preferably 0.2 to 3% by weight, of these compounds is added with reference to the weight of oil coke present in the fluidized bed. The cracking of the liquid hydrocarbons is carried out at temperatures of 630° to 850° C., especially at 680° to 780° C. The fluidizing agent may be steam and/or carbon dioxide or another inert gas, and the oxygen necessary for autothermal cracking may be added thereto. The oxygen necessary for partial combustion may be added in the form of an oxygen-containing gas, for example air. However, it is preferable to add the oxygen in pure form, i.e., a commercially pure oxygen such as is obtained for example by liquefaction of air. It has proved to be advantageous to mix a part of the oxygen necessary for cracking with the initial materials, for example the crude oil, prior to the same being introduced into the fluidized bed, and to introduce the mixture direct into the fluidized bed. For this introduction it is essential that the oxygen should be mixed completely with the initial hydrocarbon by appropriate apparatus. One or more suitable multi-substance nozzles may, for example, be used, to achieve intimate mixing of the hydrocarbon with the oxygen.

In carrying out the process it is advantageous to return at least part of the high boiling oils containing up to 50% by weight of asphalts arising in the cracking to the fluidized bed. It is especially advantageous to return the fraction or a part of the fraction boiling above 250° C. of the oil formed by cracking.

The invention is illustrated by, but not limited to, the following examples.

Example 1

A fluidized bed of oil coke is supported above a metal grate provided with fine slots arranged in a shaft furnace having a cross-section of 1 sq. m. A mixture of about 400 kg./h. of steam and about 200 m.³ (S.T.P.) per hour of oxygen is blown upwardly into the fluidized bed. 800 kg. per hour of Sahara crude oil with 0.8% Conradson carbon is sprayed in above the grate. Hydrocarbons boiling above 250° C. formed in the process are returned to the fluidized bed in an amount of 250 kg. per hour immediately above the grate. Periodically, at intervals of 4 hours, 1 kg. of primary sodium phosphate is added to the fluidized bed. The ratio of steam and oxygen supplied is regulated so that a reaction temperature of 720° C. prevails in the fluidized bed. Solids entrained from the fluidized bed by the cracking gases and vapors formed are separated in a cyclone provided above the fluidized bed and flow back into the fluidized bed through the discharge pipe of the cyclone. About 4 kg. per hour of excess oil coke is formed and is continuously removed. In the stationary state, the phosphorus content of the oil coke in the fluidized bed is 1.4% by weight.

The same amount of oil coke is formed when 500 g. of boric acid is added every four hours instead of 1 kg. of

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primary sodium phosphate. In the stationary state the boron content of the oil coke is then 0.5% by weight.

About 200 kg. of ethylene and 100 kg. of propylene are formed from each metric ton of fresh oil. 700 m.³ (S.T.P.) of gas of the calorific value 7200 kcal./m.³ and a gasoline rich in aromatics as well as oil coke are also formed.

When working under the same experimental conditions but without the supply of primary sodium phosphate or boric acid, no excess of oil coke is formed. On the contrary, the amount of oil coke decreases by 30 kg. per hour in the fluidized bed so that it is not possible to carry out the advantageous operation with a fluidized bed of oil coke formed by the process itself.

Example 2

800 kg. per hour of a crude oil from Upper Alsace (France) with 2.3% Conradson carbon contaminated with 1% by weight of salt water is cracked in a fluidized bed of oil coke in the way described in Example 1. At the same time about 400 kg. per hour of steam and about 200 m.³ (S.T.P.) of oxygen is supplied. The hydrocarbons boiling above about 250° C. formed by the process are returned to the fluidized bed in an amount of 300 kg. per hour. 100 g. of calcium ammonium phosphate is introduced into the fluidized bed per hour. At a temperature of 730° C. in the fluidized bed, 190 kg. of ethylene, 120 kg. of propylene, 650 m.³ (S.T.P.) of a gas having a calorific value of 7400 kcal. per m.³ and a gasoline rich in aromatics as well as 5 kg. of oil coke are obtained from 1 metric ton of crude oil.

An additive containing boron may be used instead of a phosphate as in Example 1. The same amount of oil coke—5 kg. per metric ton of crude oil—is formed when introducing 40 g. of boric acid per hour into the fluidized bed instead of 100 g. of calcium ammonium phosphate.

If the addition of phosphate or boric acid is omitted, no excess oil coke forms. On the contrary, the amount of oil coke contained in the fluidized bed decreases by

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about 16 kg. per hour so that continuous operation cannot be maintained without adding extraneous coke.

We claim:

1. In a method for the autothermal cracking of liquid hydrocarbons for the production of gaseous olefines in a fluidized bed of oil coke formed by the cracking at temperatures of 630 to 850° C. in the presence of oxygen and steam, the improvement which comprises adding to the oil coke in the fluidized bed from 0.05 to about 6% by weight based on the amount of said oil coke of a compound selected from the group consisting of phosphoric acid, boric acid, a salt of phosphoric acid, a salt of boric acid and mixtures thereof.

2. The method of claim 1 wherein ammonium phosphate is added to the oil coke in the fluidized bed.

3. The method of claim 1, wherein sodium ammonium phosphate is added to the oil coke in the fluidized bed.

4. In a method for the autothermal cracking of liquid hydrocarbons for the production of gaseous olefines in a fluidized bed of oil coke formed by the cracking at temperatures of 680 to 780° C. in the presence of oxygen and steam, the improvement which comprises adding to the oil coke in the fluidized bed from 0.2 to about 3% by weight based on the amount of said oil coke of a compound selected from the group consisting of phosphoric acid, boric acid, a salt of phosphoric acid, a salt of boric acid and mixtures thereof.

References Cited by the Examiner

UNITED STATES PATENTS

2,564,268	8/1951	Mathy et al.	208—114
2,587,703	3/1952	Deanesly	208—7
3,027,415	3/1962	Steinhofer et al.	260—683

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