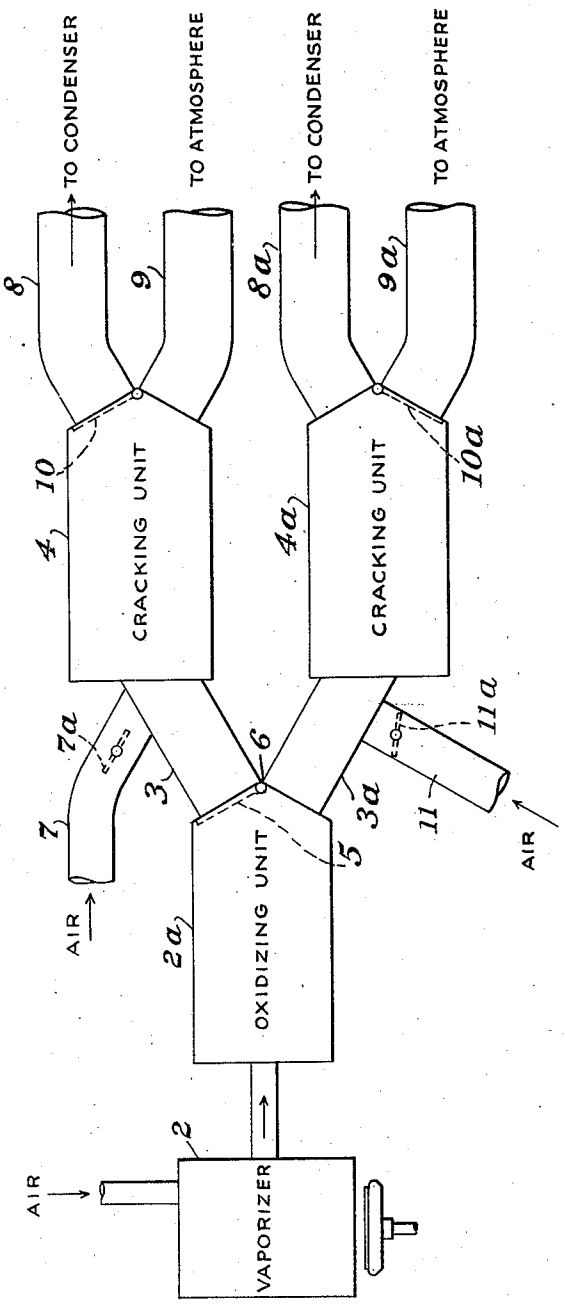
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MINERAL OIL CRACKING PROCESS

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MINERAL OIL CRACKING PROCESS

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My invention relates to cracking of hydrocarbons, especially petroleum fractions; and is designed to provide an improved process and apparatus therefor which will cheaply produce an improved product, and particularly an improved type of liquid fuel for internal combustion engines.

In many United States patents such, for example, as Reissue Patent 18,522 of July, 1932, and Patents 2,085,221, 2,054,571, and 2,036,215, I have disclosed my well known vapor phase process for partially oxidizing hydrocarbons such as petroleum fractions. I have also disclosed in United States Patents 1,836,325 and 1,836,326 partial oxidation methods wherein the oxygen tied into the hydrocarbon vapor is withdrawn from metallic oxides (termed "oxidants") in a hot zone. These metal oxides may be the same as the catalysts used in that form of my process where free oxygen is employed such as contained in air; or may be other metal oxides.

In either case, for cracking purposes, I preferably employ a mild oxidation, since any chemical tying in of oxygen such as that sufficient to produce alcohols, greatly aids in cracking under low pressures; and in both cases I preferably employ a plurality of cracking units connected to one or more units for partial oxidation; and when and if clogging of the cracking catalyst occurs I intermittently shift the exit stream from the partial oxidation step, from one cracking unit to another cracking unit, and burn out the first one by admitting air or an air containing a combustible. As soon as the first unit is "burnt out" and the coatings of tar, carbon, etc., thus cleaned out, the stream from the oxidizing unit will be shifted back and cleaning out of the other and alternate cracking unit effected.

The air or combustible mixture for burning out is preferably fed into the clogged cracking unit directly, or at a point between the oxidizing and cracking unit and the stream of burnt gases is led from the cracking unit to the open air, suitable valve means being used to switch the exit streams from the oxidizing unit and from each cracking unit to its condenser, bubble tower or equivalent.

In the oxidation step which is exothermic, the temperature is held within a reactive range, say from 250° C. up to 600° C. preferably by employing a cooling fluid, and any of the well known types of catalytic cells may be used. If a catalyst is used, it is preferably an oxide or compound or complex of a low atomic volume high atomic weight polyvalent metal, especially those having an atomic weight above forty and occurring on the descending sides of the Lothar-Meyer atomic volume curve. The main examples thereof whose oxides are catalytically active in oxidation are molybdenum, vanadium, tungsten, uranium, etc. Hereafter I shall term such metals "rare metals".

In the cracking step, I prefer to employ a catalyst consisting preferably of hydrosilicates, an acid or non-alkaline silicate or clay, an earth metal, or zeolites; since I have found these to be especially efficient in the cracking of the oxygen derivatives of hydrocarbon formed in the patrial oxidation step. The cracking temperature is preferably in the range from about 300° C. to about 550° C.

I prefer especially to employ as a cracking catalyst a silicate of a rare metal such as molybdenum, vanadium, uranium, tungsten, etc. Some of these may be prepared, for example, by adding a soluble salt of the rare metal such as a chloride or sulphate thereof to a solution of sodium silicate. The rare metal silicate will be precipitated and should be separated and washed free from the sodium salts formed. Others require special methods of preparation of their silicates. Such a cracking catalyst has certain advantages, since the catalytic properties of the silicates are combined with similar properties of the rare metals which act as activators.

I am aware that silicates or hydrosilicates have been proposed as cracking catalysts for straight hydrocarbons, but so far as I am aware, no one has discovered their peculiar advantages in cracking a mixture of oxygen derivatives of aliphatic hydrocarbons in the range from alcohols to oxygenated acids, which are produced in the partial oxidation of aliphatic hydrocarbons such as petroleum or its fractions.

In the drawing where I show diagrammatically a system of apparatus for carrying out one form of my invention, 2 represents a vaporizer wherein the raw fraction or crude oil may be vaporized and the heavy residue tapped out, and 2a the reaction chamber for partial oxidation of the mixture of vapor and air passing therein preferably in contact with a catalyst such as recited in my patents on partial oxidation. Leading therefrom are branch pipes 3 and 3a controlled by reversing valve 5 pivoted at 6 and tilted to close either conduit. Each conduit 3, 3a leads to a cracking chamber 4, 4a, one of which (shown as 4a) is connected to the oxidation chamber 2a and closed to air supply pipe 11 by valve 11a, while the other is closed to the oxidation cham-

ber and is regenerated by air or air and fuel fed through pipe 7 whose valve 7a is open. From the cracking chambers extend branched pipes 8, 8a and 9, 9a, respectively, controlled by reversing valves 10, 10a, of which 8 and 8a lead to condensers, dephlegmators, or bubble towers, while 9 and 9a open to the outer air.

In this form air and oil vapor pass through the oxidizer, the temperature of which is controlled within reactive limits, to tie free oxygen from the air into the hydrocarbon chains, preferably to a mild degree. Thence the mixture containing oxygen derivatives passes into one of the cracking units 4a where a cracking temperature is maintained and thence the cracked vapors pass to a condenser or bubble tower. During this stage unit 4 is being regenerated and burnt out, the exit stream passing into the open air. After a few minutes, for example, 6–10 minutes, the valves are reversed, the stream from the oxidizer is fed to the other cracking unit 4 and air is fed to unit 4a to burn out the coating collection on the cracking catalyst. When this burning out is completed, the valves are reversed.

In case the oxidant type of oxidation is carried out by withdrawing oxygen from an oxide as in my Patents 1,836,325 or 1,836,326, the partial oxidation unit will have means for withdrawing the oxidant and for reoxidizing and returning it to the unit for reuse. Otherwise the apparatus may be like that of the figure herein, or the oxidant may, after reduction to a lower oxide, be revivified in place or otherwise by passing air over it while hot, to reoxidize it during the revivifying of the cracking catalyst. In this case, air would be fed over the oxidation catalyst while air or air and fuel passes through the cracking catalyst, during the revivifying phase of each. This would mean in effect two lines of apparatus, one on one part of the cycle and the other on the other or revivifying part, and each connected both to the condenser or bubble tower and also direct to the atmosphere.

In case the cracking catalyst is carried into and out of the cracking zone or unit, the steps of oxidation and cracking may be carried out more continuously; and if the types of apparatus shown in my "oxidant" Patents Nos. 1,836,325 and 1,836,326 of December 15, 1931 are employed for the cracking catalyst, no reversal of periods need be used. If in such case the "oxidant" system of oxidation were also used, then both the oxidant and the cracking catalyst may be revivified as soon as used, by removal, treatment with oxygen or oxygen and fuel, and then by return to their chambers.

In all such systems heat may be supplied to the cracking unit during the cracking operation by external heat as desired; since the step here is endothermic while the oxidation step is exothermic. The layer of cracking catalyst may be and preferably is thicker or deeper than that of the oxidation catalyst. The steps may be carried out under suction or under pressure above the atmosphere. If pressure is used, it need be only that sufficient to feed the mixture through the apparatus, since the oxidation step makes the cracking step easier and operative at lower pressures than now used; though higher pressures may be used.

In another form of my invention, the condensate from partial oxidation such as my vapor phase partial oxidation (preferably carried out in mild form) may be condensed and the condensate preferably fractionated as by distillation to remove a lower fraction boiling below the range of the fuel desired such as gasoline. The heavier portion may then be cracked, preferably in the vapor phase, with a cracking catalyst such as herein described; or if desired in the liquid phase, or in both phases, with a catalyst.

One of the advantages of my process is that hydrogen is removed from the stock only in proportion to the oxygen chemically tied therein (except as to alcohol formation). Hence I can and do rerun the heavier portion remaining after gasoline removal following each run. In such case expensive high pressure cracking is not required for what is commonly called "recycle stock" as is the case where excessive dehydrogenation takes place.

Under my broader claims which include regenerating or burning out of the cracking catalyst, I may use the same catalyst for cracking as I disclose in my patents for partial oxidation; such as molybdenum oxide, vanadium oxide, etc., mounted on any suitable carrier therefor such as various refractory materials including clays, silicates, etc.; or I may use rare metal compounds or complexes such as disclosed in my several patents herein recited.

The cracking catalyst may be changed, various carriers therefor may be used; oxygen may be tied in in the absence of a catalyst; any of the oxidizing catalysts of my patents such as Reissue 18,522 of September 15, 1936; 2,054,591 of September 15, 1936; 2,085,221 of June 29, 1937; or 1,739,620 of May 20, 1930 may be used and preferably those giving a mild oxidation to vapors of heavy fractions.

In another variation of my process, the cracking of the oxidation product is carried out in the vapor phase thereof and in the presence of hydrogen.

In such a process the oxidation product, preferably in the vapor phase, whether prepared by air oxidation or with an oxidant, is mixed with hydrogen and passed over catalysts, preferably consisting of my rare metal oxides such as vanadium oxide, molybdenum oxide, uranium oxide, tungsten oxide, etc.

By the term "non alkaline" in my claims I intend to include both acid and neutral agents.

The advantage of this phase of my invention lies in the fact that the use of hydrogen prevents the formation of too great an amount of heavy hydrocarbon or heavy hydrocarbon derivatives low in hydrogen and which cannot be recycled because of their low hydrogen content. This process would also aid in lengthening the time of passage prior to such clogging action as would require revivifying of the cracking catalyst.

I claim:

1. In the treatment of petroleum, the steps consisting of vaporizing a petroleum fraction containing mainly straight chain saturated aliphatic hydrocarbons, forming a mixture of the vapor and a gas containing free oxygen, passing the vapor-gas mixture in contact with an oxidation catalyst at an elevated reactive temperature to form oxygen compounds of aliphatic hydrocarbons, and then feeding the hot exit vapor-gas stream through a hot cracking zone containing a cracking catalyst differing from the oxidation catalyst, under a pressure materially less than 200 atmospheres, and supplying external heat to the cracking zone sufficiently to thermally decompose a material percentage of the stream.

2. The method of treating mineral oil containing mainly straight chain saturated aliphatic hydrocarbons, consisting of vaporizing the same, mixing it with a gas containing free oxygen, partially oxidizing the vapor-gas stream at elevated temperature in the presence of an oxidation catalyst containing a compound of a low atomic volume high atomic weight polyvalent metal, and then thermally decomposing a material percentage of the hot vapor-gas stream in another zone and in the presence of a cracking catalyst containing material other than the said oxidation catalyst.

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