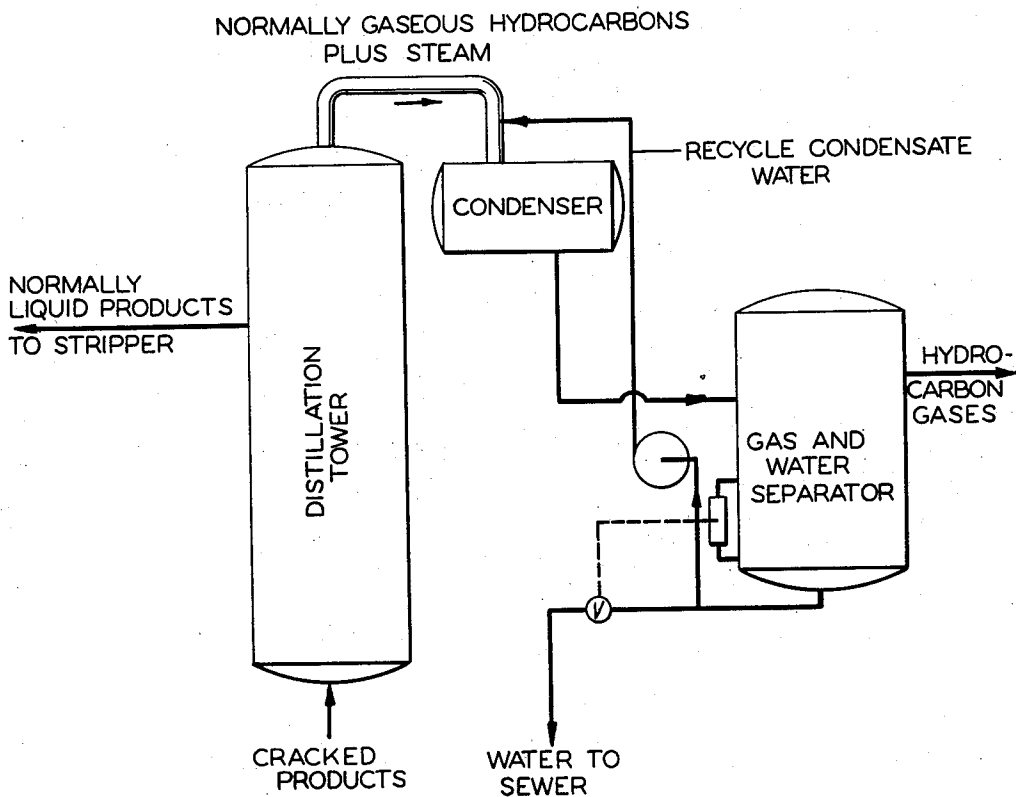


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CONTROL OF CORROSIVE CONDITIONS IN CONDENSERS  
OF A FIXED BED CATALYTIC CRACKING UNIT  
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CONTROL OF CORROSIVE CONDITIONS IN  
CONDENSERS OF A FIXED BED CATA-  
LYTIC CRACKING UNIT

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The present invention relates to an improved process of cracking hydrocarbons wherein use is made of a fixed catalytic bed that is subjected alternately to cracking and regenerating conditions, and more particularly to steps having the effect of reducing to a minimum the corrosive effects of the vaporous reaction products on the condensing equipment ordinarily employed in such a process.

The condensers in such fixed bed catalytic cracking units quickly become corroded during the operation of such units. They are made of bundles of tubes of a copper alloy, such as antimony admiralty metal (a copper, zinc and tin alloy containing 0.1% antimony as a stabilizer), and spacers and baffles of steel around which the reaction products flow. Steel ordinarily forms a protective oxide or sulfide film at pH levels above 7.0 but is subject to extensive corrosion at pH levels below about 6.5. Copper alloys, on the other hand, resist corrosion at pH levels below 7.0 but do not form oxide or sulfide films to protect them from corrosion by basic solutions. Surprisingly, both the steel and the copper alloy parts, and the condenser shell as well, become severely corroded on the oil side during the operation of fixed bed catalytic cracking units. The corrosion is, in fact, so extensive as to eventually plug the condensers up completely or cause excessive leakage and halt operation of the entire unit. This involves not only considerable expense in replacing corroded condenser tube bundles or entire condenser units but has the further disadvantage of requiring the cracking unit to be idle from time to time for repairs.

In typical fixed bed catalytic cracking units that are now used extensively in refineries, an oil charge, usually together with a certain amount of steam, is subjected to a cracking operation by passing said charge through the catalyst bed. The catalyst must be regenerated periodically by passing through it oxygen or an oxygen-containing gas. As a result it has become a more or less standard procedure to operate such units in operating cycles of say thirty minutes wherein each such cycle includes a period of catalyst regeneration and a period during which the catalyst performs its function of accelerating the cracking of the hydrocarbons introduced into the cracking chamber.

The cracked products, together with any steam initially included with the charge, pass from the cracking chamber to a fractionating tower equipped with conventional overhead condensers wherein the heavier hydrocarbons and the steam

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are condensed out. These condensates are subsequently led to an oil and water separator in order to remove the condensed water from said heavier hydrocarbons.

5 It is with the problem of inhibiting corrosion of the condenser tubes, baffles and spacers that this invention is primarily concerned.

The salient object of the present invention, therefore, is to prevent corrosion of both the steel 10 parts and the copper alloy tubes of the condenser unit to the end that the life of the condenser tubes, spacers baffles and shell will be considerably increased, the expense of replacing said units periodically will be effectively eliminated and the attendant interruptions in the operation of the 15 fixed bed catalyst cracking unit will be brought to a minimum.

Periodic analyses of the condensate water re-  
moved from the oil and water separator has shown 20 that during the cracking part of the cycle of operation of a unit of this type, wherein the cracking part of the cycle is of ten minutes duration and the initial hydrocarbon charge is a light gas oil, the pH of the water varies through a range of from about 5.0 to 8.7. It is believed 25 that this variation in the pH value of the condensate water is due to the fact that at the beginning of the cycle, when the charge comes into contact with a catalyst which has just been regenerated with air or some oxygen-containing 30 gas, organic acids are formed by a reaction of the hydrocarbons with the oxygen absorbed on the regenerating catalyst. These organic acids are apparently formed in sufficient quantity to offset, during one portion of the cracking part of the cycle, any basicity due to the formation of ammonia from nitrogen compounds in the oil charge, with the result that during said por- 35 tion of the cycle the pH of the cracked products goes below 6.5. As the cracking part of the cycle progresses and the oxygen absorbed by the catalyst is used up, the formation of these organic acids is believed to decrease so that eventually during the latter portion of the cycle the pH of 40 the cracked products reaches a peak at a level above 8.0. From that it is concluded that the steel parts of the condenser are corroded in the earlier portions of the cracking part of the cycle and that the copper alloy tubes are corroded in the later portions thereof. The situation is be- 45 lieved to be further aggravated by the fact that the periodic lowering of the pH into the range below 6.5 either prevents the formation of a protective oxide or sulfide film on the steel parts or destroys any such films that may be formed in 50

the later portions of the cycle when the pH rises above 7.0.

Attempts to remedy this situation have been frustrated heretofore because of the great number of variables involved. The characteristics, properties and composition of the initial hydrocarbons, the duration of operative cycles and, as a result, the frequency and degree of fluctuation in the pH value of the vaporous reaction products, are subject to such great changes that attempts periodically to counteract excessive acidity or alkalinity of the vaporous reaction products by adding basic or acid substances, respectively, have been found to be entirely impracticable.

One line of attack on this problem that was suggested, for example, was a proposal to dilute the vaporous reaction products with a neutral fluid such as fresh water. Calculations have shown, however, that such a step would not achieve the desired result. When the ratio of fresh water, contacted with the vaporous reaction products, to condensate water is 2:1 in a cracking operation carried out in cycles of ten minutes each, for example, the effect obtained thereby may be calculated, by methods well known in the art, to result in fluctuations of the pH from a maximum of over 8.0 to a minimum of about 5.5. These fluctuations in the pH are still too great to effectively inhibit, much less prevent, severe corrosion of the condenser parts. Attempts to further reduce the fluctuations in the pH of the vaporous reaction products by this means would involve the use of quantities of water that are prohibitive from the standpoint of economy of operation and that would necessarily overtax the volumetric capacity of existing condenser units.

It has now been found that the water collected from the conventional oil and water separator, when recycled through the oil side of the condenser, has the effect of minimizing the pH fluctuations to a far greater extent than would be expected on the basis of the aforementioned calculations.

The accompanying drawing is a self-explanatory flow diagram illustrating the method of this invention.

Trials conducted with a conventional fixed bed catalytic cracking unit operating in cycles of thirty minutes each wherein the initial hydrocarbon charge is a light gas oil and the ratio of recycle water introduced into the oil side of the condenser to condensate water condensed out from the reaction products is 2:1, revealed that the pH of the water separated from the oil and gas separator was reduced to a maximum of about 7.5 and a minimum of 6.8 and that no further appreciable corrosion of the condenser parts took place.

While the present invention is not to be limited in scope by any theory herein advanced, it is believed that this action of the condensate water, referred to hereinafter as recycle water, is probably due to the fact that it, being an accumulation of condensate from several operating cycles, contains salts which act as buffers that serve effectively to reduce the maximum pH and raise the minimum pH of the products flowing through the oil side of the condenser.

The advantages of this method of operation are tremendous both from an economic and an operational point of view inasmuch as the recycle water is readily available from the existing apparatus, no fresh water or buffering solution need be supplied from an outside source and no structural changes are required in the existing equip-

ment. Furthermore, the equilibrium pH range in the condenser may be effectively raised or lowered with facility by the addition of an acid or base to the recycle solution.

The amount of condensate water that can be recycled effectively in accordance with the present invention is ordinarily dependent only upon equipment limitations and the amount of condensate water formed. In general it has been found that the ratio of recycle water to condensate water should not be lower than about 1:1 and it may be as high as 10:1. In order to prevent the building up of excessive quantities of recycle water, a portion of it is withdrawn from the system at a rate equal to about the rate of formation of condensate water after a sufficient quantity of recycle water has been collected.

Inasmuch as innumerable variations in this process may be made without departing from the principle of the invention, it is to be understood that such variations and modifications that come within the spirit of the invention herein disclosed are intended to be included within the scope of the following claims.

I claim:

1. In a process of cracking hydrocarbons which includes alternately passing said hydrocarbons over a catalyst and regenerating said catalyst, condensing at least a portion of the vapors produced by passing said hydrocarbons over said catalyst, said vapors including steam and being excessively corrosive to the condensing apparatus, and separating the condensate water from the condensed hydrocarbon products, the steps which comprise collecting said condensate water and contacting said vapors with from about one to about ten parts of said collected condensate water to one part of steam condensed from the reaction products.

2. In a process of cracking hydrocarbons which includes alternately passing said hydrocarbons over a catalyst and regenerating said catalyst, condensing at least a portion of the vapors produced by passing said hydrocarbons over said catalyst, said vapors including steam and being excessively corrosive to the condensing apparatus, and separating the condensate water from the condensed hydrocarbon products, the steps which comprise collecting said condensate water and contacting said vapors with about two parts of said collected condensate water to one part of steam condensed from the reaction products.

3. In a process of cracking hydrocarbons which includes alternately passing said hydrocarbons over a catalyst and regenerating said catalyst, condensing at least a portion of the vapors produced by passing said hydrocarbons over said catalyst, said vapors including steam and being excessively corrosive to the condensing apparatus in fluctuating over a wide pH range, and separating the condensate water from the condensed hydrocarbon products, the steps which comprise collecting said condensate water, selectively raising and lowering the equilibrium pH range thereof to a level that is non-corrosive to the condensing apparatus, and contacting said vapors with from about one to about ten parts of said collected condensate water to one part of steam condensed from the reaction products.

4. In a process of cracking hydrocarbons which includes alternately passing said hydrocarbons over a catalyst and regenerating said catalyst, condensing at least a portion of the vapors produced by passing said hydrocarbons over said catalyst, said vapors including steam and being

excessively corrosive to the condensing apparatus, and separating the condensate water from the condensed hydrocarbon products, the steps which comprise collecting said condensate water, contacting said vapors with from about one to about ten parts of said collected condensate water to one part of steam condensed from the reaction products, and withdrawing said collected condensate water from the system at a rate approximately equal to the rate at which steam is condensed from the reaction products to maintain the ratio of collected condensate water to condensed steam substantially constant and prevent

the building up of an excessive quantity of recycle water.

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