

UNITED STATES PATENT OFFICE

2,072,801

GAS PYROLYSIS

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No Drawing. Application November 30, 1934,
Serial No. 755,413

6 Claims. (Cl. 196—10)

This invention relates to the pyrolysis of hydrocarbon gases and particularly to a method of effecting such pyrolysis in which the gases to be pyrolyzed or cracked are subjected to high conversion temperatures while passing through metal tubes located in a heating furnace or other metal apparatus maintained at the desired temperatures.

It has been known for some time that gaseous hydrocarbons may be pyrolyzed at elevated temperatures to effect a conversion thereof to products of greater value or to intermediate products which may subsequently be converted to products of greater value. Thus, gaseous paraffins such as the fixed gases produced in the pyrolytic decomposition of petroleum oils and comprising such individual paraffins as ethane, propane and butane may be converted to gaseous olefins by heat treatment at temperatures of from 1200° to 1500° F., and the gaseous olefins thus produced may subsequently be polymerized to form valuable low-boiling hydrocarbon liquids suitable for use as motor fuel. Or, gases containing paraffins or olefins or a mixture of both may be subjected to such temperatures or even higher temperatures to effect the direct pyrolysis of such hydrocarbon gases to low-boiling normally liquid hydrocarbons.

In such processes, which for the purpose of the present invention I prefer to designate generally as "gas pyrolysis" processes, the pyrolysis is ordinarily conducted while gases are passing through metal tubes of such character as to be sufficiently refractory under the temperatures employed, and it is ordinarily preferred to employ tubes constructed of metal which is as free as possible from oxidation which would result in the formation of oxide film having an unfavorable catalytic action upon the desired pyrolysis reactions. During the course of the process, however, I have observed that the effectiveness of the tubes decreases. A considerable part of this loss in efficiency is due to the fact that more or less deposition of carbon takes place in the tubes, this deposition of carbon interfering mechanically with the use of the tubes and causing a tendency toward local overheating and possibly also interfering with any beneficial catalytic effect the tube metal may have upon the reactions taking place.

The formation of a film of oxide on the interior surface of the tubes, however, also tends to reduce the efficiency of the latter. Whether this is due to the direct effect of the oxide film itself or whether the effect is more complicated I am

not able to say, but nevertheless the presence of oxide film does reduce the beneficial catalytic effect of the tubes. While I do not wish to limit my invention by any theory, I am inclined to believe that such film exerts a catalytic action tending to reduce the rate of the desired pyrolysis reactions.

I have further observed that this decrease in efficiency is especially apparent after the tubes have been "burned out" for the purpose of removing carbon. Thus, in the course of the gas-pyrolysis process, the formation of carbon may make it desirable to occasionally interrupt the process and to pass air or other oxygen-containing gas through the tubes to remove carbon therefrom while the tubes are maintained at a sufficiently high temperature to promote combustion of the carbon deposits within the tubes. The passage of oxygen-containing gas through the tubes at high temperatures causes the formation of a considerable amount of oxide film on the interior surfaces of the tubes and tubes which have been thus treated are found to be greatly impaired in respect of their effect upon the gas-pyrolysis reactions when the gas pyrolysis operation is resumed.

It is therefore an object of my invention to provide a method for maintaining the activity and efficiency of metal tubes employed for gas pyrolysis, whereby the pyrolysis of the gases may be conducted over a considerable period of time without material decrease in efficiency, and my invention has for further objects such additional operative advantages and improvements as may hereinafter be found to obtain.

According to a preferred embodiment of my process, the pyrolysis of the hydrocarbon gases is conducted at the desired elevated temperatures, for example 1200° F. or higher, while the gases are passed through metal tubes. While the tubes employed may be made of various metal alloys adapted to withstand the temperatures employed, it is ordinarily preferred to employ a metal tube free from unfavorable catalytic properties with respect to the gas-pyrolysis reactions, and in particular alloys which have been found highly suitable are high-chromium steel alloys and alloys of steel, nickel and chromium, for example a low-carbon steel alloy containing approximately 18% of chromium and 8% nickel. These tubes, when initially employed, possess no detrimental catalytic effect upon gas pyrolysis, but after continued use, and especially after being burned out for the purpose of removing carbon therefrom or after any other occurrence which may result in a for-

mation of oxide film on the interior surfaces of the tubes, suffer considerable loss in efficiency as has been pointed out hereinabove.

It may here be observed that while my invention is especially adapted to be employed as an adjunct to the use of such high-chromium alloy tubes for gas pyrolysis and more especially the use of tubes made from the chromium-nickel alloy specifically mentioned hereinabove, my invention is not in its broadest aspects limited in application to tubes of this particular character but may advantageously be employed in conjunction with the use of apparatus constructed of any metal which is subject to the formation of oxide films with resultant unfavorable effect upon catalytic efficiency insofar as gas pyrolysis is concerned.

When, during the course of the gas-pyrolysis operation, it becomes evident that the formation of oxide film has taken place to such extent as to reduce the efficiency of the tubes, the tubes are subjected in accordance with my invention to pickling for the purpose of removing the undesirable film of oxide. This may be accomplished in various ways but I prefer to accomplish it by subjecting the tubes to the action of acid, and I have employed a solution containing 10% by weight of H_2SO_4 and 20% by weight of $NaCl$ with good results.

More specifically, after the operation has been interrupted and the tubes have been allowed to cool to the desired extent, a solution of the character indicated may be introduced into the interior of the tubes, the tubes being maintained in contact with the solution for a period of, for example, from one to two hours, or at any rate until the oxide film has been removed.

This may readily be accomplished by merely pumping the acid solution through the tubes in the furnace or other heating element employed. After the tubes have been pickled to the desired extent, the interior surfaces are then washed with water to remove the acid and then after removal of water and drying if necessary they may be utilized once more for gas pyrolysis.

I have found, however, that it is extremely beneficial to subject the interior surface of the tubes, before they are again placed on stream in the gas-pyrolysis operation, to the action of a purifying medium such, for example, as concentrated nitric acid. The nitric acid may be passed through the tubes in the manner heretofore described with respect to the pickling solution. This procedure has been found to be of considerable advantage in reducing the subsequent tendency of the tubes to form oxide film and greatly reduces or eliminates the precautions which might otherwise be necessary to prevent the formation of slight oxide films upon mere contact with the atmosphere.

While the pickling in the tubes may be carried out as indicated hereinabove, whenever the tubes have accumulated sufficient oxide film to reduce their efficiency under ordinary circumstances, I have found that it is desirable to accomplish this only after the tubes have been subjected to the action of oxygen-containing gas for the removal of carbon therefrom. Under these circumstances, the gas-pyrolysis operation is interrupted at such a time as may seem expedient for the removal of carbon and the carbon is first removed by passing air or other oxygen-containing gas through the tubes at an elevated temperature, for example at a temperature around $1000^\circ F$. After the removal of carbon has been effected, the tubes may then be cooled to the desired extent and pickled in

accordance with my invention as set forth hereinabove before being employed again for further gas pyrolysis.

It may be observed that the process constituting my invention has been employed to benefit even in connection with tubes made of alloys which are ordinarily regarded as free from oxidation at the temperatures employed for burning out carbon. Furthermore, it is quite possible that it is not the direct effect of oxides which reduce the efficiency of the metal tubes but some effect of a more obscure nature. Consequently, while I have explained my invention in terms of a theory which appears to me to be reasonable, I do not predicate the success of my process upon any particular theory but on the contrary upon the actual advantageous results which have been secured by its use.

Moreover, it will be apparent to those skilled in the art that, while I have described my invention with respect to a gas pyrolysis operation in which a conversion of hydrocarbon gases is effected while the gases are being passed through an elongated coil or tube or series of tubes, my invention may be employed with good results in conjunction with the use of other types of metal apparatus such as enlarged reaction vessels and the like, and in conjunction with various types of processes for the pyrolysis of hydrocarbons. The advantages of the process are, however, more apparent in conjunction with the pyrolysis of hydrocarbon gases to olefins or to normally liquid products as aforesaid.

Furthermore, while I have given hereinabove various specific examples of procedures and pickling materials, it will be obvious to those skilled in the art that my invention is not in its broadest aspects limited to the details of the illustrative examples given hereinabove, but may variously be practiced and employed within the scope of the claims hereinafter made.

I claim:

1. In a process for effecting the pyrogenic conversion of gaseous hydrocarbons in metallic apparatus, the effectiveness of which becomes reduced during the course of the operation, the steps which comprise interrupting the gas-conversion operation when the effectiveness of the apparatus becomes thus reduced, passing an oxygen-containing gas through the apparatus to remove carbon, cooling the apparatus, pickling the interior surfaces of the apparatus and re-employing the apparatus for gas conversion.
2. In a process for effecting the pyrogenic conversion of gaseous hydrocarbons in metallic apparatus, the effectiveness of which becomes reduced during the course of the operation, the steps which comprise interrupting the gas-conversion operation when the effectiveness of the apparatus becomes thus reduced, cooling the apparatus, pickling the interior surfaces of the apparatus, treating said surfaces with a purifying agent, and re-employing the apparatus for gas conversion.
3. In a process for effecting the pyrogenic conversion of gaseous hydrocarbons in metallic apparatus, the effectiveness of which becomes reduced during the course of the operation, the steps which comprise interrupting the gas-conversion operation when the effectiveness of the apparatus becomes thus reduced, cooling the apparatus, pickling the interior surfaces of the apparatus with an acid solution to remove oxide film, removing said acid and re-employing the apparatus for gas conversion.
4. In a process for effecting the pyrogenic con-

75

version of gaseous hydrocarbons in metallic apparatus, the effectiveness of which becomes reduced during the course of the operation, the steps which comprise interrupting the gas-conversion operation when the effectiveness of the apparatus becomes thus reduced, passing an oxygen-containing gas through the apparatus to remove carbon, cooling the apparatus, pickling the interior surfaces of the apparatus, treating said surfaces with a purifying agent and re-employing the apparatus for gas conversion.

5. In a process for effecting the pyrogenic conversion of gaseous hydrocarbons in high-chromium alloy tubes, the effectiveness of which becomes reduced during the course of the operation, the steps which comprise interrupting the gas-conversion operation when the effectiveness of said tubes becomes thus reduced, passing an

oxygen-containing gas through the tubes to remove carbon, cooling the tubes, pickling the interior surfaces of the tubes with a solution of sulphuric acid and sodium chloride, treating the tubes with nitric acid to purify the interior surfaces thereof, removing said acid and re-employing the apparatus for gas conversion.

6. The method of maintaining the catalytic efficiency of metallic chromium alloy tubes employed for the pyrogenic conversion of hydrocarbon gases, which comprises passing air through said tubes at high temperature to remove carbon therefrom, then passing an acid pickling solution through the tubes to remove oxide film therefrom, and removing said acid solution.

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