June 20, 1939. S. A. GUERRIERI 2,163,170

METHOD OF CRACKING HYDROCARBON GASES AND VAPORS

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Fig. 1

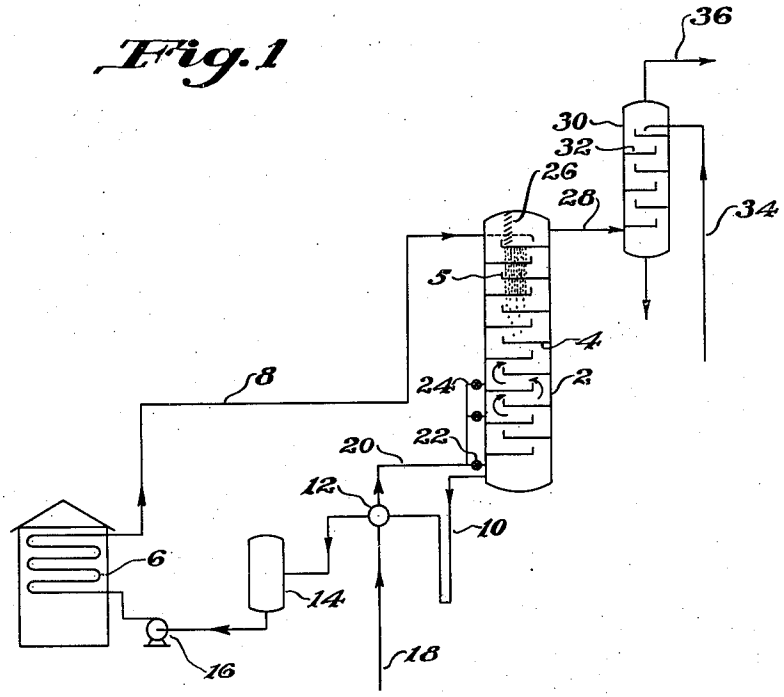
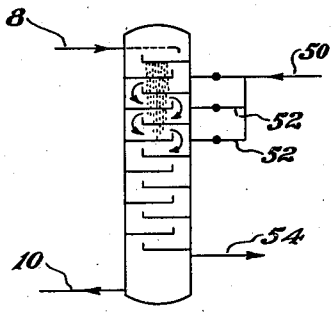


Fig. 2



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METHOD OF CRACKING HYDROCARBON GASES AND VAPORS

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1 Claim. (Cl. 196—70)

The present invention relates to a method for heating gases or vapors to elevated temperatures and more particularly to a method of gas or vapor phase cracking.

Ordinary methods of heating gas or vapor to elevated temperatures, as in a furnace or pipe still, present serious difficulties, primarily because of the inherently low coefficient of heat transfer through the relatively non-conductive film adjacent to the tube wall. It is necessary to use high gas velocities in order to reduce to a minimum the temperature drop through the film, otherwise overheating and failure of the tubes may result. The high velocities cause high pressure drops, and wide variations in pressure in the tubes. The equipment is expensive and is necessarily inflexible in operation.

One object of the present invention is to provide a simple, reliable and easily controlled method and apparatus for heating gas or vapor to elevated temperatures. To this end, the invention contemplates the heating of vapors by intimate prolonged contact with a heated non-volatile liquid in an enlarged chamber. In the preferred form of the invention, the liquid is a non-reactive material, such as molten metal, having a melting point below and a vaporizing point well above the temperature to which the vapors are to be heated. The heat transfer is preferably effected by countercurrent flow between the gas or vapor and a shower of the liquid. Since the heating takes place in an enlarged chamber, the pressure drops are small, and any desired pressure may be maintained with substantial uniformity throughout. The liquid is easily heated in any suitable manner, as in a pipe still. The still for heating the liquid is of smaller and simpler construction, and may be more easily operated than one used for direct heating of the gas or vapor according to usual methods.

The present invention is particularly suitable for cracking of petroleum hydrocarbons and oils in the gas or vapor phase. The usual cracking methods by direct heating involve the same principal difficulty mentioned above, namely, inherently low heat transfer with necessity for high vapor velocity and consequent non-uniformity of pressure conditions. The danger of tube failure is aggravated by the possibility of severe cracking of the relatively non-conductive vapor film, resulting in carbonization within the tube. Apart from such matters, however, the most serious disadvantage of the usual system is its inflexibility, there being no suitable control over the variable factors which enter into any cracking operation, namely, temperature, time of reaction and pressure.

According to the present invention, the disadvantages of the usual vapor phase cracking system are avoided. All parts of the gas or vapor are subjected to the same cracking conditions, and the variable factors which affect the reaction are amenable to independent control within narrow limits. Coke formation, which is a serious problem in the usual system, is of minor importance in the present invention, since coke forms, if at all, in the contact chamber from which it may be readily removed, as will be later described.

In the accompanying drawing, Fig. 1 is a diagram of the preferred form of apparatus for practising vapor-phase cracking according to the present invention, and Fig. 2 is a diagram of a modified system.

The illustrated embodiment of the invention comprises a cracking tower 2 having a series of perforated baffles or shower plates 4. Each plate has a lip 5 to maintain a pool of liquid thereon. Liquid introduced at the top of the tower is caused to shower or cascade in small streams or drops through the column. Liquid, such as molten lead, is heated in a furnace or pipe still 6 and run through a line 8 into the top of the column. The liquid collecting at the bottom of the column is passed by a line 10 through a heat exchanger 12 into a surge drum 14, from which it is continuously pumped by a pump 16 through the pipe still into the column.

The hydrocarbon oils to be cracked are run through a charging line 18 to be heated in the heat exchanger 12 to a temperature sufficient for complete vaporization upon introduction into the cracking tower 2. The oil is run through a line 20 into one or more branch lines 22 and 24, for introducing the oil into the tower at the bottom or at one or more intermediate points. If the hydrocarbons are initially in the gas or vapor phase, they are run directly from the charging line into the tower.

The vapors pass between decks in the column, as indicated by the arrows, and contact intimately with the descending shower of molten liquid. The transfer of heat is exceptionally good, because of the extremely high contact surface afforded by the streams or drops of lead.

The cracked vapors pass through a mist separator 26 of any suitable form and are then run by a vapor pipe 28 into a quench tower 30 wherein the vapors are immediately cooled by contact with a non-volatile liquid. The quench tower

comprses an enlarged chamber having baffles or decks 32. The quenching liquid is preferably a non-reactive hydrocarbon oil, such as gas oil, having a vaporizing temperature above the temperature which is to be maintained in the top of the tower 30. The liquid is introduced into the top of the tower by the pipe 34 to flow downwardly over the decks 32. The gases and uncondensed vapors are removed from the tower at 36, and are passed to any suitable fractionating equipment. The residue collecting in the bottom of the tower comprises the quenching liquid in mixture with some of the higher-boiling cracked products, including possibly some tar and coke. The quenching liquid may be cleaned by steam distillation or in any other suitable manner to render it fit for re-use in the process.

Under cracking conditions accompanied by coke formation, the major part of the coke forms in the cracking tower 2. The coke floats above the pools of lead on the plates 4 and falls over the lips 5 to descend from plate to plate into the bottom of the column. The space above the lead in the bottom of the column permits collection of a considerable quantity of coke which can be periodically removed. Such coke as appears in the quench tower is that which forms prior to cessation of the cracking reaction and it is readily washed down with the quenching liquid. It is unnecessary to introduce steam for the purpose of inhibiting coke formation as in conventional vapor phase cracking systems, and the avoidance of steam is a decided advantage in the manufacture of certain cracked products where moisture is detrimental.

In the system above described, wherein the contact is by countercurrent flow, gas or vapor meets lead at progressively increasing temperatures, the maximum being at the top of the cracking tower. This method provides for a gradual increase in vapor temperature during passage through the column. For some purposes, however, parallel current contact may be desired, as shown in Fig. 2. The lead is introduced at the top and withdrawn at the bottom, as in the construction first described. The gases or oils to be cracked are introduced by a pipe 50 connected with feed lines 52 entering selected decks near the top of the column. The cracked vapors are withdrawn at 54 to be passed to a quench tower in the same manner as previously described. In parallel flow operation, there is a greater temperature difference between liquid and vapor at the beginning of the reaction. As a consequence, the vapors are first more rapidly heated than in countercurrent flow, after which they contact relatively cooler lead during the remainder of their passage through the cracking tower.

In either form of the invention, the variable factors, temperature, reaction time and pressure are subject to close and independent control. Of these, the primary variables affecting the cracking reaction proper are temperature and time, and their control within close limits is of the greatest importance.

The temperature of the reaction is controlled by the temperature and rate of circulation of the lead. The heating of the lead to a closely controlled temperature presents no difficulty. In general, the lead is preferably introduced into the tower at 100 to 200° F. above the desired temperature of the cracking reaction. It is to be observed that the vapors are subjected to uniform conditions in the tower, that is, all parts of the vapor are heated to the same temperatures under the same pressures. This is to be contrasted with the non-uniform conditions obtaining in direct fired stills, where temperatures and pressures may vary widely from point to point, with the result of unequal and uncontrollable cracking of different portions of the vapors.

The time of reaction is controlled by the point at which the material to be cracked is introduced into the cracking tower. Thus for a short time of contact, the vapor is introduced at one of the upper feed points (referring to the countercurrent flow of Fig. 1), and for a longer time of contact, the vapor is introduced near the bottom. It will be understood that the term "prolonged contact" as used herein, means a contact over several successive passes of liquid and vapor, although the total time of passage of vapors through the column may not in some instances be more than a fraction of a second.

No specific temperatures and reaction times are given herein, since these factors are determined by the desired severity of cracking and the products to be obtained.

With respect to pressure, it is generally understood that its principal effects are secondary to the cracking reaction, in accelerating the polymerization of some of the cracked compounds. In conventional systems, the pressures are necessarily high, in order to overcome the pressure drops due to the high vapor velocities through the tubes, and the secondary effects cannot ordinarily be avoided. According to the present invention, however, the pressure drops in the enlarged reaction chamber are small and the secondary effects may be minimized by operation at or near atmospheric pressure, or even at sub-atmospheric pressure by connecting the final fractionating equipment with any suitable vacuum pump. The invention is not to be considered as limited to low pressure operation, and any super-atmospheric pressure may be maintained if, as is frequently the case, the secondary reactions are desired. In any event, whatever the pressure may be, the invention offers the advantage of uniform, or nearly uniform, pressure conditions in the reaction zone.

An important operating advantage of the present invention resides in the fact that the cracking operation may be started immediately. In the usual cracking systems, some time is usually required to reach the desired operating conditions and therefore a considerable amount of slop or uncracked oil is obtained. According to the present invention, after the lead has been put into circulation, the material to be cracked may be introduced and the desired cracking conditions are immediately obtained.

The invention having been thus described, what is claimed is:

A method of cracking hydrocarbon gases and vapors which consists in introducing molten metal into a cracking zone and causing it to pass downwardly through the zone in a series of vertical showers extending across a substantial part of the width of the zone and passing hydrocarbons to be cracked in successive horizontal paths through the showers in prolonged intimate contact with the molten metal.

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