

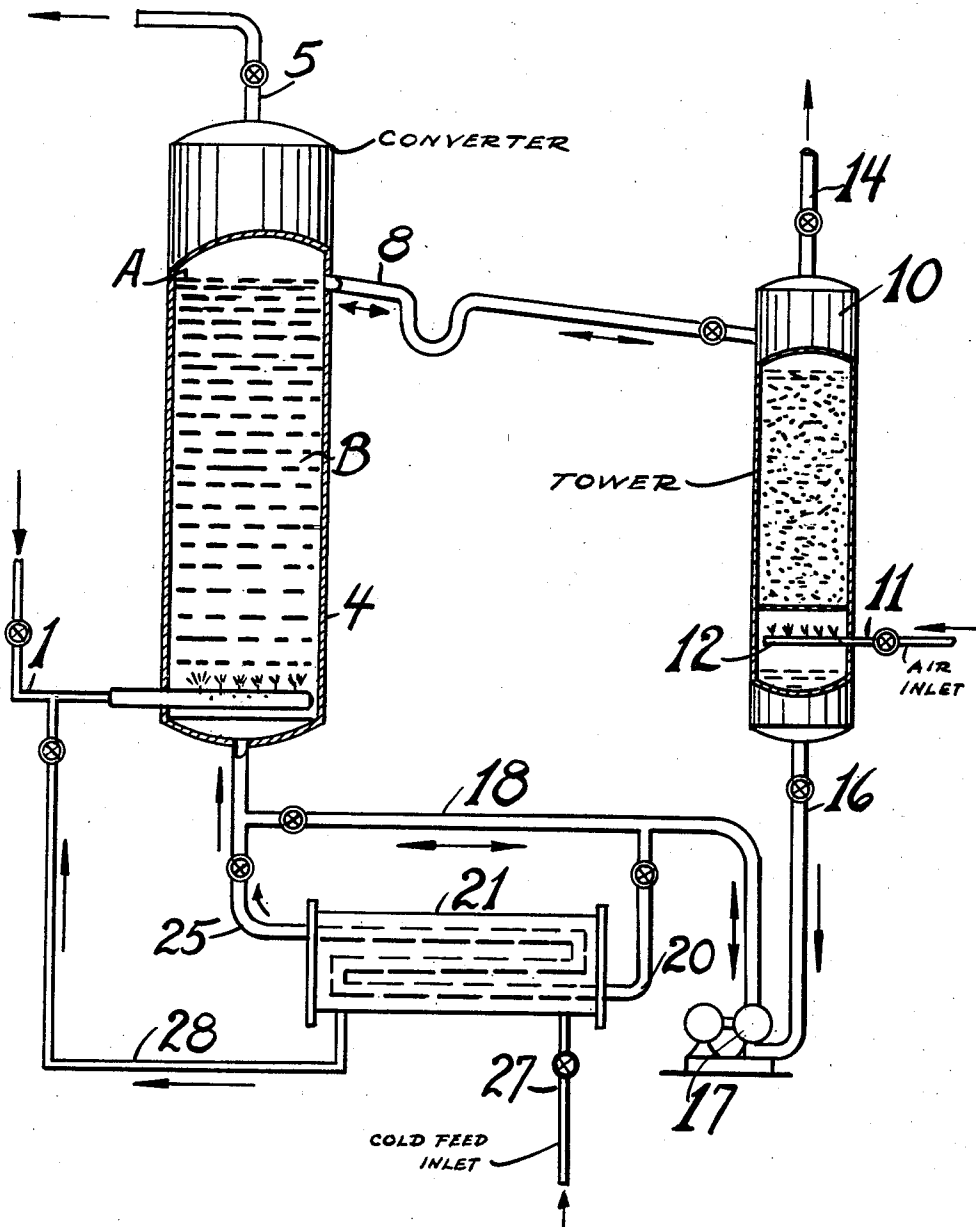
Nov. 16, 1943.

E. D. REEVES

2,334,583

PROCESS FOR CONVERTING HEAVY PETROLEUM OIL INTO VAPORS AND COKE

Filed July 27, 1940



Edward D. Reeves Inventor
By McSmall Attorney

UNITED STATES PATENT OFFICE

2,334,583

PROCESS FOR CONVERTING HEAVY PETROLEUM OIL INTO VAPORS AND COKE

Edward D. Reeves, Cranford, N. J., assignor to
Standard Oil Development Company, a corporation of Delaware

Application July 27, 1940, Serial No. 347,833

2 Claims. (Cl. 196—70)

The present invention relates to improvements in the art of treating hydrocarbon oils such as petroleum oil. More particularly, this invention relates to the conversion of relatively high boiling petroleum oils into hydrocarbon oils of lower boiling range, and in its preferred modification relates to the coking of a reduced petroleum crude oil or heavy residual oil in a continuous manner under closely controlled conditions.

My invention is fully described in the following specification and claims, reference being had to the accompanying drawing.

In refining crude petroleum oil, the usual practice is to first heat the oil to cause the vaporization of the lower boiling fractions such as naphthas, kerosene and gas oil fractions, and to remove these fractions from the crude stills to form what are known as virgin fractions which may be employed after refining in the industrial arts as such, or thereafter further chemically converted to produce additional products such as motor fuel, range oil, domestic heating oils and the like. The material remaining in the still after the naphthas, gas oil, and kerosene have been removed is commonly referred to as reduced crude. This material has such a high boiling point that it cannot be wholly vaporized at any reasonable temperature, and therefore the practice is to convert this reduced crude to hydrocarbons of lower boiling range, generally, by one of two processes, namely, either by a viscosity reducing treatment or by a coking operation. The viscosity reducing operation results in the formation of gasoline, gas oil, etc. and a tarry material which latter is removed from the viscosity reducing operation and is often further treated to produce petroleum asphalt or fuels such as bunker fuel. The coking operation, on the other hand, results not only in the production of gas oil, gasoline and naphthas, but also in the production of a solid coke. The latter operation is usually performed in a drum, and periodically the operation must be discontinued due to the deposition of considerable quantities of coke, which coke must be removed manually. The coking operation, therefore, is a batch or intermittent process, at least in the case where only one drum is employed as the coking vessel.

In my improved process for coking reduced crudes, I operate continuously in a one drum coking system. I accomplish this end by feeding the reduced crude oil into the bottom of an elongated body of molten metal or salts heated to a temperature sufficiently high to cause disruption

of the long chain hydrocarbons present in the reduced crude to form gas oil, gasoline and a solid coke within the body of the molten metal or salt. In this operation, the molten metal or salt becomes contaminated with coke particles, and I remove these coked bodies from the molten metal or bath by discharging same into a vessel where the molten bath is subjected to the influence of air which causes the oxidation and combustion of the coke to form CO, CO₂, and other gaseous products of combustion, after which the purified molten metal or salt is returned to the coking zone for reuse in the latter process. In operating my process, I discharge the hot regenerated metal or salt at regenerated temperatures into the reaction vessel, and in this manner I take advantage of the heat contained in the hot regenerated metal or salt to supply a portion of the heat which is lost in the reaction zone by virtue of the endothermic reaction therein taking place. In other words, the hot regenerated molten material as withdrawn from the regeneration vessel ordinarily is at a temperature in excess of the temperature prevailing in the reaction zone, and I am thus enabled to add heat to the reaction zone at the relatively high level therein prevailing, which, of course, is not readily accomplished, because it is difficult to add heat to a body which is at a relatively high temperature such as that prevailing in the reaction zone.

One object of my invention is to coke continuously a reduced crude in the presence of a molten metal or a molten salt.

Another object of my invention is to coke a reduced crude continuously in a molten bath of lead.

Since the coking operation in its essence is analogous to the cracking of a gas oil, it is another object of my invention to employ a molten bath in the coking zone, which molten bath consists of inorganic salts known to have catalytic activity in the cracking of hydrocarbon oils.

Other and further objects of my invention will more fully and at large appear from the following detailed descriptions.

To the accomplishment of the foregoing and related ends, I provide a process and a suitable apparatus consisting essentially of preheating a reduced crude to a temperature of 700° F., more or less, and then discharging the reduced crude into a point at near the bottom of a molten bath of lead, whereupon the lead bath which is maintained at a temperature of say 1000° F. becomes the depository for liquid fractions and solid coke

resulting from the temperature conditions to which the oil is subjected, while the gaseous decomposition products of the original oil pass upwardly through the bath of lead and are withdrawn overhead as a vapor fraction. The amount of liquid oil remaining in the lead bath under best operating conditions is very small, and the lead bath containing the solid coke and a small amount of unvaporized or unchanged oil is discharged into a burning zone or regeneration zone where the lead bath is freed from carbonaceous material of all kinds by subjection under proper conditions of heat to the influence of air.

My invention will be best understood by describing an operation following the apparatus set forth in the drawing, in which a combination of suitable apparatus elements are shown diagrammatically.

Referring in detail to the drawing, a reduced crude, say an East Texas crude having an A. P. I. gravity of about 18° is introduced into the system through line 1 at a temperature of about 700° F., and thence discharged into the bottom of converter 4, which converter contains a bath of molten lead maintained at a temperature of say about 900° F. to 1050° F. The inlet pipe 1 is preferably constructed of a refractory material such as porcelain, for at least that portion projecting into the converter 4 and a short portion extending outside the said converter. Atmospheric or super atmospheric pressure may be maintained within the converter 4. Under the conditions of temperature and pressure stated, the reduced crude undergoes a transformation to form gasoline, gas oil and coke. The time the oil is resident in the molten bath B varies according to the nature of the feed stock, but in most cases the reduced crude should remain in the molten bath for 1-15 seconds depending on the volume of the charging stock. In other words, the charging stock is resident in the molten bath for a relatively short period of time. The gas oil upon formation is vaporized and passes upwardly through the bath into the upper portion of converter 4 and is eventually withdrawn through a vapor line 5. All of the vapors in line 5 are not gas oil vapors but contain as well fractions boiling within the gasoline range or lower fractions. In the case where a non-catalytic molten bath is employed, best operating conditions require that the amount of gasoline and dry gas be held to a minimum, since the gasoline will not have a high anti-knock value, and the dry gases represent, in most instances, a loss of material. The gas oil recovered from converter 4 may be catalytically cracked to produce a high grade motor fuel, in an apparatus which is not illustrated in the drawing. The molten bath in the converter 4 is a moving body which moves upwardly to a level A maintained substantially constant and then is withdrawn from the converter through conduit 8 and discharged into the top of a tower 10. This tower is preferably packed with ceramic material over which the molten metal flows downwardly. At the same time, an oxidizing gas, such as atmospheric air, is discharged into the tower 10 through line 11 where it emerges within the tower through a series of nozzles 12 and then passes upward against the downflowing molten material containing coke and unvaporized oil. The air causes the oxidation of the carbon contained in the lead or other molten material without causing oxidation of the said molten material. The carbonaceous material therefore

contained in the molten material is converted to gaseous products of oxidation which pass upwardly through the tower and are withdrawn therefrom through vent pipe 14. The purified lead is withdrawn from the bottom of the tower through line 16, thence discharged into pump 17, thence into a line 18, and finally into the bottom of tower or converter 4 in a purified condition suitable for reuse in the coking operation. If desired, however, the purified material in line 18 may be discharged into a line 20, thence into a heat exchanger 21 where it may be either heated or cooled to bring it to the proper temperature for use in chamber 4, whereupon it is withdrawn from the heat exchanger through line 25 and redischarged into line 18 leading into the converter 4, as previously stated. In the case where heat exchanger 21 acts to cool the molten material in line 20, the cooling medium may be cold oil discharged into the heat exchanger through line 27 in such a manner that it passes in countercurrent heat exchange relation with the hot molten lead or inorganic salt, whereupon the oil is heated to a temperature of 500° F.-700° F. and thence withdrawn through line 28 for charging through line 1 into the converter 4.

It is to be noted that the direction of flow of molten material from converter 4 to regeneration vessel 10 may be the reverse of that shown in the drawing. In other words, the molten material in converter 4 may flow therefrom through pipe 13 and then upwardly through 16 and through regeneration tower 11. For some purposes the latter direction of flow is preferable, since the concurrent flow of air would have a tendency to reduce the energy requirements below that required to force the molten bath in the circuit shown from the reaction vessel to the regeneration vessel.

Referring to the revivifying or purifying tower 10, it is pointed out that it may be desirable in certain instances to mix a hydrocarbon, such as a normally gaseous hydrocarbon, with the air in line 11 in order to form an easy combustible mixture which will facilitate the burning or oxidation of the carbonaceous material contaminating the molten metal or salt. The tower 10, like the converter 4, may operate under superatmospheric pressure, say a pressure of 30 lbs. per square inch gauge.

With respect to the contact material which may be used as the molten bath material B, it is pointed out that not only lead and sodium chloride may be used, but also non-oxidizable salts such as NaAlCl_4 and ZnCl_2 .

It is also pointed out that my invention is not limited to coking of reduced crudes but includes also operations such as cracking of gas oil to form gasoline. In the case where a gas oil is cracked to form gasoline products, it is of course preferable to use a salt bath consisting of a salt which has catalytic activity, such as NaAlCl_4 , in order to produce a gasoline of high anti-knock rating.

Many modifications of my invention will readily occur to those skilled in this particular art.

What I claim is:

1. A process for converting heavy petroleum oil into vapors and coke which comprises passing the oil through a body of molten solids within a cracking zone, maintaining said molten solids within the cracking zone at a temperature above the active cracking temperature of said oil, maintaining said oil in contact with said molten solids within said cracking zone for a period sufficient to convert the same into vapors and coke, re-

moving the cracked vapors from the cracking zone, removing a mixture of molten solids and coke from the cracking zone, passing said mixture of coke and molten solids through a body of solid ceramic material, burning the carbonaceous deposits from said molten solids during passage through said body of ceramic material, and thereafter returning said molten solids to said cracking zone.

2. A process for converting heavy petroleum oils into vapors and coke which comprises passing the oil to be converted through a body of molten material maintained within a cracking zone, keeping said molten material within said cracking zone at a temperature above the cracking temperature of said oil, keeping said oil in contact with said molten material within said crack-

ing zone for a period sufficient to convert said oil into cracked vapors and coke, removing said cracked vapors from said cracking zone, removing a mixture of molten solids and coke from the cracking zone, passing said last-named mixture through a body of solid ceramic material, burning carbonaceous deposits from said molten material during passage through said body of ceramic material, heating said molten material during the burning of said carbonaceous deposits to a temperature materially above the temperature maintained in said cracking zone, and thereafter returning said molten material while at said last-named temperature to said cracking zone.

EDWARD D. REEVES.