June 4, 1963 P. T. ATTERIDG 3,092,568

METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

Filed Jan. 7, 1960 5 Sheets-Sheet 1

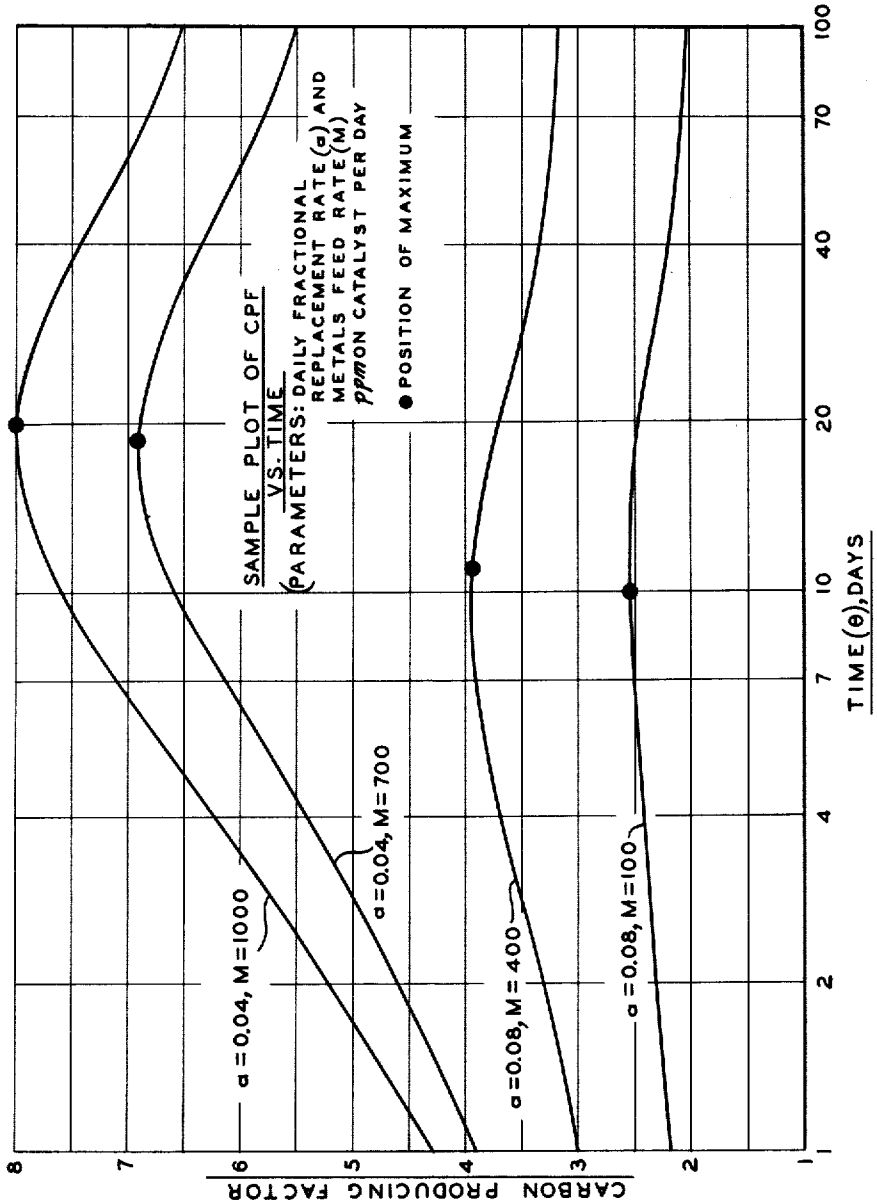


FIG. 1

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METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

Filed Jan. 7, 1960 5 Sheets-Sheet 2

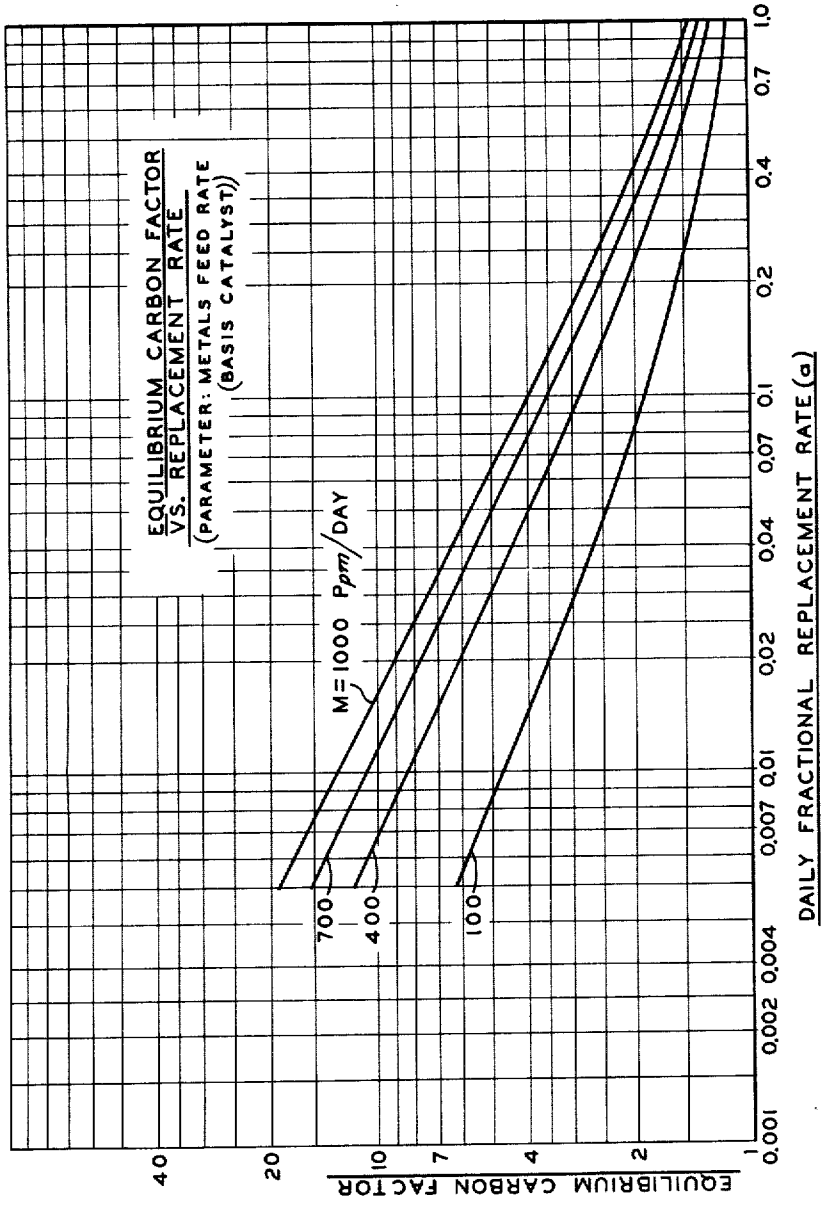


FIG. 2

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METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

Filed Jan. 7, 1960 5 Sheets-Sheet 3

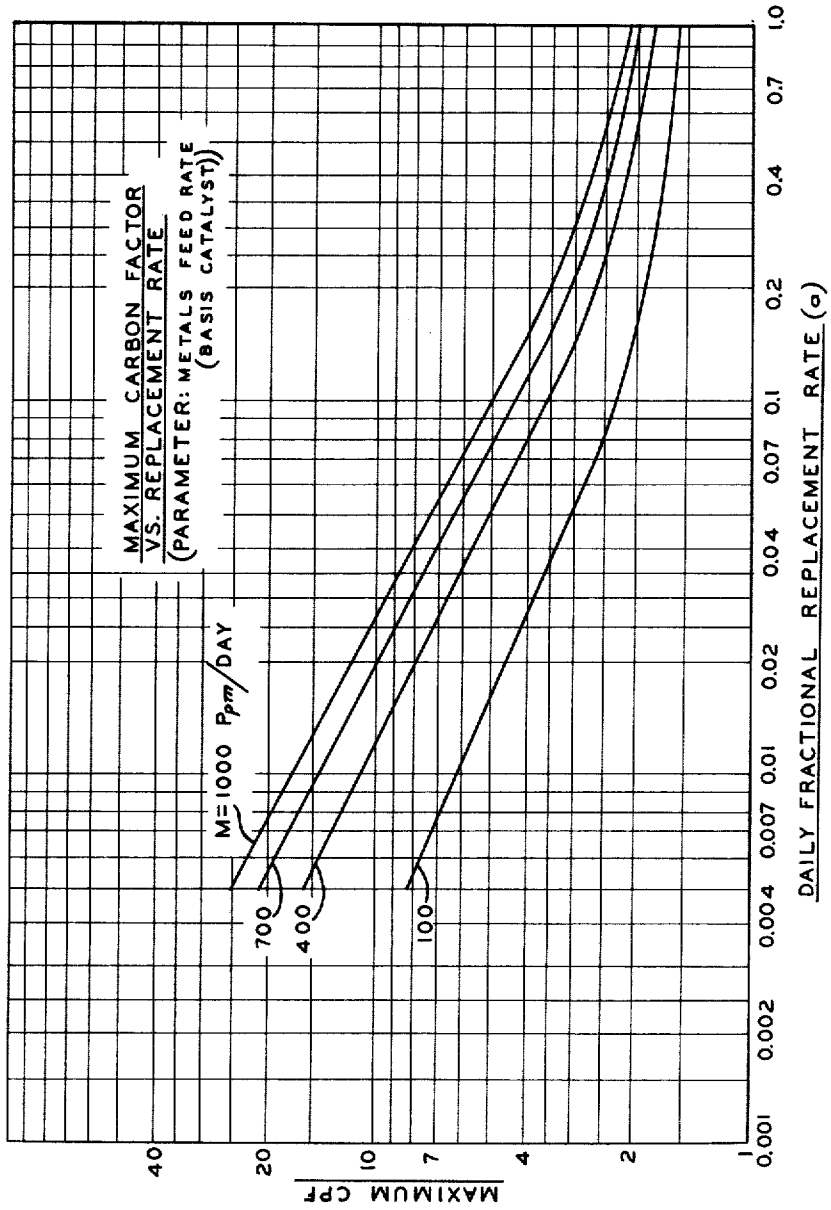


FIG. 3

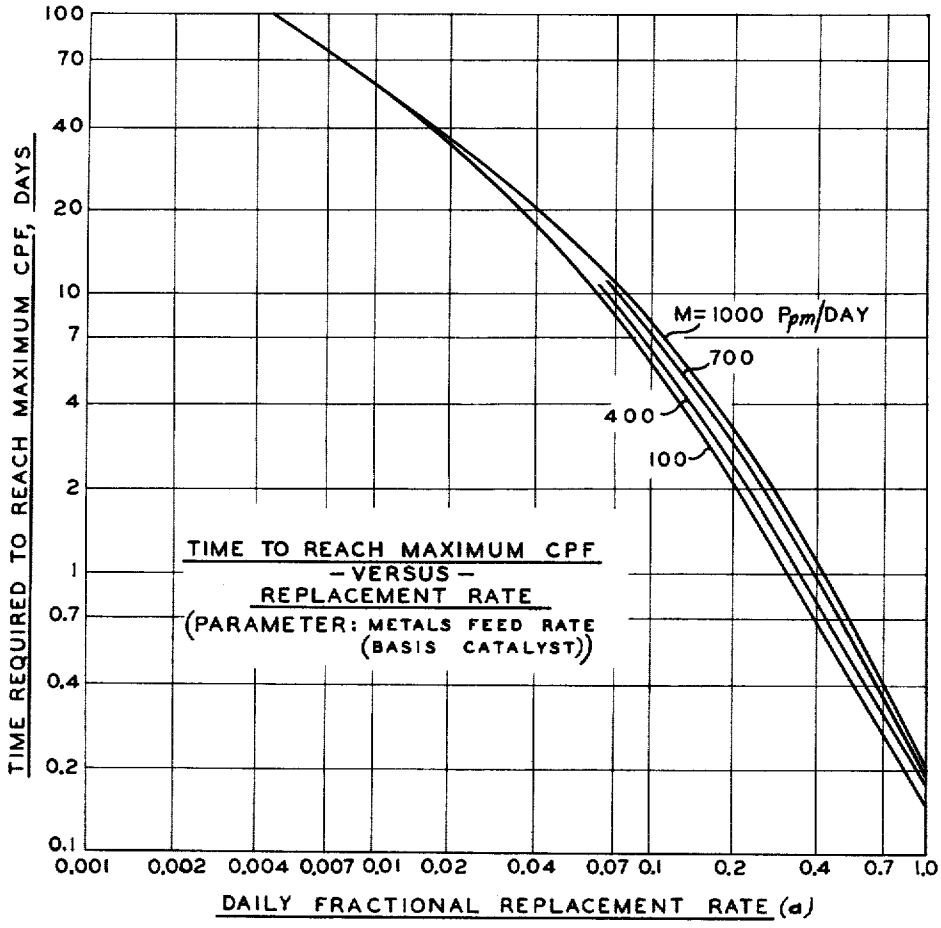
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METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

Filed Jan. 7, 1960 5 Sheets-Sheet 4

FIG. 4



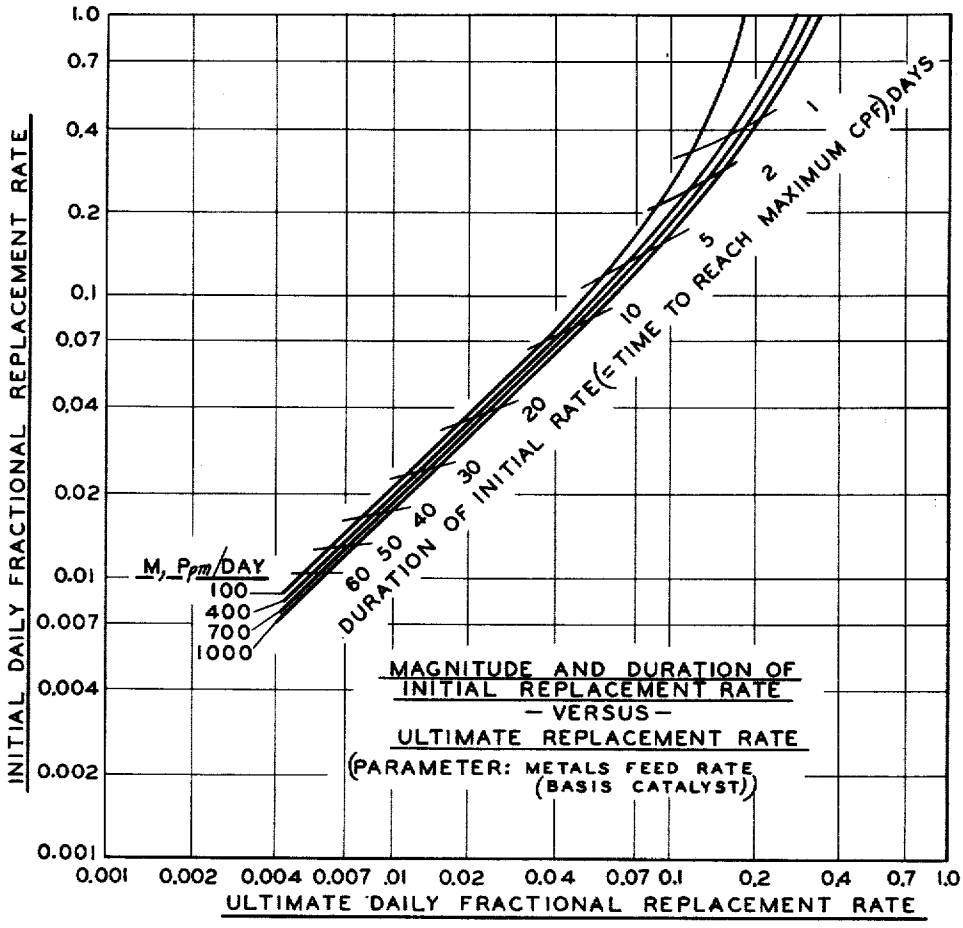
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METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

Filed Jan. 7, 1960 5 Sheets-Sheet 5

FIG. 5



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United States Patent Office 3,092,568 Patented June 4, 1963

3,092,568

METHOD FOR CRACKING HIGH BOILING HYDROCARBONS

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Filed Jan. 7, 1960, Ser. No. 1,051
9 Claims. (Cl. 208—113)

This invention relates to a method for treating hydrocarbons containing metal contaminants. More particularly, the invention relates to a method of converting relatively heavy or high-boiling hydrocarbons including topped or reduced crudes or similar heavy hydrocarbons to gasoline boiling range products and higher boiling fractions substantially free of metal contaminants which are suitable as feeds for further conversion to desired products including gasoline boiling range products of high quality.

Control over the quantity of fuel oil produced and improvements in gasoline quality and quantity has been, for many years, a serious problem of the petroleum industry. In some areas the demand for gasoline and distillate fuel has considerably increased, whereas the demand for fuel oil has actually decreased. Reduction of fuel oil yields has been accomplished by a variety of processes including vacuum distillation, visbreaking, coking, solvent decarbonizing or a combination of these techniques. Whenever catalytic processes have been considered for further reduction or elimination of fuel oil products one major stumbling block has been encountered which is directed to the metal contaminants in these feeds and their deleterious effect on product distribution, as well as economic considerations. Accordingly, a major problem associated with the petroleum industry is treating high-boiling hydrocarbons such as a total crude or portions thereof referred to as residual oils or reduced crudes which contain appreciable quantities of metal contaminants sometimes referred to as organic metal contaminants including nickel, vanadium, copper, chromium and iron.

Accordingly, it is a principal object of this invention to provide an improved process or method for converting high-boiling hydrocarbons containing metal contaminants to produce high quality gasoline products, as well as higher boiling distillate fractions substantially free of metal contaminants which may be subjected to further cracking to produce high yields of high quality gasoline.

Other objects and advantages of the improved process of this invention will become obvious from the following discussion.

In treating high-boiling hydrocarbon feed materials including total crudes, residual oils, topped and reduced crudes in accordance with one embodiment of this invention, the feed is preheated to a temperature in the range of from about 200 to about 800° F. and thereafter the preheated feed, either as a liquid or partially vaporized, is passed in contact with a sufficient quantity of hot finely divided solid particulate material to provide the resulting mixture with a sufficiently elevated temperature to accomplish the desired degree of conversion or cracking of the feed. While the ratio of finely divided particulate material to oil feed may be as low as 2:1, it is prefererd that the ratio be in the range of from about 5 to about 20:1. Accordingly, a sufficient amount of hot finely divided solid particulate material is employed to supply relatively large amounts of heat required to convert the hydrocarbon feed in the endothermic cracking operation. Another very important reason for using a relatively large amount of contact material is to provide intimate contact of porphyrins in the feed and to

effect their resultant decomposition with the contact material.

In another embodiment, the present invention is based on the discovery that the high-boiling hydrocarbons defined herein and containing metal contaminants may be converted to high yields of desired products substantially free of metal contaminants by cracking in the presence of a cracking catalyst under conditions whereby the carbon producing factor of the catalyst is maintained within a range of from about 2 to about 8, preferably from about 3 to about 6, by continuously adding fresh cracking catalyst to the system at a rate which is dependent in part upon the level of metal contaminants (in part per million) in the feed. More specifically, the invention is directed to cracking relatively high-boiling hydrocarbons containing metal contaminants in the presence of a fluidized catalytic material under conditions to maintain a relatively high catalyst replacement rate initially or during start-up of the process and thereafter reducing the replacement rate to a lower value consistent with maintaining desired economic operating conditions, as well as maintaining the catalyst at a desired equilibrium condition.

In accordance with one embodiment of this invention, the conversion of the high-boiling hydrocarbons containing relatively large quantities of metal contaminants in the range of from about 5 to about 5,000 parts per million (p.p.m.), more usually from about 10 to about 500 p.p.m. is accomplished in the presence of a relatively large amount of synthetic and/or naturally occurring cracking catalyst, either alone or in admixture. It is also contemplated employing the cracking catalyst in admixture with finely divided inert solid material under conditions to control conversion of the hydrocarbon within a desired range and maintain the catalyst carbon producing factor (CPF) within the range herein defined.

When employing finely divided inert solid material in conjunction with the catalytic material, the inert solids may be of the same or different particle size and may be selected from the group comprising coke, pumice, kieselguhr, clay, spent cracking catalyst, sand, or any other suitable finely divided solid material, which may be partially or completely fluidized with the catalyst in the reactor by the gasiform or vaporous materials introduced thereto. In addition to the above, it is contemplated within the scope of this invention to employ an absorptive material which may or may not have catalytic activity but which has a relatively high surface area and has a relatively low resistance to attrition such that it is being continuously eroded and lost from the process. As hereinbefore discussed, naturally occurring cracking catalyst may be combined with synthetic cracking catalyst and employed in a ratio such that the major portion of the catalyst mixture comprises the naturally occurring cracking catalyst.

During conversion of the residual oils, relatively large amounts of carbonaceous material, as well as metal contaminants, are deposited on the catalyst. Carbonaceous material is removed from the catalyst by burning in the presence of air or an oxygen-containing gas in a suitable regeneration zone such that during combustion of the carbonaceous deposits the finely divided solid material is heated to an elevated temperature suitable for recycling to the conversion zone. Generally, during combustion of the carbonaceous material in the regeneration zone the finely divided solids will be heated to an elevated temperature in the range of from about 1050° F. to about 1400° F., preferably about 1150° F. to about 1250° F.

It is well known at this stage of the art that fluid type operations afford the greatest advantages with respect to heat transfer, temperature control, economy and continuity of operation. In the conversion of residual oils and reduced crudes to lower boiling hydrocarbons in a

fluid-type operation, it is desirable to employ a gasiform diluent material with the oil feed in sufficient amounts to facilitate vaporization and/or atomization of the feed, thereby breaking up the high boiling feed into relatively small droplets for intimate contact with the finely divided solid material. In addition, the use of gasiform diluent such as steam with the high-boiling oil feed desirably reduces the partial pressure of the feed during conversion to within the range of from about 1 to about 15 p.s.i.a. Accordingly, intimate contact of the hydrocarbon feed with the catalyst recovery of conversion products and fluidization of the finely divided contact material is greatly enhanced by the use of a feed diluent by reducing the tendency of hydrocarbon feed-catalyst agglomerants forming in the fluid bed. Suitable feed diluents which may be used in the method of this invention include steam, low-boiling gaseous hydrocarbons, hydrogen-rich product gases, nitrogen, flue gases, etc.

Hydrocarbon feeds suitable for cracking operations usually contain metal contaminants in varying proportions, depending in part upon the source of the hydrocarbon feed. Generally the metal contaminants found in various hydrocarbon crudes will be found in the range of from about 2 to about 3000 p.p.m., with the highest concentration being found in the residual oils. By "metal contaminants" it is intended to include those metals which are found in most crude oils, such as vanadium, nickel, iron, copper, chromium, etc., which are concentrated upon distillation into the higher boiling distillate and residue fractions, generally known as the reduced crude or residual oil fraction. In residual oils, the metal contaminants may be further concentrated in the range of from about 5 to about 5000 p.p.m. When cracking these metal contaminated residual oils, the metal contaminants collect on and even become embedded in the catalyst, thereby poisoning the catalyst. The thus poisoned catalyst tends to increase the production of coke and gaseous materials.

The hydrocarbon feed materials which may be effectively processed in accordance with this invention include total crudes, residual oils, topped and reduced crudes wherein the feed may constitute from about 1 percent to about 100 percent, more usually from about 10 percent to about 65 percent of the total crude, and generally may have a gravity in the range of from about 5 to about 25° API. As hereinbefore indicated, residual oils may be readily used in fluid operations without taking extreme measures to insure complete vaporation or atomization of the feed material by using a gasiform feed diluent and a sufficient quantity of catalyst with the feed to form a relatively dry mixture. Generally, the residual oils to be processed in accordance with this invention will contain components boiling above about 700° F. in an amount ranging from about 30 percent to about 100 percent and will contain compounds of a highly asphaltic nature, sulfur-containing compounds or metal organic compounds such as porphyrins, salts of metals, which poison the catalyst and have an adverse effect upon the cracking catalyst activity and carbon producing factor. In general, the carbon residue of the residual oil is at least about 1 percent by weight and more usually will be in the range of from about 2 percent to about 30 percent by weight, with the sulfur content depending upon the source of the crude varying in the range of from about 0.5 to about 5 percent by weight.

In a catalytic cracking operation the conversion level serves to describe the severity of operation. The severity desired may be obtained by regulating the temperature, the amount of gaseous diluent, the time of contact and/or space velocity, the catalyst to oil ratio and the level of catalyst activity. It is the relative effect of these variables and particularly the catalyst addition rate to maintain the catalyst carbon producing factor within a desired range with which I am particularly interested in this invention. One method to describe severity in a cracking operation is by reference to the conversion level, which is defined as:

$$\text{Percent conv.} = 100\frac{(Vf - Vp)}{Vf}$$

wherein Vf is the volume of feed and Vp is the volume of product boiling above 400° F. For the cracking operation contemplated by this invention, the conversion level is desirably maintained above about 20 percent and preferably from about 30 to about 55 percent and may even be from about 50 percent to about 70 percent in a recycle operation.

It is generally known that in commercial cracking operations, as known today, such as gas oil cracking operations, finely divided catalyst is continuously lost from the system as fines, which are recovered in part from the decanted oil of the fractionating tower and the recovered fines are then returned to the reactor in the form of a slurry. In addition to this catalyst loss, there is a loss of catalyst fines in the regenerator flue gases, which loss is minimized through the use of rather elaborate cyclone separator equipment for the recovery of these catalyst fines. However, in such operations, the recovered fines are returned to the process and the catalyst loss is minimized such that only a relatively small fraction of the catalyst inventory is loss from the process and must be replaced by make-up catalyst. Generally, this catalyst loss in gas oil cracking operations amounts to less than about .5 pound of catalyst per barrel of oil feed, and most usually is less than this value, of the order of about .3 pound of catalyst per barrel of oil feed, or less. This invention is concerned, however, with replacing used catalyst with fresh catalyst at a rate generally above about .5 pound of catalyst per barrel of oil feed without return of the thus replaced and used catalyst to the system.

The cracking of high-boiling hydrocarbons such as residual oils, topped and reduced crudes is accomplished by this invention at a temperature below about 1000° F., generally in the range of from about 850° F. to about 1000° F., and preferably from about 900° F. to about 950° F., using a pressure in the range of from about atmospheric to about 50 p.s.i.g., and preferably from about 5 to about 15 p.s.i.g. Under these conditions of operation sufficient gasiform diluent material such as steam is used with the hydrocarbon feed to maintain the partial pressure of the feed below about 15 p.s.i.a., usually below about 10 p.s.i.a., depending upon the residual oil being treated and preferably from about 2 to about 8 p.s.i.a. The relationship of the oil feed rate to the amount of finely divided solid material which is present in the reaction zone is known as the weight space velocity and is measured as the pounds of oil feed per hour per pound of contact material in the reaction zone. Generally cracking of the contaminated high-boiling oil feeds herein contemplated is effected at weight space velocities in the range of from about 1 to about 10, and preferably from about 3 to about 6. When employing an inert finely divided solid material diluent with the catalyst as hereinbefore indicated, it is contemplated employing from about 5 percent to about 75 percent inerts and preferably from about 25 percent to about 50 percent inerts with the active cracking catalyst. It is to be understood as herein discussed that a synthetically prepared or naturally occurring catalyst substantially free of inert material may also be employed in accordance with this invention.

Applicant's efforts to resolve the problems associated with the catalytic cracking of high-boiling oils, particularly residual oils, topped and reduced crudes contaminated with metals was initiated by treating a suitable cracking catalyst with various reagent metal salt solutions and determining their influence on the catalyst carbon producing factor. It was determined in an early part of this investigation based on the product distribution obtained with catalysts of different carbon factors

that the catalyst carbon factor should be maintained in the range of from about 1.5 to about 10 and preferably in the range of from about 2 to about 6 or 8. By "carbon producing factor" I mean the ratio of the carbon produced by the catalyst relative to the carbon yields from a standard catalyst employed under the same conversion conditions. The test procedure for determining the carbon producing factor (CPF) involved contacting 50 grams of powdered catalyst for 10 minutes with a Standard Mid-Continent gas oil at 925° F., 1 atmospheric pressure and a space velocity of 2.3 w./hr./w. It was found in this investigation that iron as iron oxide physically admixed with catalyst had little or no effect, but that catalyst treated with iron, nickel, copper and vanadium salt solutions seriously hurt catalyst CPF after calcining. By "calcining" we mean heating the catalyst in air atmosphere at temperatures in the range of from about 1000° F. to about 1400° F. for periods of from about one to about four hours. Vanadium was found to be considerably less deleterious than copper and nickel with iron intermediate between nickel and vanadium. Relative to nickel, the effects were

$$Ni/Fe/V=1/0.55/0.091$$

with copper having substantially the same effects as nickel. The term "nickel equivalents" used herein refers to the total metals content of the catalyst expressed as equivalent nickel (p.p.m.) parts per million using the above effects ratio.

The problems associated with the catalytic cracking of high-boiling hydrocarbon feed material containing metal contaminants were investigated by determining the effect of metals content on carbon factor and determining the carbon factor when the equilibrium metals content and activity had been attained. This work showed that the carbon factor of a catalyst depended, not only on the metals content, but also on the ability of the catalyst to deactivate: fresh catalysts, which lose a large portion of their activity in a relatively short time, have lower carbon factors (for a given metals concentration) than used catalysts whose activities are low but stable. From these findings, suitable equations were developed which could be relied upon for predicting the catalyst carbon producing factor in reduced crude cracking when (1) starting with fresh catalyst and replacing with fresh catalyst, (2) starting with used catalyst and replacing with used catalyst, and (3) starting with used catalyst and replacing with fresh catalyst. It was recognized that (3) would be the most frequently encountered case, since most refiners would have an existing inventory of used catalyst, or would prefer to use it to keep within gas-handling limitations. While such a situation or method of operation would be identical at equilibrium conditions with the situation in which one starts with fresh catalyst and replaces with fresh catalyst, a maximum carbon producing factor would be attained shortly after commencing reduced crude cracking and would be higher than the equilibrium carbon producing factor.

The extensive calculations employing the equations developed in this investigation have not been presented for purposes of simplification, however, the carbon producting factor (CPF) values obtained for various values of "a" and "θ" at levels of "M" equal to 100, 400, 700 and 1000 p.p.m. per day are presented in Table I below. In the table, "a" is the catalyst replacement rate, fraction of inventory per day; "θ" is the time in days; and "M" is the metals feed rate, pounds per day per million pounds of catalyst (or p.p.m. basis catalyst per day).

TABLE I

Carbon Factors in Reduced Crude Cracking

[Tabulated at various levels of daily fractional replacement rate (a), metals feed rate (basis catalyst) (M), and time in days (θ)]

a	M	Time (θ), in Days									
		1	2	4	7	10	20	40	70	100	00
0.005	100	2.4	2.9	3.5	4.2	4.8	6.2	7.7	8.4	8.4	6.2
0.005	400	3.6	4.5	5.7	7.2	8.4	11.2	14.4	15.9	15.9	11.7
0.005	700	4.3	5.5	7.2	9.1	10.7	14.5	18.7	20.8	20.9	15.3
0.005	1,000	4.9	6.3	8.3	10.7	12.5	17.1	22.2	24.6	24.7	18.4
0.01	100	2.4	2.8	3.3	4.0	4.4	5.3	6.0	6.0	5.7	4.6
0.01	400	3.5	4.3	5.4	6.7	7.6	9.5	10.9	11.0	10.5	8.4
0.01	700	4.2	5.3	6.7	8.5	9.6	12.2	14.1	14.3	13.7	11.0
0.01	1,000	4.8	6.1	7.8	9.8	11.3	14.3	16.6	16.8	16.1	13.0
0.02	100	2.4	2.7	3.2	3.6	3.9	4.3	4.4	4.1	3.8	3.4
0.02	400	3.4	4.1	5.0	5.9	6.5	7.5	7.7	7.2	6.7	6.0
0.02	700	4.1	5.0	7.3	7.5	8.2	9.5	9.9	9.2	8.6	7.7
0.02	1,000	4.6	5.8	7.2	8.7	9.6	11.2	11.6	10.8	10.1	9.0
0.03	100	2.3	2.6	3.0	3.3	3.5	3.7	3.6	3.2	3.1	2.9
0.03	400	3.3	3.9	4.7	5.4	5.8	6.3	6.1	5.5	5.2	5.0
0.03	700	4.0	4.8	5.8	6.7	7.3	8.0	7.8	7.0	6.5	6.3
0.03	1,000	4.5	5.5	6.7	7.8	8.4	9.3	9.1	8.2	7.7	7.4
0.04	100	2.3	2.5	2.8	3.1	3.2	3.3	3.0	2.8	2.7	2.6
0.04	400	3.2	3.8	4.4	4.9	5.2	5.5	5.1	4.6	4.4	4.3
0.04	700	3.9	4.6	5.4	6.1	6.6	6.9	6.4	5.8	5.6	5.4
0.04	1,000	4.3	5.2	6.2	7.1	7.6	8.0	7.5	6.8	6.5	6.4
0.05	100	2.3	2.5	2.7	2.9	3.0	3.0	2.7	2.5	2.4	2.4
0.05	400	3.2	3.6	4.2	4.6	4.8	4.9	4.4	4.1	3.9	3.9
0.05	700	3.8	4.4	5.1	5.7	6.0	6.1	5.6	5.1	4.9	4.9
0.05	1,000	4.2	5.0	5.9	6.6	6.9	7.1	6.5	5.9	5.7	5.7
0.06	100	2.2	2.4	2.6	2.8	2.8	2.7	2.5	2.3	2.3	2.3
0.06	400	3.1	3.5	4.0	4.3	4.4	4.4	4.0	3.7	3.6	3.6
0.06	700	3.7	4.2	4.8	5.3	5.5	5.5	4.9	4.6	4.5	4.5
0.06	1,000	4.1	4.8	5.5	6.1	6.4	6.3	5.7	5.2	5.2	5.2
0.08	100	2.2	2.3	2.4	2.5	2.4	2.1	2.1	2.0	2.0	2.0
0.08	400	3.0	3.3	3.7	3.9	3.9	3.7	3.3	3.2	3.1	3.1
0.08	700	3.5	4.0	4.4	4.7	4.8	4.6	4.1	4.0	3.9	3.9
0.08	1,000	4.0	4.5	5.1	5.4	5.5	5.3	4.7	4.5	4.4	4.4
0.10	100	2.1	2.2	2.3	2.3	2.3	2.1	1.95	1.90	1.90	1.90
0.10	400	2.9	3.2	3.4	3.5	3.5	3.2	2.9	2.8	2.8	2.8
0.10	700	3.4	3.8	4.1	4.3	4.3	4.0	3.6	3.5	3.5	3.5
0.10	1,000	3.8	4.3	4.7	4.9	4.9	4.6	4.1	4.0	3.9	3.9

[Tabulated at various levels of daily fractional replacement rate (a), metals feed rate (basis catalyst) (M), and time in days (θ)]

a	M	Time (θ), in Days									
		1	2	4	7	10	20	40	70	100	00
0.20	100	1.92	1.93	1.88	1.79	1.71	1.58	1.54	1.54	1.54	1.54
0.20	400	2.5	2.6	2.6	2.5	2.4	2.2	2.1	2.1	2.1	2.1
0.20	700	2.9	3.1	3.1	3.0	2.9	2.6	2.5	2.5	2.5	2.5
0.20	1,000	3.3	3.4	3.5	3.4	3.2	2.9	2.8	2.8	2.8	2.8
		0.1	0.2	0.4	1	2	4	7	10	20	00
0.50	100	1.63	1.67	1.68	1.62	1.53	1.38	1.29	1.26	1.25	1.25
0.50	400	1.89	1.99	2.1	2.0	1.92	1.74	1.59	1.54	1.52	1.52
0.50	700	2.1	2.2	2.3	2.3	2.2	1.96	1.79	1.72	1.69	1.69
0.50	1,000	2.2	2.4	2.5	2.5	2.4	2.1	1.94	1.86	1.83	1.83
1.00	100	1.57	1.57	1.52	1.39	1.25	1.16	1.14	1.13	1.13	1.13
1.00	400	1.80	1.82	1.78	1.64	1.47	1.32	1.28	1.27	1.27	1.27
1.00	700	1.95	2.0	1.96	1.84	1.60	1.43	1.37	1.36	1.36	1.36
1.00	1,000	2.1	2.1	2.1	1.94	1.71	1.51	1.44	1.43	1.43	1.43

FIGURE 1 presented herewith is a plot of the data presented in Table I wherein the carbon producing factor is plotted against "θ," the time in days, for various values of "a" and "M."

FIGURE 2 is a plot of the equilibrium carbon factor for different daily fractional replacement rates "a" and the same four levels of metals feed rate "M." From FIGURE 2 the equilibrium carbon factor for the different metals feed rates is readily determinable for the different daily fractional replacement rates "a."

FIGURE 3 is a plot of the maximum carbon producing factors for different daily fractional catalyst replacement rates dependent upon the metals feed rate.

FIGURE 4 is a plot of the time required in days to reach maximum carbon producing factor for the different daily fractional replacement rates "a" at different metals feed rates.

FIGURE 5 was obtained by cross-plotting FIGURES 2, 3 and 4 to show the magnitude and duration of initial replacement rate vs. ultimate replacement rate for the different metals feed rates.

It is to be noted from a study of FIGURE 1 that after a relatively short time, a maximum carbon factor is obtained, reflecting a balance between (1) impregnation of used catalyst with metals from the feed, and (2) elimination of the used catalyst and replacement with more rapidly deactivating (and hence lower carbon factor) added catalyst. As time increases the initial catalyst inventory is completely purged from the system and the equilibrium carbon factor is approached asymptotically, with the magnitude of the equilibrium carbon factor being determined from the plot of FIGURE 2. The maximum carbon producing factors readable from FIGURE 1 (and from similar plots of other levels of "a" and "M"), are listed in Table 2 and are plotted in FIGURE 3. The time elapsing before the maxima are reached are plotted in FIGURE 4. By cross-plotting FIGURES 2, 3 and 4, FIGURE 5 was constructed to show:

(1) What replacement rate must be used initially in order that the maximum carbon producing factor just equals the equilibrium carbon factor, and

(2) How long this rate must be used before the maximum carbon factor is reached.

EXAMPLE

As a specific example of the improved method of this invention and to demonstrate how the figures and data presented herein are to be used, the following example is presented. A catalytic cracking unit designed to contain 200 tons of catalyst and to treat 10,000 b.p.d. of a reduced crude weighing 310 pounds per barrel and containing 52 parts per million of nickel equivalent is to be operated. An economic analysis of the proposed operation indicates that make-up catalyst should be fresh synthetic catalyst and that a replacement rate of 1 pound per barrel at equilibrium is desirable. In this example the unit is to be started up with a charge of used catalyst. What is to be determined is (1) the ultimate carbon factor, (2) the initial replacement rate in order that the carbon factor does not exceed its ultimate value, and (3) how long this initial replacement rate must be used. The metal feed rate ("M") will be

$$\frac{\text{Ni Equiv. p.p.m.} \times \text{p.b.d. feed} \times \text{feed density}}{\text{Tons of Cat.} \times \text{lbs./ton}}$$

$$= \frac{52 \times 10{,}000 \times 310}{200 \times 2000}$$

or 400 p.p.m. (basis catalyst) per day. At equilibrium, the catalyst replacement rate fraction of inventory per day ("a") will be

$$\frac{1 \times 10{,}000}{200 \times 2000}$$

or 0.025. FIGURE 2 shows that for a fractional replacement rate of 0.025 the ultimate carbon factor will be 5.4.

As herein discussed, a carbon factor of about 5.4 falls within applicant's preferred range and is a desired condition under which to operate. From FIGURE 5 it is now determined that for a daily fractional replacement rate of 0.025 the initial replacement rate for example at start-up of the process will be 0.043. From this value of 0.043, the replacement rate in terms of pounds of catalyst per barrel of feed is readily determined; that is

$$\frac{0.043 \times 200 \times 2000}{10{,}000} = 1.7 \text{ pounds cat./barrel feed}$$

must be used. As shown by FIGURE 5 this higher rate must be used for about the first 17 days of operation (this value falls between 10 and 20 and closer to 20 on the curve). Thereafter, the catalyst replacement rate may be reduced to 1 pound of catalyst per barrel of feed as initially determined to be economically desirable—that is, after this time has elapsed, the refiner may slowly reduce his replacement rate until gradually it has reached 1 lb./bbl.; from the 17th day on, a constant carbon factor of 5.4 would thus be maintained.

Note that if 1 pound per barrel were used from the start, a maximum carbon factor of 7.0 (FIGURE 3) would be reached after 28 days (FIGURE 4)—a distinctly unattractive level in a unit designed for 5.4.

Having thus given a general description of this invention and specific examples thereof, it is to be understood that many modifications may be made thereto without departing from the spirit thereof.

I claim:

1. A method for converting high-boiling hydrocarbons containing metal contaminants to lower boiling hydro-

carbons which comprises passing a high-boiling hydrocarbon feed in contact with a cracking catalyst maintained in a fluidized condition, (*a*) replacing catalyst when the hydrocarbon feed is initially supplied to the process at a predetermined initial fractional replacement rate of catalyst per day for a predetermined initial time, (*b*) thereafter reducing the catalyst replacement rate to another lower predetermined ultimate rate and carrying out the cracking process at said lower rate, the ultimate rate for step (*b*) being within the range of 0.004 to 0.2 and the catalyst replacement rate and time of use for step (*a*) being in accordance with the correlation of the ultimate catalyst replacement rate and metals feed rate according to the curves of FIGURE 5.

2. A method for converting high-boiling hydrocarbons containing metal contaminants to lower boiling hydrocarbons which comprises passing a high boiling hydrocarbon feed in contact with a cracking catalyst maintained in a fluidized condition, (*a*) replacing catalyst when the hydrocarbon feed is initially supplied to the process at a predetermined initial fractional replacement rate of catalyst per day for a predetermined initial time, (*b*) thereafter reducing the catalyst replacement rate to another lower predetermined ultimate rate and carrying out the cracking process at said lower rate, the ultimate rate for step (*b*) being within the range of 0.004 to 0.2, and the initial catalyst replacement rate for step (*a*) being correlated with the ultimate catalyst replacement rate for a given time and metals feed rate in accordance with FIGURE 5.

3. The method of claim 2 wherein the ultimate catalyst replacement rate is correlated with the catalyst carbon producing factor and the metals feed rate "M" according to FIGURE 2.

4. A method for cracking hydrocarbon feed materials including residual oils, topped and reduced crudes containing metal contaminants to lower boiling range materials which comprises cracking a hydrocarbon feed material containing metal contaminants in the presence of a cracking catalyst wherein the catalyst employed in the cracking step is initially replaced with a fresher catalyst at a higher catalyst replacement rate than the catalyst replacement rates are made for the metals feed rate in accordance with the correlations of FIGURE 2 and FIGURE 5.

5. The method of claim 4 wherein cracking of the hydrocarbon feed is effected in the presence of a mixture of synthetic and naturally occurring cracking catalyst.

6. The method of claim 4 wherein cracking of the hydrocarbon feed is effected in the presence of cracking catalyst containing a major portion of a relatively inert solid particulate material admixed therewith.

7. The method of claim 4 wherein cracking of the hydrocarbon feed is effected at a temperature in the range of from about 850° F. to about 1000° F. and in the presence of a sufficient quantity of a relatively inert gaseous material to maintain the partial pressure of the hydrocarbon feed during contact with the catalyst within the range of from about 2 to about 10 p.s.i.a.

8. The method of claim 4 wherein the catalyst initially employed is used catalyst which is replaced with a fresh synthetic catalyst.

9. The method of claim 4 wherein conversion of the hydrocarbon feed is maintained within the range of from about 20 to about 55 percent.

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