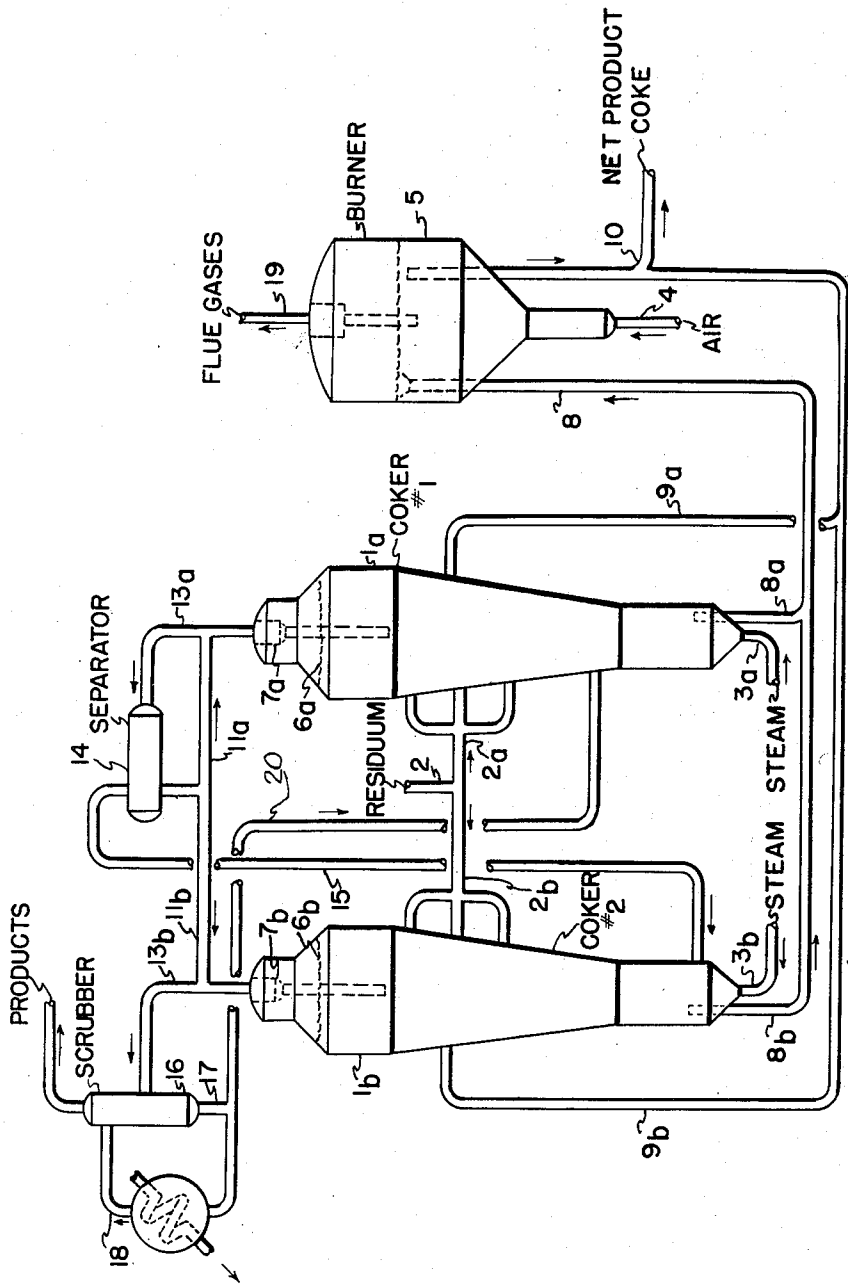


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REDUCTION OF VAPOR PHASE CRACKING BY USE OF  
A MULTI-STAGE FLUIDIZED COKING PROCESS  
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## REDUCTION OF VAPOR PHASE CRACKING BY USE OF A MULTI-STAGE FLUIDIZED COKING PROCESS

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This invention relates to the coking of hydrocarbon oils, particularly petroleum residual oils containing refractory constituents and catalyst contaminants that render other methods of upgrading unattractive. More specifically, this invention proposes a conversion process wherein a heavy oil is pyrolytically converted by contact with high temperature fluidized particulate solids in a plurality of coking zones.

The charging stock which is to be converted according to the present invention comprises preferably, low value, high boiling residual oils having an API gravity between about  $-10$  and  $20^\circ$ , a Conradson carbon between about 5 and 50 wt. percent and an initial boiling point between  $850^\circ$  and  $1200^\circ$  F. Broadly, however, the present invention may find applicability in the converting of charging stocks comprising shale oils, synthetic oils, pitches, tars, coal tars, asphalts, cycle stocks, extracts, recycled heavy ends from the coker effluent, whole crudes, heavy distillate or residual fractions therefrom, and mixtures thereof.

The prior art is familiar with residual oil coking processes wherein an oil is upgraded by contact with fluidized solids maintained at a high temperature in a coking zone. The oil, upon contact with the solids, undergoes pyrolysis evolving relatively lighter, normally liquid hydrocarbon vapors and depositing carbonaceous residue, i. e., coke on the solids. The necessary heat for the pyrolysis is usually supplied by circulating a stream of the solids through an external heater, generally a combustion zone, and back to the coking vessel. Steam, or an equivalent relatively inert gasiform medium, is used to fluidize the solids and to effect circulation of the solids.

The heat-carrying particulate solids that form the high temperature fluidized coking bed of the present invention, may comprise any suitable, finely divided, substantially catalytically inert refractory solids such as spent catalyst, sand, metal particles, glass beads, ceramics, etc. Preferably, however, coke particles produced by the process are the solids used. References herein to coke particles will be understood to be by way of illustration only and to be non-limiting. As this is a fluidized solids process, these coke particles have a size preferably in the range of 40 to 500 microns by screen analysis, although the size in some applications may vary considerably beyond this range, e. g., from 10 to 1000 microns.

The coking temperatures used may vary from  $850^\circ$  to  $1200^\circ$  F. Low temperatures in the range of  $850^\circ$  to  $1000^\circ$  F. are preferred when heavier distillates, e. g., gas oils are desired as a primary product and higher temperatures in the range of  $1000^\circ$  to  $1200^\circ$  F. are preferred when lighter distillates, e. g., gasolines, are desired.

The coking process of the type described has found application principally in upgrading heavy oils such as vacuum residua to materials suitable as charging stocks to catalytic cracking units. Generally, the material is treated to an extent sufficient only to de-ash and decarbonize the oil to convert it into a proper feed stock for catalytic cracking. It is desired that the conversion

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of the heavy oil into a gas oil occurs primarily in the liquid phase as this results in better product yields and qualities. Vapor phase cracking is desirably avoided or at least substantially reduced as much as possible.

It is believed that the heavy oil feed upon introduction into a fluid coker is initially uniformly distributed on the particles throughout the bed because of the rapid mixing obtained in the fluidized bed. The cracking or coking of the oil, therefore, takes place substantially uniformly throughout the coking zone, and the gas oil produced near the bottom of the coking zone is subjected to undesirable vapor phase cracking in passing upwardly through the top part of the fluidized bed. With this concept in mind, it becomes apparent that as the size of the coking zone is increased to obtain greater capacity, there is a corresponding loss in liquid product percent yield and quality because the vapor residence time of the conversion products increases.

To alleviate this problem, it has been previously suggested to use larger amounts of fluidizing gases, e. g., steam, and to operate at higher fluidizing gas velocities in order to more rapidly sweep out the conversion products. Operation in this manner is to be avoided, however, because the use of large amounts of extraneous gases adds considerably to the expense of the process. It has also been suggested that some of the lighter gases removed overhead from the coking zone can be repressurized and recycled to replace some of the extraneous fluidizing gas to increase the effective fluidizing gas rate. This is also uneconomical because the cost of compressing this recycle is generally greater than the cost of an equivalent amount of steam.

It has now been found that the vapor phase cracking of the conversion products from coking operations can be greatly reduced by effecting the coking in a series of coking zones of limited size. Through the use of a plurality of coking zones to secure the desired capacity and by partially condensing the products from each zone and passing the noncondensed portion to the next succeeding stage, the requirements of extraneous fluidization or dilution gas to significantly reduce the vapor phase cracking are greatly reduced while obtaining low vapor times.

The present invention proposes to secure low vapor phase residence time by staging the coking reaction and to utilize the lighter portions of the conversion products from a prior stage as fluidizing media in the next stage. In this manner, the present process secures maximum conversion of heavy oils to gas oils with a minimum consumption of steam and with a minimum production of normally gaseous hydrocarbons.

It can be seen, then, that this invention obtains the desired reduction in vapor phase cracking time with a low amount of fluidizing steam and uses no more steam than would a single stage coker of equivalent capacity. This decrease in vapor phase cracking time is also achieved without the necessity of recycle operation. Through this staged arrangement using coking zones of limited size, the effective steam rate to each stage is increased without exceeding permissible economic limits.

Further, because the naphtha fraction from an initial conversion zone is subjected in the next coking zone to further thermal treatment, this naphtha is advantageously reformed to a product of higher octane without, however, any appreciable loss in product quality or yield. As the gas oil fraction is condensed from each stage and is not subjected to further thermal treatment, it is of higher quality for catalytic cracking.

It is, accordingly, an object of this invention to upgrade by pyrolysis hydrocarbon oils. A more particular object is to upgrade petroleum residua in a multi-stage

fluidized solids coking process effecting partial condensation of the effluent from each stage.

The drawing, attached to and forming a part of this specification, will serve to illustrate this invention. The drawing depicts a two-stage coking process adapted to achieve the objects of this invention. It is to be understood that this drawing is for purposes of illustration only and that the invention is not to be limited thereto.

In brief compass, this invention proposes a fluid coking process which comprises maintaining fluidized beds of particulate solids at a coking temperature in a plurality of coking zones, introducing a charging stock into each of the coking zones whereby the charging stock undergoes pyrolysis evolving lighter normally liquid hydrocarbon vapors, withdrawing vapors from each of the zones and separately partially condensing the vapors. The noncondensed portion of the vapors is then sequentially introduced into the lower portion of the next succeeding zone operating at a somewhat lower pressure to serve as fluidizing media therein, and the condensed portion serves as a quench medium to cool the conversion products from the next succeeding zone to a temperature below incipient cracking.

Succinctly, this invention presents to the art a novel sequential multi-stage coking process which comprises, in essence, coking an oil at a coking temperature in a plurality of fluidized solids zones and passing the lighter portions of the conversion products from each zone boiling below a temperature in the range of 200 to 500° F. to the next zone to fluidize the solids therein, said coking being conducted with vapor phase cracking times under 30 seconds.

For convenience, the ranges of pertinent operating conditions applicable to the attached drawing are summarized in Table I.

Referring now to the attached drawing, the major items of equipment shown are first and second-stage coking zones, 1a and 1b, and a burner 5 used to reheat the contact solids. It is to be understood that more than two zones can be used as desired, as will more clearly appear, and that the zones can be of different cross-sectional area and/or capacity, e. g. the initial zone can be of somewhat lesser capacity. The charging stock to be converted is admitted to the process by line 2 and may be suitably preheated to a temperature in the range of 600° to 800° F. This charging stock is introduced in substantially equal amounts via lines 2a and 2b into each of the coking zones, preferably through a plurality of injection points to obtain good distribution. Each zone contains fluidized dense beds of finely divided inert particles, preferably particulate coke. The beds have definite upper levels indicated at 6a and 6b with dilute or disperse phases thereabove. The conversion gases, emerging from the beds, pass through cyclone systems 7a and 7b wherein entrained solids are removed and returned to the fluidized beds.

External cyclone systems or other solid gas separating devices may be used to remove entrained solids from the conversion products.

An extraneous fluidizing gas, e. g., steam is admitted by line 3a to the first stage coker 1a. The gas so admitted will comprise a major amount of the extraneous fluidizing gas consumed by the process. If desired, small amounts of additional extraneous gas can be introduced, e. g., for control purposes, into the second stage 1b via line 3b. Considering the fluidizing gas rate as based on total feed to the process, this method of operating permits the stages to operate at a much higher fluidizing gas rate than in conventional processes without exceeding permissible economic limits. The gases admitted to the coking zones serve first to strip the coke particles in the lower stripping sections and then ascend upwardly fluidizing the solids in the cokers.

The coking zones are preferably upwardly tapered as illustrated. This further reduces steam requirements as

the conversion products created in the lower part of the zone will serve as fluidizing gases in the upper portion.

To supply the necessary heat for the pyrolysis, relatively cool coke is circulated from the cokers by lines 8a and 8b to the burner vessel 5.

To avoid having to provide for stripping zones in each vessel, the cool solids from one can be transferred to the stripping zone of the next coker to have occluded hydrocarbons removed before being transferred to the burner.

Thus, the contents of line 8b may be transferred to coker 1a to be stripped therein. In the burner vessel, the solids are engaged by free oxygen-containing gasiform medium, e. g., air, supplied by line 4, which serves to fluidize the solids and to partially combust them, thereby raising their temperature 50° to 400° F. above the coking temperatures. The amount of coke consumed in this manner will normally amount to about 10 to 50% of the coke produced by the process. The remaining reheated particles are circulated to the cokers by lines 9a and 9b. The excess coke produced by the process is removed from line 9b through line 10. The flue gases, after having entrained solids removed, are vented overhead by line 19.

Other means of supplying heat to the coker may, of course, be used. Thus, transfer line burners, gravitating bed burners, shot circulation heating systems, etc., may also be used. Other direct or indirect heating means, either integral with the coker or separate therefrom, may be used in certain applications. Further, when the value of other extraneous liquid or gaseous fuels is less than that of the coke produced by the process, these fuels may be preferentially combusted in burner 5, or by other means, to heat the circulating solids.

The conversion products from each stage, in lines 13a and 13b, after having the entrained solids removed, are quenched by a quench oil, more completely described hereinafter, supplied by lines 11a and 11b. It is desirable to quench the vapors to a temperature below about 300° to 600° F. to prevent any further vapor phase cracking. The quenched products from the first-stage coker are then partially condensed in a separator 14. The condensed fraction boiling above a temperature in the range of 200° to 500° F. then serves as a quench oil. The non-condensed portion is transferred by line 15 to the base of the second-stage coker 1b and serves as a fluidizing medium therein and is subjected to thermal reforming to increase its octane number. The next succeeding coker in the series is operated at a somewhat lower pressure so as to avoid the necessity of pressurizing the non-condensed fractions.

This non-condensed fraction contains a major portion of the naphtha boiling in the gasoline range produced by the process. By passing this naphtha again through a thermal cracking or coking zone, it is thermally reformed and its octane number is advantageously increased with, however, no substantial increase in total unsaturation of the naphtha or with no appreciable decrease in yield of naphtha. It is known that vapor phase thermal reforming of the coker naphtha substantially decreases the aniline point, thus improving its octane value. It has been found, however, that the bromine number of the naphtha remains substantially constant which indicates that there is no appreciable increase in unsaturation.

Assuming the second-stage coker to be the last one in the series, then the effluent from this coker is passed to a product recovery system. A simple separation system is shown for the purposes of illustration. The quenched material in line 13b is introduced into a scrubber 16 wherein the heavier high boiling ends of the vapors are removed. These heavy ends, boiling above about 900° to 1150° F. are removed by line 17. A portion of these ends are cooled and recycled via line 18 to serve as a scrubbing liquid. The remaining portion of the ends are transferred by line 20 to the first-stage coker to be retreated therein. In order to prevent undue build-up

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of extremely refractory constituents and metal contaminants in the recycled ends, a portion of these ends may be bled from the process. The material thus removed may conveniently be used as a fuel source.

It is contemplated that the cokers will operate at substantially the same temperatures. However, the coker to which the recycled ends are delivered may conveniently be operated at somewhat more severe conditions, i. e., at higher temperatures, so as to more completely convert the refractory ends. In the alternative, these recycled ends may be substantially equally divided and delivered to each coker in the series.

Table I presents a summary of the operating conditions applicable to the above-described process and presents a specific example of conditions for the two-stage process illustrated. Table II illustrates the products attainable according to this invention from the feed stock indicated when the process is operated in accordance with the example of Table I.

Table I

	Range	Example
Coking temperature in each stage, ° F.....	850-1,200	950
Pressure at outlet of first stage, p. s. i.....	0-400	15
Pressure at outlet of second stage, p. s. i.....	0-400	6
Oil injection rate, lbs./hr./lb. coke in coker.....	0.1-1.0	0.4
Solid to oil ratio, each stage.....	5-20	10
Temperature of reheated solids, ° F.....	950-1,600	1,125
Coke partic size range, microns.....	10-1,000	250 Avg.
Total steam consumption:		
Wt. percent of total feed.....	5-50	5
Superficial fluidization gas velocity, F./S.....	0.5-2.0	1.0
1,015° F. conversion per pass, percent <sup>1</sup> .....	50-90	85
Average vapor time of liquid products, seconds.....	Under 30	16.5
Initial boiling point of condensate fraction from each stage, ° F.....	200-500	400

<sup>1</sup> 1,015° F. conversion is defined as: 100 vol. percent fresh feed minus products boiling above 1,015° F., excluding coke.

Table II

Charging Stock -----	Elk Basin residuum
Inspections:	
Gravity, °API.....	2.0
Conradson carbon, wt. percent.....	30
H/C atomic ratio.....	1.35
Initial boiling point, °F.....	970
Sulfur, wt. percent.....	3.5
Ash, wt. percent.....	0.1
Products—percent on feed:	
C <sub>3</sub> and lighter..... wt. percent.....	10.7
C <sub>4</sub> ..... vol. percent.....	4.1
C <sub>5</sub> /430..... vol. percent.....	18.7
430/1015° F..... vol. percent.....	44.2
Gross coke make..... wt. percent.....	33
Net coke product..... wt. percent.....	27

Note.—(1) The 1015° F. ends from the separation of the products are recycled to extinction equally to each stage. (2) A portion of the gross coke make has been burnt to supply heat.

In the above example, it is to be noted that the average vapor time of the liquid conversion products is 16.5 sec. Under equivalent conditions in a single stage coker, the vapor time would be about 24.4 sec. This advan-

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tage in vapor time gained by the present invention is sufficient to increase the gas oil yield by 2-3 volume percent, besides increasing its quality. While a two-stage process has been illustrated, it will be apparent to those skilled in the art that additional staging can be used to reduce the vapor time even more.

In summary, it can be seen that this invention proposes a multi-stage hydrocarbon oil process leading to increased yields through decrease in vapor phase cracking times and is characterized by injection of a charging stock into a plurality of fluidized solids coking zones with partial condensation of the effluent from each zone and utilization of the non-condensed portion of the effluents as fluidizing media in the next succeeding coker.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A fluid coking process comprising maintaining dense, turbulent fluidized beds of particulate solids at a coking temperature in the range of 850° to 1200° F. in a plurality of separate coking zones including a first coking zone, the coking zones operating at substantially the same temperatures, introducing residual oil charging stock into each of said zones whereby said charging stock undergoes pyrolysis evolving lighter, normally liquid hydrocarbon vapors, withdrawing said hydrocarbon vapors from each of said zones, circulating the particulate solids through an external heating zone wherein they are heated and back to the coking zones to supply heat thereto separately partially condensing the vapors so withdrawn, utilizing the condensed fractions from each zone to quench the effluent from the next succeeding zone to a temperature below 300° to 600° F., sequentially introducing at least a portion of the non-condensed fractions which have a final boiling point within the limits of 200° to 500° F. from the condensation into the lower portion of the next succeeding zone to serve as fluidizing gas therein, and finally withdrawing the effluent from the last of said coking zones as conversion products, the total vapor phase cracking time being under 30 seconds.

2. The process of claim 1 wherein an extraneous fluidizing and stripping gas, including steam, is introduced into the lower portion of the first of said coking zones.

3. The process of claim 1 wherein said charging stock comprises a low value, high boiling residual oil having an API gravity between about -10° and 20°, a Conradson carbon between about 5 and 50 wt. percent and an initial boiling point between 850° and 1200° F.

4. The process of claim 1 wherein at least a major portion of the heavy ends boiling above a temperature in the range of 900° to 1150° F. is separated from the products and recycled for further treatment.

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