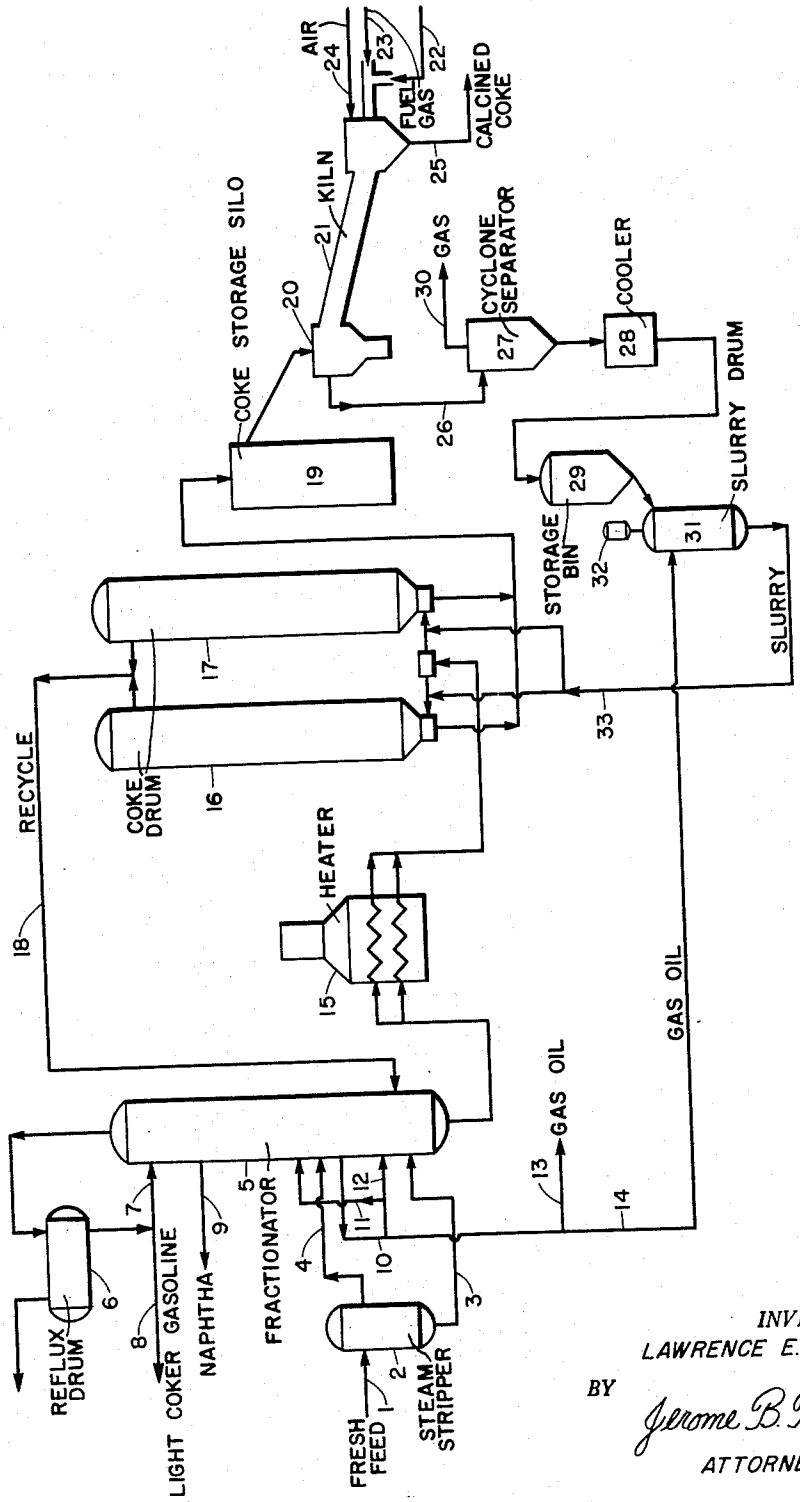
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MANUFACTURE OF PETROLEUM COKE

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MANUFACTURE OF PETROLEUM COKE

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This invention relates to the manufacture of petroleum coke. More particularly, it relates to an improved process for the manufacture of petroleum coke wherein the coke fines produced during the process are recovered and recycled to the coking step in order to increase yields and minimize the problem of disposing of such fines.

In the delayed coking process a petroleum fraction is heated to a temperature at which it will thermally decompose. The oil is then fed into a drum under conditions which prevent the oil from vaporizing until it has partially decomposed. This thermal decomposition produces a very heavy tar which undergoes additional decomposition depositing a porous coke mass in the drum.

In the usual application of the delayed coking process, residual oil is heated by exchanging heat with the liquid products from the process and is fed into a fractionating tower where any light products which might remain in the residual oil are distilled out. The oil is then pumped through a furnace where it is heated to the required temperature and discharged into the bottom of the coke drum. The first stages of thermal decomposition reduce this oil to a very heavy tar or pitch which further decomposes into solid coke. The vapors formed during this decomposition produce pores and channels in the coke thru which the incoming oil from the furnace may pass. This process is continued until the drum is filled with a mass of coke. The vapors formed in the process leave from the top of the drum and are returned to the fractionating tower where they are fractionated into the desired cuts.

The attrition associated with removing petroleum coke from delayed coking drums and the subsequent coke handling produces a considerable amount of undersized coke fines. Prior to development of this invention, these fines constituted a disposal problem. Their value as fuel is much less than the value of the larger lumps of coke because of the limited amount of fine coke which can be utilized economically in the various processes consuming petroleum coke.

This invention provides a method for recovering these fines and returning them to the delayed coking unit where they are cemented into a new coke being produced in such a manner that they loose their identity and are subsequently recovered as part of the useful sized coke lumps.

Broadly stated, the invention is a process for producing petroleum coke which comprises subjecting a heavy petroleum residuum to coking conditions of temperature and pressure, recovering the coke fine produced during the process, and injecting the recovered coke fines into the coker feed. One preferred embodiment consists of slurrying the coke fines in a suitable oil, delivering the slurry to the coke drum where the coke particles become suspended in the heavy tar or pitch undergoing thermal decomposition. Under these conditions, the coke particles become incorporated into the new coke being formed so that they become an integral part of the coke deposit.

The coke fines to be handled by this invention may be either wet or dry. It will normally not be necessary to dry the wet fines except to decant the excess water from settled fines. It is true, however, that dry fines are easier to handle than wet fines.

Any suitable oil can be used for the initial slurry. Normally it will be one of the oil streams available from the coking unit. While the residual oil feed to the unit is appropriate, we prefer to use gas oil merely for the sake of convenience.

Engineering factors determine the proper point for injecting the slurry into a given delayed coking unit. The major factors to be considered are heat requirements, fluid velocity, abrasion of equipment, and equipment fouling. The more important locations to be considered for injecting the slurry are:

(1) The slurry may be injected directly into the coke drum either with or without prior heating.

(2) The slurry may be injected into the furnace feed line.

(3) The slurry may be injected into the fractionator tower.

(4) The slurry may be injected into the feed stream as it enters the exchanger train.

Selection of suitable charge stocks for coking operations is well known in the art. The principal charging stocks are high boiling virgin or cracked petroleum residua such as: virgin reduced crude; bottoms from the vacuum distillation of reduced crudes, hereinafter referred to as vacuum reduced residuum; Duo-sol extract; thermal tar; and other heavy residua. Blends of these materials are often used to provide a feed which will provide a suitable coke having a sufficiently low sulfur content.

As indicated above, the preferred coking process is the well-known delayed coking process. In this process, which is one of the most commonly-used and most economical at the present time, the charge stock is pumped at 150 to 500 p.s.i. into a furnace where it is preheated to 850 to 950° F. and then discharged into a vertical coking drum through an inlet at the base. The pressure in the drum is maintained at 20 to 80 p.s.i., and the drum is well insulated to minimize heat loss, so that the reaction temperature lies between about 830° F. and 900° F. The hot charge stock decomposes over a period of several hours, liberating hydrocarbon vapors which rise through the mass continuously, stirring the contents of the coker vigorously.

After removing the coke from the drum (usually by means of a high impact water jet), the coke is broken into lumps and may be calcined, generally at a temperature of 1000° C. to 1500° C.

The preferred mode of operation is illustrated in the drawing. The fresh feed from line 1 is stripped in steam stripper 2, in which the feed is split into two streams 3 and 4, which are introduced into fractionator 5. The overhead from the fractionator, at about 300° F., is passed to the reflux drum 6, and a portion of the light coker gasoline therefrom is refluxed through line 8. Naphtha is removed through line 9, a portion thereof being refluxed (not shown) from a naphtha stripper (not shown), if desired.

Gas oil is removed from the fractionator through line 10, and portions thereof are refluxed by means of lines 11 and 12. The bulk of the remainder of the gas oil is removed at 13, but a small quantity from line 14 is used to form a slurry of coke fines for injection into the coker, as will be described hereinafter.

The bottoms from the fractionator, at about 550° F., are passed through heater 15, and then into one or the other of coke drums 16 and 17 at a temperature of about 910° F. at the beginning of the coke run and about 925° F. at the end of the run. A stream of vapor, at about

830° F. and about 30 p.s.i.g., is recycled to the fractionator through line 18.

When the coke drum is full, the coke is cooled and then removed from the drum by means of high impact-producing water jets incorporated in special boring and cutting tools. After the raw coke is dewatered, it is then crushed and screened to 1½ inches and smaller, and is then passed to raw coke storage silo 19.

The coking operations thus described (except the above reference to the use of gas oil stream 14) comprise the standard coking process known as delayed coking, and no claim to novelty is made thereto.

Coke is fed from the silo by gravity feed into feed end housing 20 and from there into inclined rotary kiln 21, in which the coke is calcined at a temperature of about 2500° F.

Coke passes downwardly through kiln 21, while hot gases pass upwardly through the kiln and countercurrently to the flow of coke. The hot gases are created partially by combustion of fuel gas introduced at 22. Primary and secondary sources of air are supplied through lines 23 and 24, affording an excess of air over that required to combust the fuel gas introduced at 22. Hot gases are also created by combustion of the volatile hydrocarbons from the raw coke with the excess air. In normal operations, the combustion of these volatile hydrocarbons with the excess air affords approximately 60–70 percent of the heat required to maintain the kiln temperature.

The calcined coke is removed from the lower end of the kiln at 25 and is cooled and then conveyed to storage.

The hot gases, containing coke fines, after passing through the kiln, are removed through line 26 and introduced to cyclone separator 27, which is a cylindrical vessel with a cone-shaped lower portion. The gases are introduced horizontally and tangentially to the inside surface of the cyclone. The fines drop to the bottom, are cooled in cooler 28, and are elevated to fines storage bin 29. The preferred cyclone is referred to as a "hot cyclone" because no water is injected into it; however, if desired, a "wet cyclone" may be employed wherein water is injected into the cyclone to aid in the separation of fines from gas.

Cyclone separators are standard dust-collecting equipment and may be purchased from a number of sources and may be adapted for use in the separation of coke fines with relatively little effort in the line of engineering skill.

The gas is removed from the top of the cyclone and is passed, through line 30, to an incinerator (not shown) and to a waste heat boiler (not shown).

Fines from the storage bin 29 are fed to slurry drum 31, which is equipped with a propeller-type agitator driven by motor 32. Gas oil from fractionator 5 is used to form a slurry of coke fines which is fed through line 33 directly to the particular coke drum being charged. The slurry is preferably maintained at or below 40 percent fines. All of the fines recovered may be used without detrimental effect upon the quality of the coke produced.

Fines from areas other than the cyclone 27 may also be recycled to the coking operations. For example, wet fines resulting from the dewatering of the raw coke hydraulically removed from the coke drum may be dried or drained of most of the water, slurried with oil, and then fed to the coke drum as indicated above. Wet fines may also be slurried with oil, and the slurry boiled to remove the water, thus affording an oil slurry which may be injected into the coke drum. Fines from the bottom of the feed end housing 20 may also be recycled to the coking operations by the slurry method.

As an alternate to the slurry method, the dry fines may be introduced into the coke drum as a fluidized solid by the use of superheated steam, or other suitable gas. Wet fines, from the hydraulic removal of coke from the drum, may first be dried in the calciner or other drying equipment and recovered in the cyclone as previously described.

The following examples are set forth to illustrate the invention, it being understood that they are not to be construed as limiting its scope.

EXAMPLE 1

Nine pilot coking runs were performed using vacuum reduced residuum as the coker feed stock having the following properties:

Gravity, ° A.P.I.	17.0
Viscosity, S.S.U. at 210° F.	226.3
Distillation—	
IBP	510
5	786
10	850
20	888
30	920
40	954
50	983
60	997

Fines previously recovered in a wet cyclone (located at the discharge end of the rotary kiln) were first dried and were then slurried with the feed prior to introduction into the coker.

The results of these runs are shown below in Table I. It will be noted that runs 1–4 were made without recycle, whereas runs 5–9 employed injection of fines.

Table I

	1	2	3	4	5	6	7	8	9
Feed:									
Wt. percent	100	100	100	100	97.1	97.1	97.1	97.1	97.1
Pounds	39.5	43.0	40.5	40.5	42.5	39.7	43.0	29.4	27.8
Fines, wt. percent	0	0	0	0	2.9	2.9	2.9	2.9	2.9
Run Data:									
Time, hrs.	3	3	3	3	3	3	3	2¼	2¼
Coker Temp., ° F.	950	930	930	930	925	925	930	900	925
Pressure, p.s.i.g.	32	33	30	30	33	33	33	30	30
Yield Data:									
Coke, wt. percent	9.0	9.3	11.4	9.4	12.3	12.4	10.9	16.0	17.0
Distillate, wt. percent	76.0	72.0	74.4	74.2	70.8	72.5	72.8	69.7	69.2
Volatile Matter—raw coke	9.4	5.7	13.2	10.8	11.8	----	16.2	5.8	----

Friability tests conducted upon the raw coke indicated that the injection of fines did not affect the coke strength within test repeatability.

EXAMPLE 2

Three test runs were conducted substantially as shown in the drawing, employing a feed comprising a blend of Duo-Sol extract and vacuum reduced residuum in the ratio of 0.19 to 1.0 and having the following properties:

Gravity, ° A.P.I.	16.5
IBP	460
5%	680
10%	770
20%	870
30%	915
40%	947
50%	975
60%	1000
S.S.U. at 210° F.	262
Sulfur, wt. percent	0.74
C.C.R., wt. percent	6.61

During this run partially-wet coke fines from the water settling pit (which had been previously separated and then drained) were slurried with gas oil to provide a 22 wt. percent slurry, which was injected directly into the coke drums as shown in the drawing. While injecting fines the furnace transfer temperature of the heater charge was raised 20° F. above normal to affect the quenching effect of the cold gas oil and coke fines.

Table II shows material balances and operating data for the three test runs. The gas oil used in the slurry is not shown as a charge because it was just a small recycle stream within the coker.

Table II

MATERIAL BALANCE AND COKER OPERATING DATA COKE FINES INJECTION TEST RUNS

	Run I				Run II				Run III			
	BPD	LV, percent	Lbs./Hr.	Wt. percent	BPD	LV, percent	Lbs./Hr.	Wt. percent	BPD	LV, percent	Lbs./Hr.	Wt. percent
Charge:												
Fresh Feed	9,148	99.0	127,805	98.7	8,002	99.2	111,194	98.9	7,689	99.1	107,194	98.9
Coke Fines (BFOE) [1]	(96)	1.0	1,667	1.3	(72)	0.8	1,250	1.1	(72)	0.9	1,250	1.1
Total	9,244	100.0	129,472	100.0	8,074	100.0	112,414	100.0	7,761	100.0	108,444	100.0
Yield:												
Gas (BFOE)	(1,099)	11.8	12,386	9.5	(1,225)	15.2	14,429	12.8	(1,205)	15.5	14,190	13.0
Gasoline	2,000	21.6	21,883	16.9	1,783	22.1	19,427	17.2	1,685	21.7	18,436	17.0
Naphtha	781	8.5	9,353	7.3	660	7.5	7,245	6.4	625	8.0	7,567	7.0
Gas Oil	4,929	53.4	64,323	49.6	3,363	41.6	43,971	39.2	3,348	43.2	43,565	40.2
Coke (BFOE) [1]	(1,356)	14.6	23,475	18.2	(1,532)	16.4	23,075	20.6	(1,284)	16.5	22,232	20.5
Loss	921	9.9	1,948	1.5	229	2.8	4,297	3.8	386	3.9	2,454	2.3
Total	9,244		129,472		8,074		112,444		7,761		108,444	
Heater Charge, BPD	11,000				10,000				10,000			
Recycle Ratio	0.2				0.2				0.3			
Furnace Transfer: Pressure, p.s.i.g.	[2] 35–56				[2] 46–60				[2] 40–60			
Furnace Transfer, Temperature, °F.:												
Initial	925				925				925			
After 16 hrs	935				935				935			
After 20 hrs	940				940				940			
Coke Drum Outlet, Temperature, °F	[2] 810–830				[2] 810–835				[2] 817–828			
Coke Drum Pressure, p.s.i.g	[2] 31–41				[2] 34–42				[2] 33–39			

[1] Conversion factor used: 4.812 BFOE Coke=1 ton coke.
[2] The lower figure would apply at the start of the 24-hour run and gradually work up to the higher figure by the end of the run.

Table III gives the total quantity of fines injected and total coke produced during the three test runs.

Table III

Run	Fines Injected		Coke Made (Tons)
	Tons	Tons per hr.	
I	20	1.17	281.7
II	15	.88	276.9
III	15	.88	266.8

Friability tests conducted upon the raw coke showed that the injection of fines had no adverse effect upon the strength of the coke produced.

EXAMPLE 3

Sustained operations were conducted in accordance with the process shown in the drawing, employing a mixed feed of the same type as that of Example 2 and typically having about the same properties. During a period of six months of such continuous operations, the hot cyclone fines charged amounted to about 54 wt. percent of the fines produced or about 0.6% of the coker feed, reducing the net fine production from about 5.4 wt. percent of the average coke production before commencement of fines injection, to about 2.5 wt. percent of the average coke production during the period of fines injection.

During these operations it was found that if the fines were injected throughout the entire drum cycle, so that the fines injected late in the cycle did not become cemented into the coke mass, they were still present when the drum was opened. This difficulty can be improved by injecting the fines at a greater rate during the early part of the cycle and then discontinuing the injection during the latter part of the cycle.

Just prior to the six-month period mentioned above, a short period of operation was carried out in which the coke fines were slurried into normal feed stock and charged to the unit thru line 1 (refer to drawing). In this particular unit fluid velocities in the furnace feed pump and thet furnace tubes of the unit proved to be excessive causing severe erosion at these points. Otherwise this method of operations proved to be entirely satisfactory. Mechanical redesign of these two pieces of equipment using widely known engineering skills could have corrected this erosion problem, but in this particular case it proved to be more desirable to change to the method of operation described in the first portion of this Example 3.

I claim:

1. In a process for the production of petroleum coke by the delayed coking method comprising the steps of introducing a heavy petroleum residuum into the bottom of a coking drum, subjecting said residuum to delayed coking conditions of temperature and pressure to thermally decompose said residuum to produce a mass of solid raw coke filling the coking drum, removing the raw coke from the drum, calcining said raw coke, and recovering the coke fines produced during the calcining step, the improvement which comprises injecting the recovered coke fines into the coker feed during the coking step.

2. The process of claim 1 further wherein the coke fines are slurried in a hydrocarbon oil prior to injection into the coker feed.

3. The process of claim 2 in which the hydrocarbon oil is gas oil.

4. In a process for the production of petroleum coke by the delayed coking method comprising the steps of introducing a heavy petroleum residuum into the bottom of a coking drum, subjecting said residuum to delayed coking conditions of temperature and pressure to thermally decompose said residuum to produce a mass of solid raw coke filling the coking drum, removing the raw coke from the drum, recovering the coke fines produced during the step of removing the coke from the drum, the improvement which comprises injecting the recovered coke fines into the coker feed during the coking step.

5. The process of claim 4 wherein the raw coke is removed from the coke drum by means of high impact-producing jets of water.

6. The process of claim 5 wherein the coke fines are slurried in a hydrocarbon oil prior to injection into the coker feed.

7. The process of claim 5 wherein the coke fines are slurried in gas oil prior to injection into the coker feed.

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