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PROCESS OF PRODUCING DESULFURIZED COKE FROM PETROLEUM

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Fig. 1

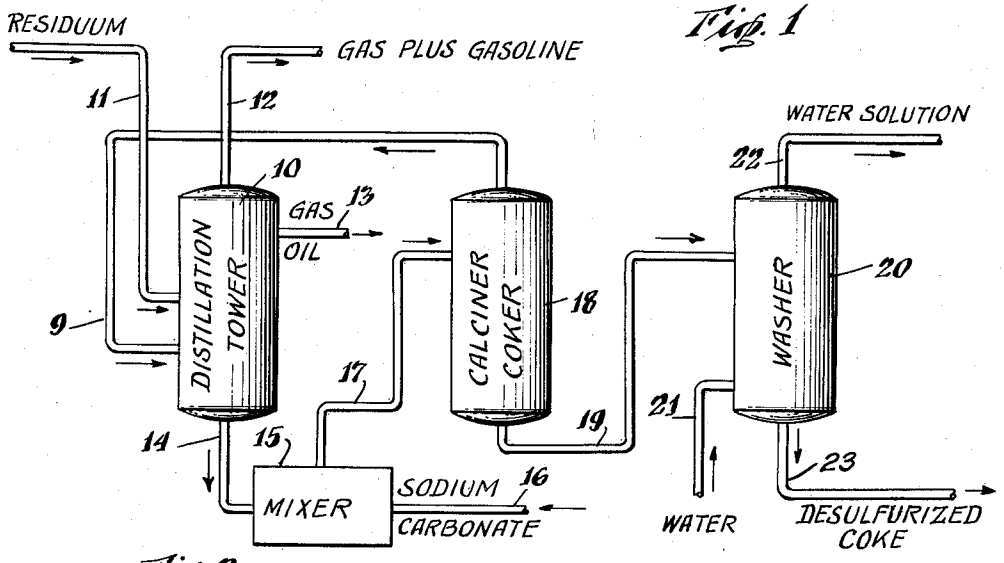


Fig. 2

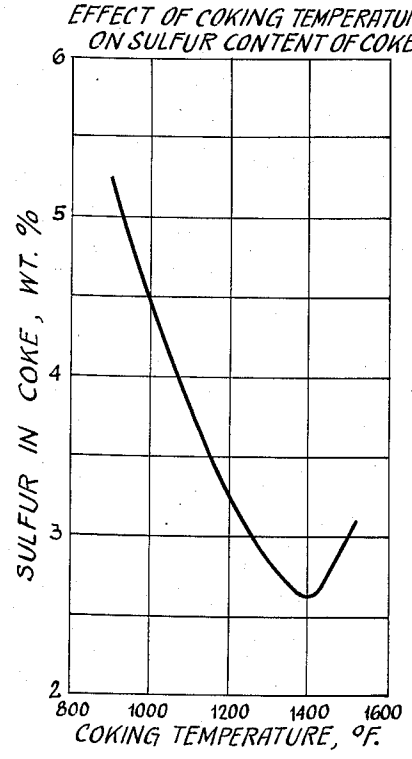
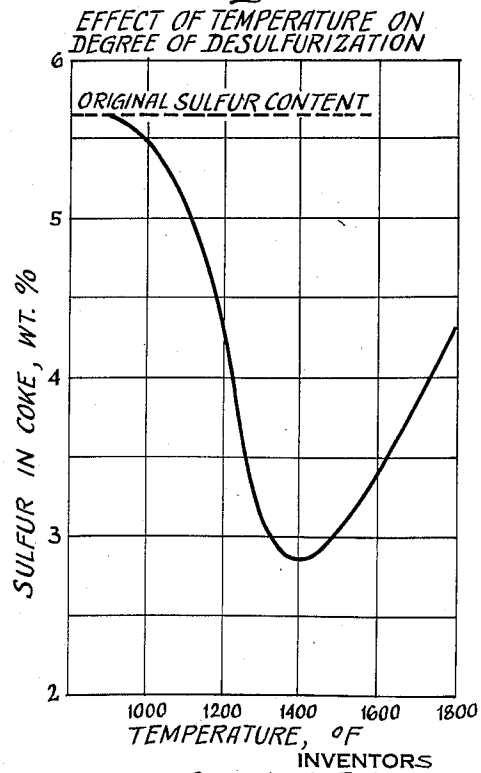


Fig. 3



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PROCESS OF PRODUCING DESULFURIZED COKE FROM PETROLEUM

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10 Claims. (Cl. 208—106)

This invention relates to the production of petroleum coke of low sulfur content from petroleum residua of high sulfur content.

In the manufacture of petroleum products the customary practice involves the separation of the crude petroleum oil into various fractions or cuts having limited boiling range, thereby providing products suitable for specific purposes. The prime products are naphtha and the distillate fuel oils useful as heating oil and diesel fuels. However, many other useful products are obtained from petroleum, including a hard brittle coke having a low ash content.

After the light products have been removed from the crude oil, there remains a heavy viscous liquid which is characterized as residuum. In one form of the conventional coking process the residuum is charged to a distillation tower with the overhead from a coker and the mixture separated into gas, gasoline, gas oil and residuum. The residuum is removed from the bottom of the distillation tower, pumped through a furnace and charged to the coker. A typical coking temperature is about 900° F. and a typical pressure is 60 p.s.i.g. The finished coke is very much in demand and the market is continually increasing. Petroleum coke is a major raw material for making anodes for the aluminum industry. Anodes for use in this industry should be low in ash and sulfur.

As crude sources are being continually exhausted, more and more crudes having a high sulfur content are being charged to processing equipment throughout the world to provide desired products. Among these are such crudes as Santa Maria Valley, West Cat Canyon, Kuwait and Slaughter. These crudes yield coke containing more than 2 percent sulfur and this amount is excessive for many uses, such as, for example, the electrodes in the aluminum industry.

We have found that the sulfur content of petroleum coke can be suitably reduced by grinding the coke and mixing it with powdered sodium carbonate, heating the mixture to a temperature of about 1400° F. for a short period of time and then water washing the product to provide a desulfurized coke. The product coke is a commercially acceptable coke.

This invention involves an improved process in which the powdered sodium carbonate is mixed with the residuum before the coking operation and the coking conditions are changed sufficiently to effect the coking and desulfurization in a single operation. The coke produced is provided in commercially acceptable form.

The object of this invention is to provide a process for producing a low sulfur content coke product from a high sulfur content crude.

A further object of this invention is to provide a simplified process for directly producing a low sulfur content coke from a petroleum which is high in sulfur.

These and other objects will become clear from a review of the following detailed description of the invention.

Figure 1 is a block diagram of the improved process which is used in the following detailed description.

Figure 2 is a plot of weight percent sulfur in the coke produced versus coking temperature for a given high sulfur residuum.

Figure 3 shows the effect of temperature on the desulfurization of coke.

Referring to Figure 1, petroleum residuum obtained from atmospheric or vacuum topping of the crude is charged to the distillation tower **10** through the path **11**. Hot vapors from the coker **18** are introduced into the tower **10** through the path **9** to heat exchange with the residuum and raise the temperature of the residuum. The gas and gasoline vis., the lightest products, are removed overhead through the path **12**. A somewhat heavier cut, such as a gas oil, is removed from the distillation tower **10** through the path **13**. The remaining heavy product or residuum is removed from the bottom of the distillation tower **10** through the path **14** and introduced into a mixer **15**. The sodium carbonate is preferably crushed or powdered first and then introduced into the mixer **15** through the path **16**. The mixture of residuum and sodium carbonate is then transferred through the path **17** to the calciner coker **18**.

Although coking will generally take place at a satisfactory rate at about 900° F. and 60 p.s.i., the temperature in the calciner coker is maintained substantially above 900° F. in this process, for example, 1400° F. being most suitable. Hot gases can be used to heat the calciner coker to this temperature. After a suitable period of time, the coke is removed from the calciner coker and transferred through the path **19** to the washer **20**. Water is introduced into the washer **20** through the path **21**. The water solution is removed through the path **22** and finally the desulfurized product coke is removed through the path **23**.

The effect of coking temperature upon the sulfur content of the coke is shown on Figure 2. It is seen that correct temperature is important and that lowest sulfur content occurs at or about 1400° F. At lower temperatures or higher temperatures the product coke contains more sulfur. The graph shown on Figure 2 was prepared from data obtained by coking a residuum containing about 6.41% sulfur. The 1400° F. temperature is also the optimum in the desulfurization of coke, as shown in Figure 3.

The amount of sodium carbonate to be used depends upon the amount of sulfur present in the residuum. The usual operating range is about 0.7 to 7.2 lb. sodium carbonate for each pound of sulfur which would be present in the coke produced from the residuum if no sodium carbonate were present. For example, if the residuum yields 14% of coke containing 5.16% sulfur, the usual amount of sodium carbonate used would be 0.51 to 5.2 lb. per 100 lb. of residuum.

The optimum operating conditions are tabulated as follows:

	Preferred Range	Broad Range
Temperature, ° F.	1,300–1,500	1,100–1,800.
Pressure	Atm.	0.1 atm.–50 atm.
Time at Reaction Temp.	15–60 min.	1 min.–4 hrs.
Amount of Sodium Carbonate.	0.7–7.2 lb./lb. of sulfur in coke made without Na_2CO_3 present.	0.7 or greater lbs./lb. of sulfur in coke made without Na_2CO_3. present.

While the process is primarily adapted for use in preparing low sulfur content coke from liquid petroleum residuum, it can also be used on residuum obtained from shale or from tar sands. The invention is particularly useful when the residuum without carbonate would yield a coke containing at least 2% sulfur.

The invention was tested using 72% Santa Maria residuum with sodium carbonate. Table I below shows the results:

Table I

Run No.	Charge	Material Added	Amount of Material Added, Wt. Percent	Coking Temp., ° F.	Time, Hr.	Sulfur in Charge, Wt. Percent	Sulfur in Product Coke, Wt. Percent	Coke Yield, Wt. Percent
38	72% Santa Maria Valley Residuum.	Na_2CO_3	20	916	1	6.41	5.16	22
43	do	Na_2CO_3	20	1,200	1	6.41	3.27	17
44	do	Na_2CO_3	20	1,409	1	6.41	2.67	14
48	do	Na_2CO_3	20	1,404	1	6.41	2.63	14
49	do	Na_2CO_3	20	1,488	1	6.41	2.96	12
62	do	Na_2CO_3	5	1,401	1	6.41	3.15	

While sodium carbonate is a suitable material useful for desulfurization in the process as described above, other alternative materials are available. These include sodium bicarbonate, sodium sesquicarbonate, sodium carbonate monohydrate, sodium carbonate heptahydrate, sodium carbonate decahydrate and sodium hydroxide. These materials have been tested with coke obtained from different crude sources and at different operating conditions, with the result that desulfurization to varying degrees has been obtained.

Table II, which follows hereinafter, shows the results of these tests.

As an alternative process the coking and desulfurization of the residuum may be carried out in two steps. For example, the residuum may be mixed with the sodium carbonate and coked at a temperature of 900° F. or thereabouts. This provides a good mixture of the sodium carbonate and coke. Then the mixture is transferred to a separate vessel where the temperature may be raised to 1400° F. to complete the coking and desulfurization. The two steps may be carried out in separate vessels or alternatively, the two stages may be carried out successively in a single vessel by raising the temperature from 900° F. to 1400° F. Afterwards, the desulfurized coke product is washed with water to remove salts, providing a finished commercially marketable coke. Suitable con-

Table II

Run	Charge	Original Coking Temp., ° F.	Mesh Size of Coke	Material Added	Amt. of Material Added, Wt. Percent	Method of Mixing	Re-coking Temp., ° F.	Time, Hours	Sulfur in Charge, Wt. Percent	Sulfur in Product, Wt. Percent	Sulfur Removal, Wt. Percent	Coke Yield, Wt. Percent
8	Houk Coke [1]	900	60–100	None	0		1,390	1.0	7.01	6.37	9	88
33	do	900	60–100	Na_2CO_3	5	Impreg.	1,405	1.0	7.01	5.57	21	86
30	do	900	60–100	Na_2CO_3	10	Impreg.	1,405	1.0	7.01	3.23	54	85
31	do	900	60–100	Na_2CO_3	20	Impreg.	1,417	1.0	7.01	3.15	55	85
32	do	900	60–100	Na_2CO_3	20	Impreg.	925	1.0	7.01	6.97	1	96
34	do	900	60–100	Na_2CO_3	20	Impreg.	1,204	1.0	7.01	4.45	37	88
75	Santa Maria Valley Coke	916	60–100	None	0		1,404	1.0	5.57	4.83	13	92
51	do	1,000	60–100	Na_2CO_3	20	Mixing	1,215	1.0	5.64	4.03	29	94
63	do	1,000	60–100	Na_2CO_3	20	do	1,227	4.0	5.64	2.77	51	92
45	do	1,000	60–100	Na_2CO_3	20	do	1,402	0.5	5.64	3.09	45	91
36	do	1,000	60–100	Na_2CO_3	20	do	1,405	1.0	5.64	2.88	49	91
37	do	1,000	60–100	Na_2CO_3	20	Impreg.	1,410	1.0	5.64	2.85	50	90
47	do	1,000	60–100	Na_2CO_3	20	Mixing	1,418	4.0	5.64	2.88	49	95
69	do	916	60–100	Na_2CO_3	10	do	1,400	1.0	5.57	2.92	48	89
46	do	1,000	60–100	Na_2CO_3	20	do	1,527	1.0	5.64	3.54	37	95
40	do	1,000	60–100	Na_2CO_3	20	do	1,600	1.0	5.64	3.45	39	96
41	do	1,000	60–100	Na_2CO_3	20	do	1,763	1.0	5.64	3.88	31	98
52	do	1,000	20–60	Na_2CO_3	20	do	1,408	1.0	5.64	3.32	41	95
54	do	1,000	100–200	Na_2CO_3	20	do	1,408	1.0	5.64	2.70	52	90
50	do	1,000	≤100	Na_2CO_3	20	do	1,407	1.0	5.64	2.32	59	89
53	Product of Runs, 45, 47	[2] 1,410	60–100	Na_2CO_3	20	do	1,407	1.0	2.98	1.83	39	97
60	Santa Maria Valley Coke	1,000	60–100	Trona [3]	28.4	do	1,410	1.0	5.64	1.85	67	91
65	do	1,000	60–100	$NaHCO_3$	20	do	1,408	1.0	5.64	3.51	38	92
68	do	1,000	60–100	$Na_2CO_3.H_2O$	23.4	do	1,400	1.0	5.64	2.79	51	89
57	Kuwait Coke	1,036	60–100	Na_2CO_3	23.4	do	1,410	1.0	7.29	2.63	64	91
71	Santa Maria Valley Coke	916	60–100	$NaHCO_3$	31.7	do	1,400	1.0	5.57	2.75	51	91
70	do	916	60–100	Trona [4]	28.4	do	1,403	1.0	5.57	2.56	54	92
74	do	916	60–100	Trona [3]	28.4	do	1,405	1.0	5.57	1.99	64	90
76	do	916	60–100	Trona [5]	28.4	do	1,404	1.0	5.57	2.59	54	91
77	do	916	60–100	Trona [6]	28.4	do	1,406	1.0	5.57	2.30	59	89
78	do	916	60–100	$Na_2CO_3.10H_2O$	54.0	do	1,402	1.0	5.57	2.35	58	90
55	do	1,000	60–100	NaCl	20	do	1,411	1.0	5.64	5.06	10	92
56	do	1,000	60–100	CaO	20	do	1,413	1.0	5.64	4.67	17	95
66	do	1,000	60–100	NaOH	20	Impreg.	1,413	1.0	5.64	1.17	79	90

[1] This is a West Cat Canyon, California crude.
[2] Average of 1402 and 1418° F.
[3] Sodium sesquicarbonate—lab. preparation.
[4] Sodium sesquicarbonate—commercial purified needles.
[5] Sodium sesquicarbonate—60–100 mesh (commercial).
[6] Sodium sesquicarbonate—commercial below 200 mesh.

ditions for conducting the process in two stages are as follows:

	Preferred	Broad
Temp., ° F., 1st stage	830–930	800–1,000.
Pressure, 1st stage	60 lbs./sq. in.	1/10th atm.—50 atm.
Sodium Carbonate	0.7–7.2 lb./lb. of sulfur in coke made without carbonate.	More than 0.7 lb./lb.
Temp., ° F., 2nd stage	1,300–1,500	1,100–1,800.
Time, 2nd stage	15–60 min	1 min.—4 hrs.

The sodium carbonate is preferably used in the form of a fine powder although small lumps can be used successfully. The coke from the low temperature stage should not be water-washed nor removed from the coker by hydraulic means, otherwise, sodium carbonate will be lost. The pressure is usually about atmospheric pressure in the high temperature step. The coke from the high temperature stage is preferably crushed before washing but may be used as lumps with consequent added difficulty in removing the salts by washing with water.

Table III illustrates the invention as a two-stage process.

Table III

Run No.	Charge	Sulfur in Charge, Wt. Percent	Material Added	Amt. of Material Added, Wt. Percent	Temperature 1st Stage	Sulfur in Product Coke, Wt. Percent	Coke Yield, Wt. Percent
67	Santa Maria Valley Crude	4.65	None		916	5.57	12.6
35	do	4.65	None		930	5.64	10
64A	72% Santa Maria Valley Residuum	6.41	Na_2CO_3	5	* 880		

Run No.	Charge	Sulfur in Charge, Wt. Percent	Material Added	Amt. of Material Added, Wt. Percent	Coking Temp., ° F. 2nd Stage	Sulfur in Product Coke, Wt. Percent	Coke Yield, Wt. Percent	Overall Coke Yield Based on Crude Step 1 and Step 2, Wt. Percent
75	Coke From Run 67.	5.57	None	0	1,404	4.83	92	12
36	Coke From Run 35.	5.64	Na_2CO_3	20	1,405	2.88	91	9
64B	Coke From Run 64A.		None		1,405	3.43	♭ 27	19

* Reflux liquid returned to coking operation.
♭ Step #1 plus Step #2.

We claim:

1. The method of producing a low sulfur petroleum coke from a high sulfur petroleum residuum which comprises the steps of mixing with the residuum a material selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium carbonate monohydrate, sodium carbonate heptahydrate, sodium carbonate decahydrate and sodium hydroxide and subjecting the mixture to high temperature coking conditions to produce a petroleum coke, washing the coke formed to effect removal of sulfur salts, whereby a petroleum coke is produced having a substantially reduced sulfur content from that of the residuum from which it is formed.

2. Claim 1 further characterized in that the coking temperature is about 1100–1800° F.

3. Claim 1 further characterized in that the coking temperature is about 1300–1500° F.

4. The method of producing a low sulfur petroleum coke from a high sulfur petroleum residuum which comprises the steps of mixing with the residuum at least a sufficient amount of sodium carbonate in particle form, subjecting the mixture to an advanced temperature for a sufficient period of time to produce a petroleum coke having a substantially lower sulfur content by weight than would be provided if the sodium carbonate were not present, and washing the coke formed to effect removal of sulfur-containing salts from the coke.

5. Claim 4 further characterized in that the coking temperature is about 1100–1800° F. and the reaction time is about 1 minute–4 hours and the amount of sodium carbonate is 0.7 or greater lbs./lb. of sulfur in the coke made without sodium carbonate present and the pressure during reaction is about 0.1 atmosphere–50 atmospheres.

6. Claim 4 further characterized in that the coking temperature is about 1300–1500° F. and the reaction time is about 15–60 minutes and the amount of sodium carbonate is about 0.7–7.2 lb./lb. of sulfur in coke made without sodium carbonate present and the pressure is about atmospheric.

7. The method of producing a low sulfur petroleum coke from a high sulfur petroleum residuum which comprises the steps of mixing with the residuum a material selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium carbonate monohydrate, sodium carbonate heptahydrate and sodium carbonate decahydrate, subjecting the mixture to low temperature coking conditions and then subjecting the mixture to a substantially higher temperature, sufficient to effectively reduce the sulfur content of the finished coke below the amount which would be present in the coke if the carbonate were not used, and washing the product to effect removal of salts from the coke product.

8. Claim 7 further characterized in that the mixture is first heated to a temperature of about 800–1000° F., the pressure being maintained at about 1/10 atmosphere–50 atmospheres, the amount of carbonate being at least 0.7 lb./lb of sulfur in coke made without carbonate, and the material is then heated to about 1100–1800° F. for a period about 1 minute–4 hours, whereby a coke is produced of substantially reduced sulfur content.

9. Claim 7 further characterized in that the mixture is first heated to a temperature of about 800–930° F., the pressure is maintained at about 60 p.s.i., the amount of carbonate is about 0.7–7.2 lb./lb. of sulfur in coke made without carbonate, and the material is then heated to about 1300–1500° F. for about 15–60 minutes, whereby a coke is produced of substantially reduced sulfur content.

10. Claim 9 further characterized in that the carbonate material is sodium carbonate.

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