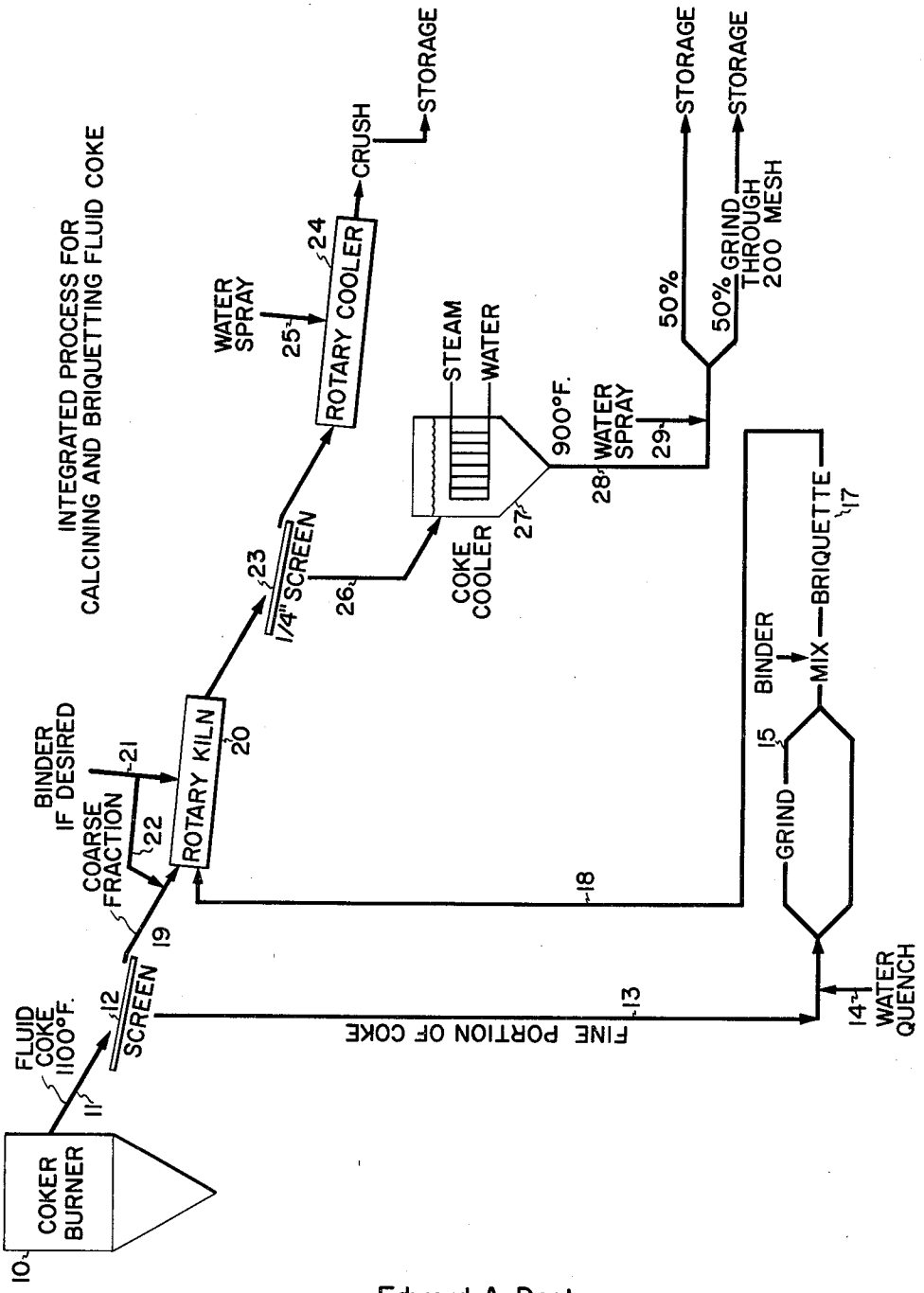
July 10, 1962 E. A. DESTREMPS ETAL 3,043,753

MANUFACTURE OF DENSE COHERENT CARBON MASSES

Filed Jan. 3, 1961



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United States Patent Office 3,043,753 Patented July 10, 1962

3,043,753
MANUFACTURE OF DENSE COHERENT CARBON MASSES

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Filed Jan. 3, 1961, Ser. No. 80,479
7 Claims. (Cl. 202—26)

This invention relates to the production of dense, coherent carbon masses and more particularly to the preparation of electrodes from fluid coke which can be utilized effectively and advantageously for the obtaining of aluminum metal from its ores.

The fluid coking unit consists basically of a reaction vessel or coker and a heater or burner vessel. In a typical operation the heavy oil to be processed is injected into the reaction vessel containing a dense turbulent fluidized bed of hot inert solid particles, preferably coke particles. A transfer line reactor or staged reactors can be employed. Uniform temperature exists in the coking bed. Uniform mixing in the bed results in virtually isothermal conditions and effects instantaneous distribution of the feed stock. In the reaction zone the feed stock is partially vaporized and partially cracked. Product vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms is usually returned to the coking vessel. The coke produced in the process remains in the bed coated on the solid particles. Stripping stream is injected into the stripper to remove oil from the coke particles prior to the passage of the coke to the burner.

The heat for carrying out the endothermic coking reaction is generated in the burner vessel, usually but not necessarily, separate. A stream of coke is thus transferred from the reactor to the burner vessel, such as a transfer line or fluid bed burner, employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or added carbonaceous matter is burned in the burning vessel to bring the solids therein up to a temperature sufficient to maintain the system in heat balance. The burner solids are maintained at a higher temperature than the solids in the reactor. About 5% of coke, based on the feed, is burned for this purpose. This may amount to approximately 15% to 30% of the coke made in the process. The net coke production, which represents the coke made less the coke burned, is withdrawn.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy crudes, atmospheric and crude vacuum bottoms, pitch, asphalt, or heavy hydrocarbon petroleum residue or mixtures thereof. Typically, such feeds can have an initial boiling point of about 700° F. or higher, an A.P.I. gravity of about 0° to 20°, and a Conradson carbon residue content of about 5 to 40 wt. percent. (As to Conradson carbon residue see ASTM Test D–180–52.)

Further details on the distinctions between fluid coking and delayed coking are given in "Oil and Gas Journal," March 22, 1954, pages 126, 127, 130 and 131.

The fluid coke product as withdrawn from the heater or burner vessel is particularly characterized by the small size of the particles, the major proportion, i.e., 30 to 90 wt. percent, being in the range of from about 20 to 80 mesh or about 175 to 850 microns diameter, and also the very low real density, about 1.4 to 1.7, which is considered too low for satisfactory electrodes, and also its high electrical resistivity. These three factors have militated against the use of fluid coke for the manufacture of electrodes.

To render fluid coke suitable for the manufacture of dense, coherent carbon masses, and especially for electrode manufacture, all of it must be calcined at about 1800–2600° F., up to 25% of it must be ground through 200 mesh, and up to 50% of it must be agglomerated. Rotary kilns are most commonly used for calcining and are used successfully for calcining delayed coke for electrode manufacture. However, because of the particle size of fluid coke, fines loss would be appreciable, i.e., 2–10 wt. percent on feed, if rotary kilns were used to calcine it. It has been proposed previously to form fluid coke particles into agglomerates to facilitate the fabrication thereof into electrodes. Unfortunately, however, these previous methods have required expensive procedures to prevent softening of the agglomerates while baking.

It is the object of this invention to provide an improved method for the production of dense, coherent carbon masses from fluid coke. It is a further object of the present invention to provide an effective method for preparing electrodes for metal manufacture from fluid coke.

It is also the object of this invention to provide a method of processing fluid coke in rotary kilns which avoids the problem of fines loss as well as the problem of softening of fluid coke agglomerates during baking.

It is a further object of this invention to provide a method of preparing dense, coherent carbon masses from fluid coke which gives good heat economy.

These and other objects will appear more clearly from the following specification.

It has now been found that fluid coke may be readily fabricated into dense, coherent carbon masses such as electrodes for metal manufacture if fluid coke is withdrawn from the coker burner at about 1100° F. and screened to separate out the finest 50% portion which is agglomerated in the usual way. The agglomerates may be any size desired but are preferably about one half to one inch in size. The coarse 50% portion and the green agglomerates are then sent to the rotary kiln for calcination. Most of the agglomerates will not fall apart in the rotary kiln because they are cushioned by the free fluid coke particles of the coarse 50% portion. Those that do fall apart or stick together will eventually wind up as missshapen agglomerates which are also satisfactory for the manufacture of electrodes. Additional binder is preferably injected into the moving mass of coke particles in the rotary kilm to form more agglomerates during the calcination. At the end of the rotary kiln or calciner, the product is passed over a stationary ceramic screen to separate the briquettes and large agglomerates from the smaller particles and the latter can be fed to a fluid bed cooler to make steam. Part of the smaller particles are then ground to proper size. The briquettes and large agglomerates are cooled in a conventional water spray rotary kilm cooler and crushed to proper size. An alternate procedure would be to pass the entire product from the rotary kiln into the fluid bed cooler without screening, and to eliminate the rotary kiln cooler. The agglomerates would be cooled by contact with the smaller particles. Upon leaving the cooler, the product would be screened, the fines ground, and the agglomerates crushed as before. The various coke particles are then recombined to give the desired particle size distribution, combined with a suitable binder and then formed into dense, coherent carbon masses in any well-known way. Electrodes for use in metal manufacture, for example, may be made either by the conventional prebaking technique or the Soderberg, self-baking technique.

In accordance with the present invention, fines loss in the calciner is greatly reduced since only the coarse coke

particles and agglomerates are passed through the rotary kiln. Also the problem of softening and breaking of the agglomerates during baking is alleviated by the coarse 50% portion of the coke particles which act as a cushion in the kiln. The entire process is particularly characterized by giving good heat economy.

Reference is made to the accompanying drawing in which the figure is a schematic flow plan of the process of the present invention.

Referring now to the drawing, vessel **10** is the usual heater or coker burner of an ordinary fluid coker system in which coke particles are heated to about 1000–1300° F. for recirculation to the coker vessel (not shown) to supply the sensible heat necessary to convert the heavy feed oil therein to vaporous products and solid coke which is, of course, deposited upon the circulating coke particles. A portion of the coke, usually equal to the net coke make of the fluid coker, is withdrawn from burner vessel **10** through line **11** and charged to a screen **12**. The screen **12**, usually 40–115 mesh, is chosen to provide that portion of coke which is to be agglomerated in **17**. If no additional binder is injected through lines **21** or **22**, the screen is chosen so that the fluid coke is divided into approximately equal parts of fine particles and coarse particles. If additional binder is injected, the screen is chosen to provide enough coke for agglomeration in **17** so that the latter plus those agglomerates formed in the kiln by the additional binder total about 50 wt. percent of the coke withdrawn from the coker burner through line **11**. In order to minimize fines loss in the subsequent calcination, the coarse particles should not be smaller than about 115 mesh.

The fine portion of coke which passes through the screen **12** is transferred through line **13**, cooled to about 300° F. by water quench **14** and supplied to grinder **15**. Although not absolutely necessary, part or all of the coke may be ground in grinder **15** to produce fines particles which increase agglomerate strength. It is desirable to have 10–30% of the particles finer than 200 mesh. The coke or ground fluid coke particles are mixed with carbonaceous binder substances supplied through line **16** and compacted into agglomerates in **17**. Carbonaceous binder substances that can be used include suitable hydrocarbon binders such as asphalt and other heavy petroleum residues, aromatic tars, e.g., vacuum-reduced thermal tars, heavy ends of coal tar, such as coal tar pitches having a minimum softening point of about 100–250° F., preferably about 150° F. and heavy ends from the coking operation, i.e., 1000° F.+ material. These carbonaceous binders are utilized in amounts of from about 5 to 25 wt. percent based on the coke charge and preferably 8 to 15 wt. percent.

The mixture of coke particles and binder is then agglomerated in **17** by molding in a hydraulic press at temperatures of about 150–250° F. and at a pressure of about 2100 to 20,000 p.s.i. Roll presses such as those commonly employed to make briquettes from coal and other materials can be used. Such hydraulic and roll presses are well known in industry.

The freshly prepared compactions or agglomerates require a heat hardening at a temperature of at least about 1000° F. to decompose the binder to a carbonaceous residue and to produce adequate strength and cohesion. Treating at these temperatures causes melting of the binder material resulting in the deformation and adhesion of the compactions or agglomerates to each other. These problems are readily overcome by the present invention.

The briquettes which are preferably one half to one inch in size are removed from **17** and conveyed through line **18** into rotary kiln **20** where they are mixed with the coarse 50% fraction of the fluid coke rejected by screen **12** which is conveyed to the kiln **20** through line **19**. If desired, additional binder such as is supplied at **16** for agglomerate formation can be supplied through line **21** directly to the rotary kiln **20** or through line **22** to the coarse fraction in transfer line **19**. The kiln is heated by firing air and fuel at the coke discharge end, the hot combustion gases flowing up the kiln countercurrently to the downward flowing coke. The gases leave the kiln at a temperature in the range of 1000 to 1500° F., and may pass through a settling chamber to recover any of the coke which may be entrained in the gas. This latter amount will be very small, i.e., about 1% on feed since all of the fines have been agglomerated. The coke and agglomerates discharge from the kiln at a temperature in the range of 1800 to 2800° F. Coke residence time in the kiln is from 10 minutes to one hour. Gas residence time is from 5 to 30 seconds.

As the agglomerates are heated in the kiln, they become rather soft or plastic. Deformation and adhesion of the agglomerates or briquettes as well as disintegration thereof through abrasion or impact of briquette upon briquette is greatly reduced by the separating and cushioning action provided by the coarse 50% coke particles.

At the exit end of the rotary kiln the calcined coke is discharged onto a stationary ceramic screen **23** of about ¼" hole size to separate the relatively fine coke particles from the briquettes or other larger agglomerates. The briquettes and large agglomerates rejected by the screen **23** are discharged into a suitable cooler such as rotary drum **24** into which a water spray is directed in order to cool the coke to about 300° F. The cooled coke agglomerates are then crushed to provide a uniform particle size distribution ranging from 10 mesh to ½ inch. The crushed coke agglomerates are then passed to storage.

The coke fines passing through ceramic screen **23** are passed via line **26** to a suitable cooler such as a fluid bed cooler **27** containing suitable heat exchange equipment for making steam. The fine coke particles are withdrawn from cooler **27** through line **28** at about 900° F. and cooled to about 300° F. by means of a water spray **29** or the like. The coke particles are then separated into about equal parts, one of which is sent to storage and the other of which is ground sufficiently to pass through a 200 mesh screen and then sent to storage.

In the manufacture of the dense, coherent carbon masses, such as electrodes, brushes, and internal lining of electric furnaces and electrolysis cells or the like, the several coke products are blended in order to give the desired particle size distribution. The blending may be carried out in either continuous or batch mixers containing rotating paddles or arms and the degree of mixing should be such as to provide a uniform, homogenous blend of the crushed briquettes, fluid coke ground to minus 200 mesh, and unground fluid coke streams. The blend of coke particles is thoroughly mixed with a suitable carbonaceous binder such as is described above for the preparation of briquettes. The binder is used in amounts of from about 15 to 45 parts by weight per 100 parts by weight of the coke blend.

In general, two types of electrodes are employed by the industry (*a*) prebaked, and (*b*) Soderberg self-baking electrodes. In the former, a mixture comprising about 78–85% of calcined coke blend and about 15–22% of coal tar pitch is molded at pressures of about 3000–6500 p.s.i. or extruded, and then baked for periods up to 30 days at 1800° to 2400° F. These preformed electrodes are then used in electrolytic cells, being slowly lowered into the molten alumina as they are consumed. Butts of the unconsumed electrodes are reground and used in subsequent electrode preparations. Some green coke can be calcined during the baking operation.

The Soderberg process involves the continuous or intermittent addition of a coke-tar pitch paste to the top of the cell as the electrode components in the lower part of the cell are consumed. In this operation the paste represents a blend of about 70% to 72% coke charge and 28%

to 30% of pitch. The cells operate usually at temperatures of 1700° to 1900° F. and electrodes are consumed at the rate of about 0.5 to 1.0 inch per day. The paste is baked into an electrode by the hot cell gases in the period between the time it is added at the top and the time it is used. The net consumption of coke represents 0.4 to 0.7 lb. per pound of aluminum metal produced. Both methods have in common the baking of the mixed coke charge and binder at a temperature in the range of 1700° to 2400° F.

The following examples are illustrative of the present invention.

Example 1

Two hundred t./s.d. of fluid coke at 1100° F. are withdrawn from coker burner **10** through line **11** and charged to screen **12** which is 80 Tyler mesh. Ninety percent of the coke is in the 20 to 200 mesh range and 45% is larger than 80 mesh. About 110 t./s.d. of coke finer than 80 mesh pass through screen **12** to line **13** where the coke is cooled to 300° F. by water quench **14**. Sixteen t./s.d. of this coke then flows to ball mill **15** where it is crushed to pass through a 200 mesh screen and then blended with the unground 94 t./s.d. The blend is mixed with 16 t./s.d. of a 150° F. softening point coal tar pitch supplied through line **16**, the mixing operation being carried out at 175° F. The mixture is then briquetted at 160° F. in conventional roll press **17** which has a capacity of 10 tons per hour and which operates at 10,000 p.s.i. Cooling of the mix from 175° F. to 160° F. occurs by heat loss to the air as the mix is conveyed to roll press **17**. The briquettes are pillow shaped and are 1" x 1" x ¾" thick.

The briquettes are conveyed through line **18** into rotary kiln **20** where they are mixed with the 90 t./s.d. coarse fraction of the fluid coke rejected by screen **12** and conveyed to kiln **20** through line **19**. The briquettes and coarse fraction are heated to 2400° F. by contact with hot combustion gases flowing through the kiln and discharged from the kiln at 2400° F. The combustion gases, which include some unburned volatile matter from the coke are discharged from the other end of the kiln at 1500° F. Coke residence time in the kiln is 45 minutes. The kiln is 10 feet in diameter and 150 feet long.

At the exit end of the rotary kiln, the calcined coke is discharged onto screen **23** which has holes about ¼" in diameter. The briquettes rejected by the screen are discharged into rotary cooler **24** and cooled to 300° F. by a water spray. The cooled briquettes are crushed in a jaw crusher set to give a particle size range from 10 mesh to ½". The fines passing through screen **23** are passed via line **26** to fluid bed cooler **27** where they are quenched to 600° F. The fines are withdrawn through line **28** and cooled to 300° F. by water spray **29**, separated into equal parts, one of which is sent to storage and the other which is ball milled to pass through a 200 mesh screen.

The three coke streams totaling about 197 t./s.d. are then blended together in a steam jacketed paddle mixer heated to 210° F. Thirty-five t./s.d. of 210° F. softening point coal tar pitch is added to this mixture and when thoroughly blended the mixture is discharged and molded at 6000 p.s.i. to form prebaked electrodes. The electrodes are baked at 2200° F. for 28 days at which time they are ready for use in an aluminum electrolytic cell.

Example 2

Two hundred t./s.d. of fluid coke at 1100° F. are withdrawn from coker burner **10** through line **11** and charged to screen **12** which is 115 Tyler mesh. Ninety percent of the coke is in the 20 to 200 mesh range and 70% is larger than 115 mesh. About 60 t./s.d. of coke finer than 60 mesh pass through screen **12** to line **13** where the coke is cooled to 300° F. by water quench **14**. Nine t./s.d. of this coke then flows to ball mill **15** where it is crushed to pass through a 200 mesh screen and then blended with the unground 51 t./s.d. The blend is mixed with 9 t./s.d. of a 150° F. softening point coal tar pitch supplied through line **16**, the mixing operation being carried out at 175° F. The mixture is then briquetted at 160° F. in conventional roll press **17** which has a capacity of 10 tons per hour and which operates at 10,000 p.s.i. Cooling of the mix from 175° F. to 160° F. occurs by heat loss to the air as the mix is conveyed to roll press **17**. The briquettes are pillow shaped and are 1" x 1" x ¾" thick.

The briquettes are conveyed through line **18** into rotary kiln **20** where they are mixed with the 140 t./s.d. coarse fraction of the fluid coke rejected by screen **12** and conveyed to kiln **20** through line **19**. Seven t./s.d. of 150° F. softening point coal tar pitch is supplied through line **21** at 200° F. to make more agglomerates in the kiln. As an alternate, the 150° F. softening point coal tar pitch can be supplied through line **22** in solid granular form at ambient temperature. The briquettes, other agglomerates, and coarse fraction are heated to 2400° F. by contact with hot combustion gases flowing through the kiln and discharged from the kiln at 2400° F. The combustion gases which include some unburned volatile matter from the coke are discharged from the other end of the kiln at 1500° F. Coke residence time in the kiln is 45 minutes. The kiln is 10 feet in diameter and 150 feet long.

At the exit end of the rotary kiln, the calcined coke is discharged onto screen **23** which has holes about ¼" in diameter. The briquettes rejected by the screen are discharged into rotary cooler **24** and cooled to 300° F. by a water spray. The cooled briquettes are crushed in a jaw crusher set to give a particle size range from 10 mesh to ½". The fines passing through screen **23** are passed via line **26** to fluid bed cooler **27** where they are quenched to 600° F. The fines are withdrawn through line **28** and cooled to 300° F. by water spray **29**, separated into equal parts, one of which is sent to storage and the other which is ball milled to pass through a 200 mesh screen.

The three coke streams totaling about 197 t./s.d. are then blended together in a steam jacketed paddle mixer heater to 210° F. Thirty-five t./s.d. of 210° F. softening point coal tar pitch is added to this mixture and when thoroughly blended the mixture is discharged and molded at 6000 p.s.i. to form prebaked electrodes. The electrodes are baked at 2200° F. for 28 days at which time they are ready for use in an aluminum electrolytic cell.

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. A method of making dense coherent carbon masses from fluid coke which comprises withdrawing a stream of green coke particles from a fluid coking system, screening the coke particles into a coase fraction and a fine fraction, adding a binder to the fine fraction and forming said fines into suitable compactions of at least one-half inch size, passing the coarse fraction and the compactions in intimate contact through a rotary kiln heated to temperatures of about 1800° F. to 2800° F., withdrawing calcined coke product from the kiln, screening the compactions and large agglomerates from the calcined product, cooling and crushing the calcined compactions, cooling the product passing through the screen, grinding at least a portion of these screenings to pass through a 200 mesh screen, blending the several calcined coke products to give the desired particle size distribution, adding a carbonaceous binder and forming the resulting mixture into a dense coherent carbon mass.

2. A method of making dense coherent carbon masses from fluid coke which comprises withdrawing a stream of green coke particles from a fluid coking system, screening the coke particles into a coarse fraction and a fine fraction, adding a carbonaceous binder to the fine fraction, and forming the resultant mixture into suitable compactions of at least one-half inch size, passing the coarse

fractions and the compactions in intimate mixture through a rotary kiln countercurrent to hot combustion gases at temperatures of about 1800° F. to 2800° F., withdrawing calcined coke product from the rotary kiln, screening the compactions and large agglomerates from the remainder of the calcined coke product, cooling and crushing the calcined compactions, cooling the calcined coke product passing through the screen, grinding at least a portion of these screenings to pass through a 200 mesh screen, blending the several calcined coke products to give the desired particle size distribution, adding a carbonaceous binder and forming the resultant mixture into a dense coherent carbon mass.

3. A method for making dense coherent carbon masses from fluid coke which comprises withdrawing a stream of green coke particles from a fluid coking system, screening the coke particles into a coarse fraction and a fine fraction, adding a carbonaceous binder to the fine fraction and forming the resultant mixture into suitable compactions of at least one-half inch size, passing the coarse fractions and the compactions in intimate mixture through a rotary kiln countercurrent to hot combustion gases at temperatures of about 1800° F. to 2800° F., adding carbonaceous binder material to the mixture of compactions and coke particles in the kiln to form additional agglomerates, withdrawing calcined coke product from the rotary kiln, screening the compactions and large agglomerates from the remainder of the calcined coke product, cooling and crushing the calcined compactions, cooling the calcined coke product passing through the screen, grinding at least a portion of these screenings to pass through a 200 mesh screen, blending the several calcined coke products to give the desired particle size distribution, adding a carbonaceous binder and forming the resultant mixture into a dense coherent carbon mass.

4. The process as defined in claim 2 in which the residence time of the coke particles in the rotary kiln is from about 10 minutes to one hour.

5. The process as defined in claim 2 in which the calcined coke product is cooled before separating the compactions and large agglomerates from the remainder of the calcined coke product.

6. The process as defined in claim 3 in which the residence time of the coke particles in the rotary kiln is from about 10 minutes to one hour.

7. The process as defined in claim 3 in which the calcined coke product is cooled before separating the compactions and large agglomerates from the remainder of the calcined coke product.

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