Feb. 19, 1957 D. S. MAISEL ET AL 2,782,105

FURNACE FOR ACTIVATING COKE

Filed Dec. 2, 1952 2 Sheets-Sheet 1

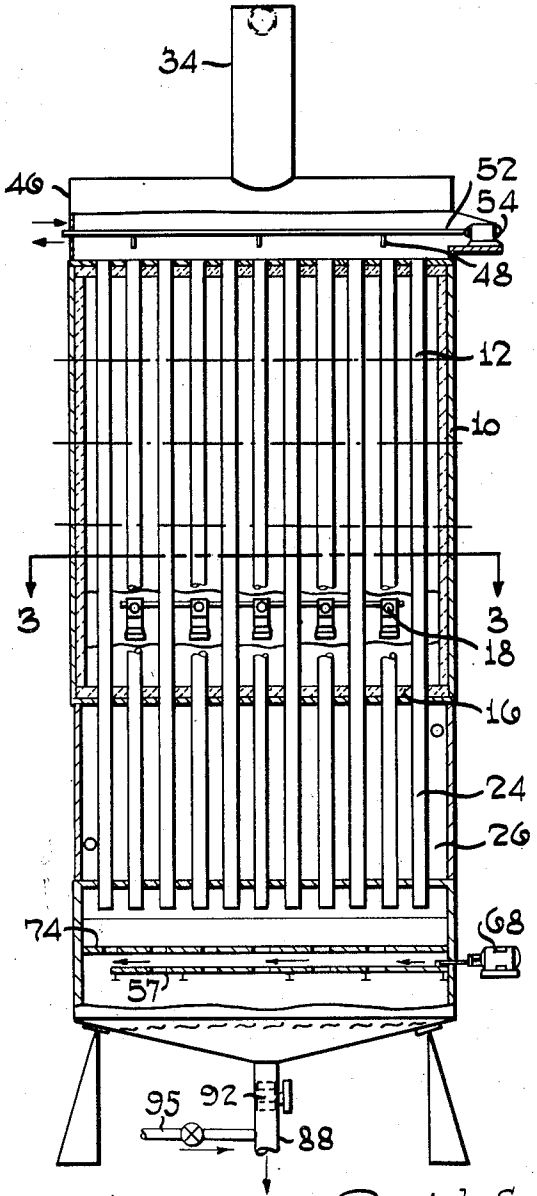


FIG. -2

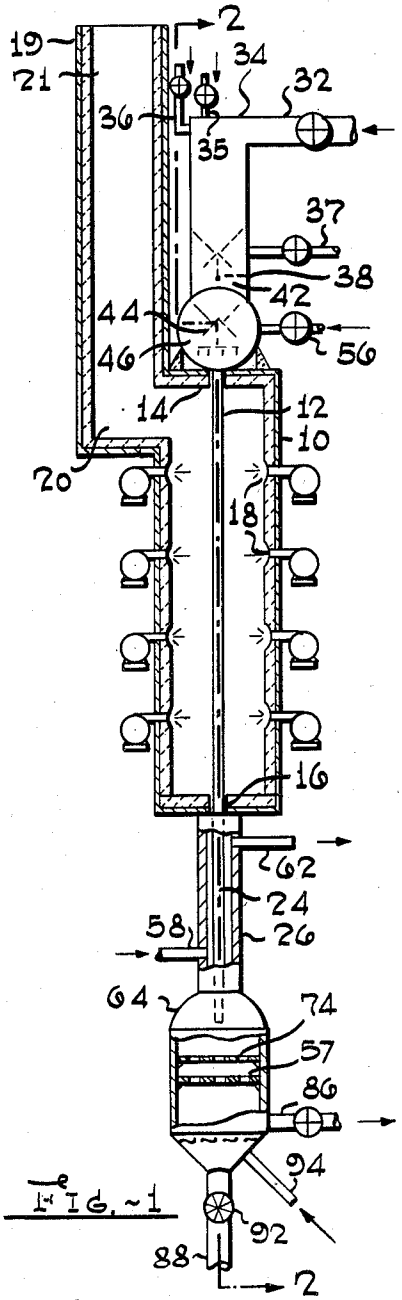


FIG. -1

Daniel S. Maisel Inventors
William M. Gorgl
By George J. Sicherman Attorney

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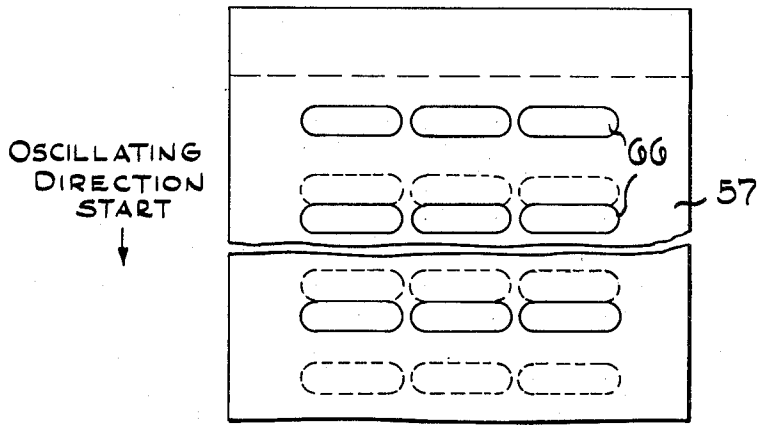


FIG.-5

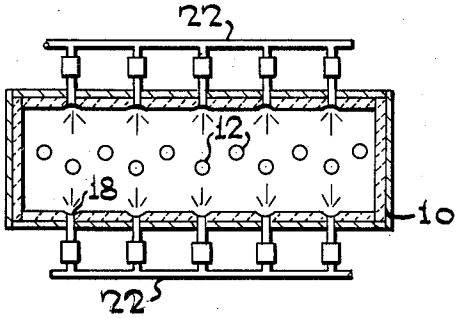


FIG.-3

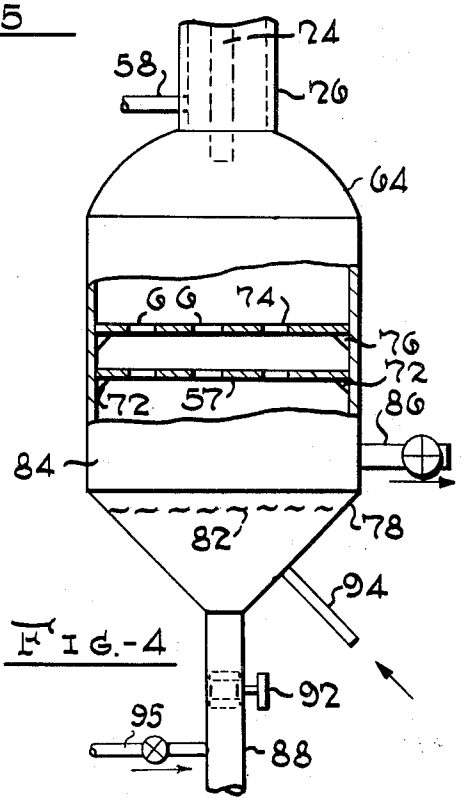


FIG.-4

Daniel S. Maisel Inventors
William M. Gorgl
By George J. Silbary Attorney

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FURNACE FOR ACTIVATING COKE

Daniel S. Maisel, Union, and William M. Goryl, Morristown, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application December 2, 1952, Serial No. 323,666

1 Claim. (Cl. 23—277)

This invention relates to activating coke and more particularly relates to an apparatus and method for close control of the quality of the activated coke product and for allowing wide flexibility of operation.

Coke particles to be activated are preferably continuously fed to the top of an activating furnace and maintained in an inert atmosphere before entering the activating section of the furnace. Steam and the coke particles flow concurrently down through the activating furnace. The activating furnace includes a plurality of spaced vertical tubes heated on opposite sides by radiant heat. With the type of firing system used and with the arrangement of tubes a wide range of control is provided and the danger of hot spot formation is avoided.

After passage through the activating furnace the coke particles are cooled by indirect heat exchange with a heat exchange medium. After cooling, the gaseous reaction products are separated and the activated coke particles are either delivered to intermediate storage prior to grinding and/or classification or packaged as in drums. An inert atmosphere is maintained around the activated coke particles during their handling.

In the drawing:

Fig. 1 represents a vertical transverse section through the apparatus of this invention;

Fig. 2 represents a vertical longitudinal section of the apparatus;

Fig. 3 represents a horizontal transverse section taken substantially on line 3—3 of Fig. 2;

Fig. 4 represents an enlarged detail of the lower discharge portion of the apparatus; and

Fig. 5 represents an enlarged detail of a portion of perforated grid used in the discharge portion of the apparatus.

Referring now to Figs. 1, 2 and 3 the reference character **10** designates a furnace section which is shown as substantially rectangular in shape as will be seen by the vertical sections in Figs. 1 and 2 and horizontal section in Fig. 3. Arranged within the furnace **10** are vertical parallel tubes **12** arranged in staggered relation as shown in Fig. 3 and extending to the top **14** and through the bottom **16** of the furnace section. The tubes are arranged in rows parallel to the longer dimension of the rectangular furnace section as shown in Figs. 1 and 3. Provided in the opposite vertical walls of the furnace section **10** are burners **18** for supplying heat to the tubes **12**. The burners are arranged in rows in the vertical walls forming the longer dimension of the rectangular furnace section **10**. As shown in Fig. 1 the burners are in vertical rows and as shown in Fig. 3 the burners are also arranged in horizontal rows. While the tubes **12** are staggered, they do not overlap so that radiant heat is supplied to each side of each tube in the radiant heating section of the furnace **10**. A stack **19** is provided for removing combustion gases from furnace **10**. The stack **19** has a horizontal section **20** and an offset vertical section **21** to permit feeding of raw coke from the top of the furnace into tubes **12**.

The burners are of the radiant heat type where the burner body has an open cavity provided with a refractory lining forming a combustion space so that a combustible mixture supplied to and burned in the combustion space to heat the lining to incandescence. A typical example of a burner of this type is known as a Selas burner. With these burners there is no impingement of flames on the burner tubes. The combustible mixture is supplied to the burners by manifolds or the like **22** and is premixed before combustion with controllable amounts of air. Valves may be provided in means **22** to supply different amounts of heat to different or selected portions of the furnace or radiant heating section **10**. With the arrangement of burners as shown, wide variation in heat flux, controllable distribution of heat and elimination of hot spots caused by flame impingement on the tubes are provided.

In general best results in activating coke are obtained in regard to yield and quality of the activated coke when the reaction is carried out within the limits of 1400–1550° F., preferably 1400–1500° F. Too low a temperature, that is below about 1350° F., causes too low a reaction rate, whereas too high a temperature, that is above 1600° F., results in over activation.

The following information is included to show the importance of close temperature control.

Temperature of Activation	Carbon Yield Wt. Percent on Coke Feed	Activating Gas	Separating Factor Between n-heptane and iso-octane 50/50 mixture
1,400–1,500° F.	83	Steam	7.5
1,600–1,760° F.	83	Steam	2.5

Preferably the horizontal temperature gradient in said heating tubes **12** above cooling section **26** is maintained at about 100° F. or below.

The heating tubes **12** are made of refractory or heat resistant material such as 25–20 chromium nickel steel but other materials may be used. The lower portion **24** of the tubes **12** extending below bottom wall **16** of the furnace **10** and into the cooling section **26** (to be described later) may be formed of carbon steel. The lower portions **24** may be formed as extensions of the refractory tubes **12** as by welding or may be attached thereto by suitable flanges. However, the transition from heat resistant material to carbon steel should be located in the cooling section **26**.

The coke particles to be treated or activated are introduced through line **32** in any suitable manner into one or more top lock hoppers **34** arranged above the furnace section **10**. Line **35** is provided for admitting inert gas into lock hopper **34** to sweep out residual traces of air introduced with the fresh feed coke. This gas may be vented through line **32**. Inert gas such as nitrogen, natural gas, hydrocarbon gases, tail gas or other gases not containing oxygen or oxides of carbon and which do not react with the carbon at the temperatures prevailing in the lock hoppers may be used and is introduced into lock hopper **34** through line **36**. Upper hopper **34** is at a pressure of about atmospheric to about 20 p. s. i. g. The valve **38** on lock hopper **34** is then opened and the coke particles are passed to lower lock hopper **42** with valve **44** closed. Then valve **38** is closed for the next charge of the coke particles. Inert gas of the type above described is introduced under pressure to lower lock hopper **42** through line **37**. Then valve **44** is opened and the coke particles under a pressure of about 10 to 50 p. s. i. g. are passed to distribution chamber **46** arranged above the top

14 of the furnace section and above the upper ends of tubes 12 for feeding the coke particles to the tubes.

The pressure in lower lock hopper 42 may be intermediate to the pressures in upper lock hopper 34 and distribution chamber 46. As an alternative method of operation of the furnace, the valve in line 35 or 36 communicating with upper lock hopper or hoppers 34 may be opened and fresh feed coke introduced into hoppers 34 through line 32. Then to displace air from the feed coke in hopper 34, inert gas from lower lock hopper 42 is passed through open valve 38 to hopper 34 and vented through line 35 or 36. When all the air has been displaced from the feed coke in hopper 34, valve 38 is closed and the pressure in the lower lock hopper 42 raised to the desired level. Upper hopper 34 is then pressurized, if desired.

The lower portion of distribution chamber 46 is shown as semi-cylindrical and the tops of the tubes open into the bottom semi-cylindrical portion and are flush with the bottom portion to permit feeding of the coke particles to the tubes. The distribution chamber is constructed to hold a pressure of about 10 to 50 p. s. i. g. on the contents thereof.

Rake elements 48 are provided in distribution chamber 46 to distribute the coke particles to the upper ends of tubes 12. The rake elements 48 are secured at intervals to a rod 52 which is oscillated back and forth by a suitable motor 54 or the like. Steam as the activating gas is introduced into distribution chamber 46 through line 56. Instead of steam, CO_2 alone may be used or a combination of CO_2 and steam or other activating gases may be used.

Since the activation process is strongly endothermic, it is necessary to transfer a large amount of heat to the coke. It is important to maintain a high degree of turbulence within the tubes 12 so as to obtain a maximum internal heat transfer coefficient. By having the flow of coke particles and activating gas cocurrent, the activation gas velocity is much greater than would be permissible if the gas flowed countercurrent to the coke without blowing the coke upward from the tubes or preventing downward coke flow. In addition cocurrent flow of gas and coke particles aids the flow of the coke particles by minimizing the potential "bridging" effect of the solids. With cocurrent flow better product quality and more reliable operation of the activating furnace is obtained.

The raw coke to be treated contains a wide range of particle sizes from about 200 mesh up to ½ inch and after activation may be ground or classified to desired size ranges from a powder for fluidized beds to larger particles up to ½ inch for moving beds. The raw coke is preferably that prepared from acid sludges produced as a result of various petroleum refining operations particularly the sulfuric acid treatment of gasoline, lubricating oil and higher boiling petroleum distillate. The acid sludge comprises a tarry residue containing carbonaceous residue with unreacted sulfuric acid, sulfonic acids etc. The sludge coke is prepared in any conventional manner. One method of preparation is given in Vesterdal et al. Patent No. 2,586,889. Other cokes and other petroleum cokes such as those obtained in refinery operations such as cracking, visbreaking, coking etc. may be used.

Positive control of the flow of coke particles through tubes 12 is obtained by an oscillating grid 57 or the like arranged at the bottom outlet of tubes 12 and presently to be described. As the coke particles pass down through the tubes 12 they enter the lower portions of tubes in cooling section 26 which comprises a heat exchange element surrounding the lower portions 24 of the tubes 12. The heat exchanger has an inlet 58 and an outlet 62 for a heat exchange medium. Water is preferred as the cooling medium but the cooling is carried out with

water boiling under sufficient pressure to prevent condensation of unreacted steam in the activated coke as otherwise condensation of water in the coke mixture would cause agglomeration. The activated coke particles in cooling section 26 are cooled to about 250° F. to 350° F.

The oscillating grid 57 is generally shown in Figs. 1 and 2 and in more detail in Figs. 4 and 5. The grid 57 is arranged in a sealed or air tight housing 64 which receives activated coke particles from the lower ends 24 of tubes 12 which extend a short distance into housing 64. The upper end of housing 64 is shown in the form of a rounded dome but other shapes may be used. The oscillating grid 57 is provided with spaced openings 66 as shown in Fig. 5 and the grid is oscillated back and forth a short distance by a motor or the like 68 (Fig. 2). Suitable mechanism is provided between the grid and the motor to effect the oscillation. In Fig. 4 grid 57 is shown as supported or mounted on supports 72 and oscillation is in a plane perpendicular to the plane of Fig. 4.

Arranged above oscillating grid 57 is a stationary grid 74 mounted on supports 76. Stationary grid is similar to oscillating grid 57 and is also provided with openings like those provided in the oscillating grid as shown in Fig. 5. The grids are so arranged that upon oscillation of the grid 57 in one direction, the holes or openings in the two grids 57 and 74 will register or aline to permit coke particles to fall through the alined openings and then upon oscillation in the other direction the openings will be out of registry or out of alinement so that no coke particles can fall through the openings. The coke particles substantially fill the space in the housing below the bottom of tubes 24 and the stationary grid 74 and are supported on upper stationary grid 74.

The cooled activated coke particles then fall into the conical hopper section 78 below oscillating grid 57 and which forms part of the housing 64. The coke particles collect in the bottom of the hopper section 78 as shown at 82 to leave a gas disengaging space 84 thereabove. The gaseous reaction products are withdrawn from disengaging space 84 and discharged through valved line 86. The coke particles are withdrawn through outlet line 88 provided with a star feeder 92 or other valve for maintaining a seal during discharge of the coke particles from hopper section 78. Steam is preferably introduced into the activated coke through line 94 above star feeder 92 as a purging or stripping medium for the coke particles. From line 88 the activated coke particles are removed to a product storage hopper or drums (not shown) and provision is made for keeping the activated coke particles under an inert atmosphere at all times. Preferably inert gas is introduced into line 88 through line 95.

A specific design will now be described for the continuous steam activation of 20 tons per stream day of coke made from acid sludge to produce activated coke. For this design an activated coke yield of 53% based on the acid sludge coke feed was selected on the basis of data indicating maximum adsorptive ability (final surface area per unit weight of raw coke) at this level. The average size of the coke particles is ⅛ inch. An analysis of a typical raw acid sludge coke is as follows:

	Wt. percent
Carbon	87.0
Sulfur	6.0
Hydrogen	1.8
Oxygen	5.0
Ash	0.2

The entire system is blanketed with an inert gas which in this design is natural gas. Two lock hoppers arranged one above the other are provided at 34 and 42. Lock hoppers are sufficiently large to hold about 2.5 to 3 tons of coke to be fed to the unit.

Raw coke is fed into top hopper **34** through line **32** and the hopper is blanketed with inert gas. Valve **38** is closed. T hen inert gas is pumped through line **32** to place hopper **34** under a pressure of about 18 p. s. i. g. Then valve in line **32** is closed and valve **38** in the bottom of lock hopper **34** is opened to discharge the coke into the lower hopper **42** having valve **44** closed. Then valve **38** is closed and valve **44** opened to discharge the coke into distribution chamber **46** where the rakes **48** distribute the coke to the tubes **12**. The pressure in chamber **46** is about 15–18 p. s. i. g. Steam at about 600° F. and at about 15–18 p. s. i. g. is introduced into chamber **46** through line **56** at a rate of about 3000 lbs. per stream hour. The charging of the lock hoppers is continued to feed about 20 tons per stream day of raw acid sludge coke to the system.

There are 18 heating tubes **12**, each 9 inches in diameter. The length of each tube in the furnace **10** is about 25 feet and the length of the cooling tubes **24** forming extensions of the tubes **12** is about 10 feet. The furnace **10** is about 8 feet by 20 feet and about 25 feet high. There are 40 radiant burners **18** with 20 on each side. Normal design operation requires 125,000 B. t. u./hr./burner. However, with the type burner used, the range is from 20,000 to 300,000 B. t. u./hr./burner so that a large amount of flexibility is provided. The tube wall temperature will be about 1600° F. to heat the coke particles in tubes **12** to about 1500° F. During activation in heating tubes the horizontal temperature gradient is maintained at about 100° F. or below. Heat flux densities can be controlled at specific points by firing rates to the individual burners.

The cooling section **26** will require about 300 gal. per minute of water at 90° F. under a pressure of about 15–25 p. s. i. g. and the steam leaving through line **62** is at a temperature of about 250° F. and a pressure of about 15 p. s. i. g.

From the cooling section **26** the coke particles move down into housing **64** above stationary grid **74**. The entire length of the tubes **12** and **24** and housing **64** contains a compact column of downwardly moving coke particles together with activating gas. The coke particles after being cooled are at a temperature of about 270° F. The stationary grid **74** and oscillating grid **57** are about 5 feet by 20 feet and the slots or openings **66** are oval shaped measuring about 9 inches by 3 inches. There are 24 rows of slots **66** with three slots in a row making a total of 72 slots. The slots are spaced 6 inches apart longitudinally of the grids. The oscillating grid **57** has a 6 inch stroke so that the slots in the two grids register in one position and are out of registry at the other position of grid **57**.

The activated coke falls into collecting hopper **78** below grid **57** and reaction gases including H_2, H_2O, CO and CO_2 at a temperature of about 270° F. leave disengaging space **84** through line **86**. About 2,000 cu. ft. per minute of gases are removed via line **86**. About 11 tons per stream day of activated coke will be obtained having the following analysis:

	Wt. percent
Carbon	93.5
Sulfur	0.8
Hydrogen	1.7
Oxygen	3.7
Ash	0.3

From hopper **78** the activated coke at a temperature of about 240°–260° F. is withdrawn through star feeder **92** and line **88** while being blanketed by inert gas introduced through line **95** into line **88**. The activated coke is then sent to storage hopper or drums or otherwise packaged, care being taken to maintain the activated coke under an inert gas blanket at all times because of the reactive nature of the product.

In the above design the coke particles being activated will pass through tubes **12** and **24** at a velocity of about 4 feet per hour and the activating steam will pass through the tubes at a velocity of about 3 feet per second. This higher velocity of the steam maintains a high degree of turbulence within the reaction or heating tubes **12** to obtain a maximum internal heat transfer coefficient. However, the velocity of the coke particles passing down through heating tubes **12** may vary between about 1 and 10 feet per hour and the velocity of the steam passing down through tubes **12** may vary between about 2 and 10 feet per second. The activation temperature for the coke particles may vary between about 1400° and 1550° F. with 1450° F. preferred. At 1450° F. the velocity of the coke particles passing through the heating tubes is lower to permit maintaining the coke particles at the activating temperature for about 8 hours whereas at the 1550° F. activation temperature the velocity of the coke particles is higher to maintain the particles at this higher temperature for about 4 hours.

The process may be varied to produce activated coke or carbon having different characteristics. For example, to produce an activated coke for gas adsorption work where a certain gas or gases such as ethylene, propylene is recovered from mixtures containing such gas or gases, a very highly activated coke containing 1000–1300 sq. meters of surface per gram is desired and will be obtained on operating the process under the conditions given above in connection with the specific design. When a less active coke such as one containing 300–700 sq. meters per gram is desired as for liquid decolorization of sugar, the conditions are changed, the temperature being about 1400° F., the velocity of the coke particles being about 10 ft./hr. and the steam velocity being about 4 ft./sec.

Generally to produce particles with less surface area, the rate of flow of the coke to be activated in tubes **12** is increased two or three times while maintaining the other conditions as given in the specific design. The process may be carried out to obtain different yields of 50 to 90% activated coke from the 53% given for the specific design above described.

From the above it will be seen that the present invention gives wide flexibility of product control by variation of the coke flow rate through heating tubes **12** (coke residence time), by affording control of temperature level and steam conversion.

A wide range of operating conditions may be used. The raw coke feed rate, fractional yield of product and reaction temperatures can be varied considerably to give a wide range of activated carbon from low to high surface area.

The system can also be used for heat activation of cracking catalysts, hydroforming catalysts etc.

In the preferred construction the tubes **12** and **24** are not supported by the furnace but are free to expand and contract without interference from the furnace. The tubes therefore support the lock hopper and feed equipment. The furnace may be supported by conventional steel framework.

While a specific design has been disclosed it is to be expressly understood that this is by way of illustration only and variations may be made without departing from the spirit of the invention.

What is claimed is:

An apparatus of the character described including in combination, a rectangular furnace oblong in horizontal cross section, a plurality of spaced vertically arranged metal heating tubes in said furnace and parallel to and spaced from the long vertical side walls of said furnace, said heating tubes being arranged in two rows in staggered relation to receive radiant heat on both sides of said tubes, sets of burners opening into said furnace and extending through said long side walls of said furnace, each set of burners being arranged in a horizontal row with each row being spaced vertically one above the other

for supplying radiant heat directly to opposite sides of each of said metal heating tubes, means for controlling said burners for supplying different amounts of heat to selected portions of said metal heating tubes, an elongated feed hopper communicating with the upper ends of said metal heating tubes for supplying solids to be treated to said metal tubes and for downward passage therethrough, rake means in said feed hopper for insuring equal distribution of solids to said metal heating tubes, means including a pipe for introducing activating gas into the upper portion of said metal heating tubes for passage down through said tubes at a greater velocity than that of the downwardly moving solids, vertically arranged cooling tubes forming extensions at the lower ends of said metal heating tubes and extending below said furnace, an indirect heat exchanger for said cooling tubes, a discharge chamber for receiving treated solids from said cooling tubes, grid means in said discharge chamber communicating with the lower outlet ends of said cooling tubes and for maintaining a column of solids in each of said

tubes, said grid means including a stationary upper grid and a spaced lower oscillatable grid for controlling the removal of treated and cooled solids from said cooling tubes, a pipe for introducing inert blanketing gas into said discharge chamber, said discharge chamber being provided with a gas disengaging space and means for removing gas from said disengaging space.

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