F. D. LINDQUIST.

METHOD OF FIXING NITROGEN.

APPLICATION FILED APR. 15, 1916.

1,298,363. Patented Mar. 25, 1919.

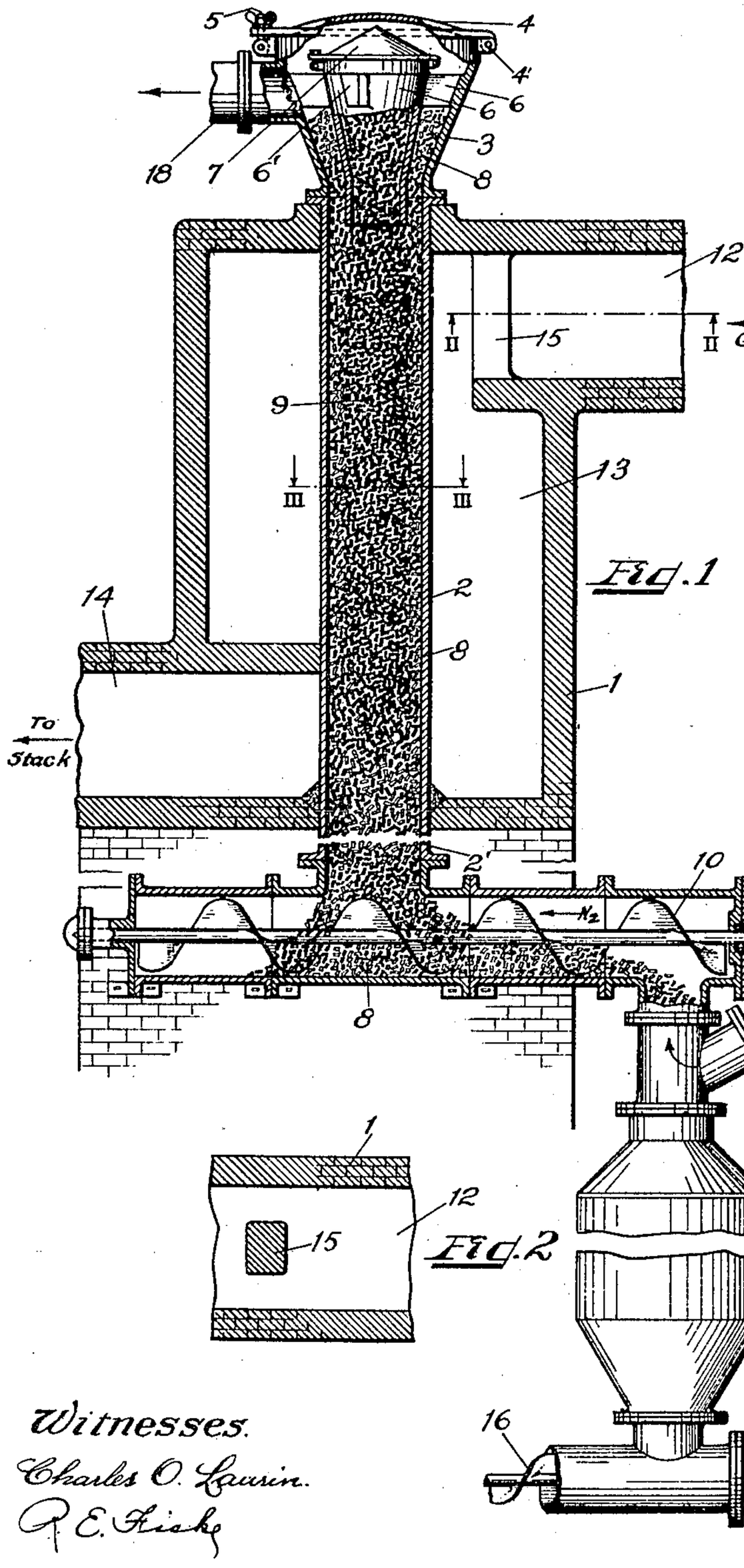

Fig. 1

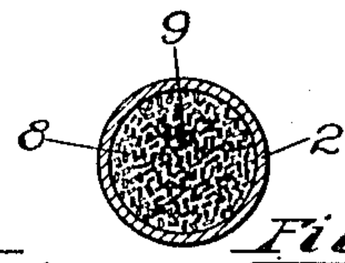

Fig. 3

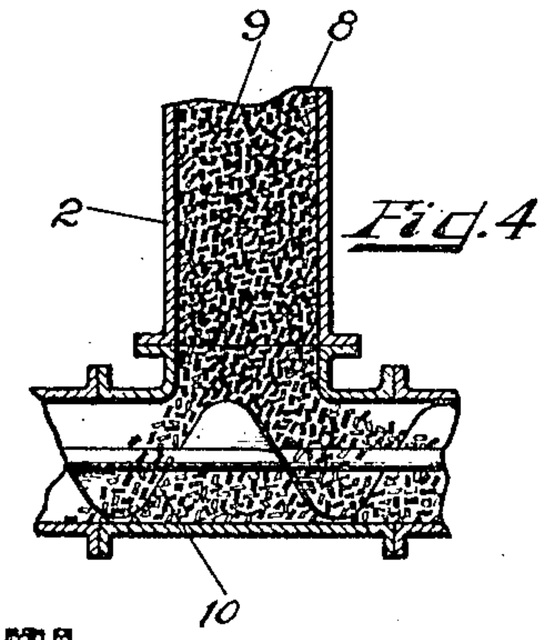

Fig. 4

Fig. 2

Witnesses.

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METHOD OF FIXING NITROGEN.

1,298,363. Specification of Letters Patent. Patented Mar. 25, 1919.

Application filed April 15, 1916. Serial No. 91,446.

To all whom it may concern:

Be it known that I, FRANK D. LINDQUIST, a citizen of the United States, residing at New York, in the county of Bronx and State of New York, have invented certain new and useful Improvements in Methods of Fixing Nitrogen, of which the following is a specification.

This invention relates broadly to a method of conducting chemical reactions in a retort and, also, to means for facilitating such reactions; the retort, for example, being such as is used in the method of fixing nitrogen, described in the U. S. patent to John E. Bucher, No. 1,120,682, dated December 15, 1914. The present method, while obviously applicable to operations of a different character from that described in said patent, is primarily intended to overcome certain difficulties encountered in the working of said patented process upon a large scale. In its more limited aspect, therefore, the present invention is an improvement in processes of fixing nitrogen by the formation of alkali metal cyanid, or the like; but in view of its novelty and evident utility in various other connections, I do not desire to be limited to such processes except where in certain of the claims appended hereto, such limitation is specifically indicated by the setting forth of steps of the present improvement in combination with the steps of known processes, whereby to favor these latter.

In the accompanying drawing which forms a part hereof and in which like reference characters designate like parts in the respective views, I have illustrated one form of apparatus in which my said process may be effectuated. The apparatus shown is given merely by way of exemplification, however, as I am aware of various modifications which may be made therein and in the process as hereinafter described.

Referring to the drawing:

Figure 1 is a vertical section of a furnace of the substantially continuous feed type.

Fig. 2 is a detail section taken on line II—II of Fig. 1.

Fig. 3 is a detail section taken on line III—III of Fig. 1; and

Fig. 4 is a fragmentary detail section showing the delivery of what are hereinafter termed, rich or core briquets,—to the screw conveyer.

In said patented process, free nitrogen is fixed by treating with nitrogen a heated mass of briquets preferably consisting of finely divided iron, or equivalent catalyzer; powdered carbon, *e. g.*, graphite or coke, etc.; and a binder which also supplies the base of a cyanogen compound to be formed, *e. g.*, sodium carbonate.

These briquets are caused by gravity to descend through a preferably vertical retort, or in some equivalent manner, relative movement is established between the receptacle or retort and the mass being treated while the nitrogen is preferably supplied either substantially pure; or mixed with carbon monoxid, as, for example, in producer gas.

By reason of their composition, the briquets become plastic when heated and while this has its advantages, as described in said patent to Bucher, it also has certain attendant disadvantages, which become more pronounced as the temperature is raised and as the height of the briquet column in the retort is increased. When overplastic, as when overheated, said briquets tend to adhere to the walls of the retort, while as the column is extended in height, pressure upon the lower briquets is increased, which tends to deform them and close the interstices therebetween through which the current of nitrogen gains access to the catalytic solution surface provided by the iron or its equivalent, within the briquets.

Electrical internal heating of the briquets as per the process of said John E. Bucher, disclosed in U. S. Patent No. 1,174,667, dated March 7, 1916, favors an equable distribution of heat; but the electric current is not cheaply available in many localities and it is, hence, frequently to be preferred to heat by gas or oil combustion, or the like; while the present process may be used to advantage in almost any case and regardless of the source of heat. In the absence of my method, particularly where external heating is used as shown in the accompanying drawing, there is a marked tendency for the retort to overheat in spots and, as a result,— after even sometimes only a few days' use,—

to burn out; necessitating stopping the process and replacing the retort or pipe with a new one—both of these operations being wasteful and more or less costly.

This briquet mass, as described in said patents, while heat conductive,—is not a specially good conductor of heat, and it is by reason of this, very largely, I believe, that the retorts are thus overheated in places; the heat not passing into and through the reaction mass quickly enough. When the briquets become over plastic and adhere to the retort walls, so that less highly heated briquets are not free to flow directly into contact with parts of said walls, this tendency to overheat becomes more apparent.

Now, in order to obtain the best results in the reaction, the content of, for example, sodium carbonate or soda ash in said briquets should be quite high; the relative proportions of the iron, carbon and soda ash (or as I shall hereinafter briefly term the latter—ash), being about 2:2:1; but I have discovered that if briquets of but, for example, six parts by weight of iron, to twelve of carbon and two of soda ash, be used, such briquets do not become over plastic nearly so readily as do those in which a high content of the fusible binder is used; since all of this binder does not fuse at once, if the process is conducted with due regard to temperature, and the low carbonate content briquets are less soggy or, in other words less charged with liquid carbonate, although they are not capable of yielding as high a percentage of cyanid in the reaction; and are hence softer when chilled.

When using the 2:2:1 briquets, considerable of the choking or sticking in a downwardly moving or movable column of the same, occurs at the top and also at the bottom of the retort. At the top the sticking is due to excessive fluidifying and to the distillation and recondensation of alkali and cyanid, while the sticking at the bottom seems to be due to the hardness of the cylindrical mass, resulting from the pureness of the cyanid more than from the cyanid content.

Taking advantage of these discoveries, I prefer to so conduct the movement of the briquet mass with respect to the retort, as to provide and maintain an annular wall of low carbonate content briquets next to the retort walls to protect the latter from the more plastic high carbonate content briquets which are disposed, and which preferably move along, the axis of said retort.

Thus, in the center of the retort there is, in the preferred embodiment of my process, a downwardly moving column of briquets rich in the material which supplies the base of the cyanid or its equivalent, while around this is a substantially concentric column of protective briquets, which moves down with the core and shields the retort walls from the latter.

These relatively impoverished protective briquets are further, more absorbent of the carbonate or its equivalent, and hence if the briquets in the core become too plastic, especially in the zone where condensation of the volatilized carbonates and even cyanid, occurs, and too much liquid is hence present therein, which tends to flood the catalytic solution surfaces in their pores,—such excess liquid, at least in the outer layer of briquets in the core, is soaked up or otherwise absorbed by the protective column, which favors the process both physically and chemically. Again, since the protective briquets are less plastic than normal, the interstices therebetween are better maintained than in the core; with the advantage that the nitrogen supplying gas current, passes upward, for example, quite freely through the annular column and finds its way therefrom laterally in toward substantially all parts of the core.

To further absorb any excess of carbonate in the pores of the rich briquets, particularly when the latter are over-rich in carbonate, or the furnace is too hot, or if for any other reason said briquets in the core are found to be too plastic when in use and too hard when chilled,—this is in large measure overcome by the addition of the low carbonate content briquets thereto, to the extent of from, for example, ten to twenty-five per cent.

This addition of absorptive briquets to the core takes place automatically to a certain extent in the charge as the lower part of the retort is approached, as indicated in Fig. 4 of the drawing; and it aids to make the charge more friable and hence less likely to cake or clog when cooled preparatory to removal from the retort by a conveyer or the like.

With a view to still further increase the longevity of the retorts, I have used briquets for the protective wall or screen, in which not only was the content of carbonate, or the equivalent thereof, materially reduced; but, further, the carbon or coke content was cut down while that of the iron was increased. Such briquets would have, for example, relative proportions of—Fe 10–12: C 8–6: ash 2.

The result of this latter change is to make such briquets still less reactive but, to compensate, far more heat conductive; resulting in a very prompt transfer of heat from the retort walls into the body of the charge. This provision of the protective briquets, with an excessive metallic content, or in other words the metallizing of the loose bodies which form the protective wall, is however, in so far as the application of my

invention to the formation of cyanid is concerned, not without its attendant disadvantages, such as the consequent loss in efficiency in the reaction with respect to the charge, as a whole. Nevertheless, as it is available for use, it is herein referred to. A protective-wall briquet mixture of this latter character, which I have found to yield quite excellent results is one in which the carbon and iron are in substantially equal proportions, while the sodium carbonate or equivalent content is relatively low; as far example where the proportions are—Fe 9: C 9: ash 2. Herein, it will be noted that both the iron and carbon content have been increased at the expense of the ash.

While the protective wall or screen, of whatever nature, may be formed in the retort by pouring in the materials therefor and for the core, separately, by hand; it is obvious that such a procedure would be undesirably slow and otherwise objectionable. I have accordingly devised a simple means for effecting the desired arrangement of charge material, which is exemplified in the drawing.

Referring to the latter, the furnace wall 1 may be of brick-work or the like, and contains a pipe-like retort 2, which may be closed, substantially gas tight, by a cover 4, hinged at 4′ and fastened by a pivoted bolt 5. Within the hopper 3 is a second or core-briquet hopper 6, which may be provided with lateral lugs or supports 6′ to engage an inner surface of hopper 3 and center the smaller hopper within the latter. Hopper 6 is preferably also provided with a cover 7, preferably cone shaped to aid in directing the protective or screen forming briquets 8 into the space provided between the walls of the inner and outer hoppers; whence said protective briquets,—which may, for example, be those of low carbonate content, above described,—are fed down into the retort around the rich or core briquets 9 which are loaded into and pass out from the hopper 6.

To start the operation, a simple way of charging the retort is to load it from bottom to top with protective or low carbonate content briquets 8, assuming of course that it be desired to form cyanid from the carbonate. The screw conveyer 10 is then started, whereupon the briquets 8 move downwardly through the retort and thence through said conveyer to the receptacle 11. While this settling action is occurring in the retort, briquets 9, rich in carbonate, are loaded into the hopper 6, and pass thence into the retort along with the briquets 8, emerging from hopper 3; the briquets 8 in the retort laterally supporting the briquets 9 in the latter and thus forming the core and the protective wall or screen which separates said core from the walls of the retort.

Fig. 1 shows the retort with the briquet core traveling down to but not vet in contact with the conveyer screw. Fig. 4, however, shows the core, shortly thereafter, passing into the conveyer.

Gas from a gas producer is led in through passage 12, passing thence into the space 13 in the furnace, in which said gas is burned; the combustion products passing out through the conduit or flue 14, to the stack. To protect the retort from the direct impingement of the blast emerging from the passage 12, a column-like screen 15 of fire brick or the like may be provided.

The treated briquets, both 8 and 9, pass together into the receptacle 11, from whence they may be removed bv a conveyer 16 or the like, preparatory to lixiviation or other treatment for the recovery of the cyanid therefrom.

The nitrogen current is supplied through a pipe 17, to the conveyer and passes through the latter to the retort up which it flows through the interstices between the briquets, into the hopper 3 and thence out through a pipe 18.

The retort is preferably exposed to the air, as at 2′, for a sufficient distance to partially chill the briquets; while the incoming nitrogen also tends to cool said briquets and in turn to become preheated thereby.

As described in the said patents to John E. Bucher, the nitrogen fixing reaction in the heat zone of the retort, preferably involves the formation of cyanid, or in certain cases, depending for example upon the supply of carbon,—cyanamid, etc.,—by the reaction of the alkali metal, *e. g.*, sodium, or its equivalent, upon the carbon contained in the catalytic solution surface afforded by the finely divided iron, nickel, cobalt or the like, in the presence of nitrogen; the preferred reaction temperatures depending upon the ingredients of the charge,—mixtures of for example, sodium and potassium carbonates permitting lower working temperatures. In the preferred nitrogen fixing operation, however, it is desirable that the temperature should never exceed the eutectic point of the carbon containing catalyzer; so that in practice said temperature may range from for example, 800° C. to 1100° C. and when using soda ash, coke and iron, it is preferably held around 1000° C. The temperature limits given are, it will be understood, merely by way of exemplification, as they may be varied in accordance with the charge to be treated.

The base supplying substance, which is preferably an alkaline compound, is usually, —and especially when in the solid phase—a heat insulator and hence in the nitrogen fixing operation as practised prior to my invention, there was, at times, not sufficient opportunity for the heat to pass away from an overheated portion of the wall of the re-

tort, into the charge. Where, however, the briquets, as used in the auxiliary or screening charge, or elsewhere, as described, are relatively poor in alkali or its equivalent, not only is the ratio of conductive metal, *i. e.*, the metallic catalyzer, increased with respect to the whole mixture per unit of volume,—say per cubic inch,—but, further, the thickness of the insulating layers of the liquefiable salt, *e. g.*, sodium carbonate, are decreased; permitting of better initial contact of the iron and carbon particles and especially of the iron, and resulting in a marked improvement in heat conductivity.

From practically every view point therefore, is there an advantage in using, what I have termed in practice, impoverished briquets, as a protective layer around a core of highly active and rich briquets in which latter the bulk of the cyanid is produced; although the protective briquets nevertheless participate in the reaction and yield cyanid.

To avoid circumlocution in certain of the appended claims, the term alkaline compound will be understood to comprehend not only such substances as sodium or potassium carbonate, hydrate, etc., but also equivalents thereof, such as barium carbonate or the like.

Having thus described my invention what I claim is:

1. The method of chemically reacting upon plastic material in a retort, which comprises effecting relative movement between said retort and said material while screening the interior walls of said retort from said material by less plastic bodies which are loosely movable along with said material, to prevent adhesion of said material to said walls, heating said plastic material, and reacting thereon while heated with a fluid reagent.

2. The method of chemically reacting upon plastic material in a retort, which comprises effecting relative movement between said retort and said material in the direction of the axis of said retort while screening the interior walls of said retort from said material by less plastic and more heat conductive loose material, to prevent adhesion of said plastic material to said walls, effecting a corresponding relative movement between said retort and said less plastic material, heating said plastic material, and reacting thereon while heated with a gaseous reagent.

3. The method of chemically reacting upon briqueted material which includes as a constituent thereof a chemically reactive substance which tends to fluidify and to render said material increasingly plastic, as its temperature is raised within determined limits,—which comprises at least partly surrounding said briqueted material with bodies capable of absorbing the excess of said substance which may exude from the briqueted material, to aid in reducing its plasticity and in maintaining the interstices thereof open, subjecting said briqueted material to heat, and passing a current of a gaseous reagent through said interstices, to react on said substance.

4. The method of chemically reacting upon briqueted material which includes as a constituent thereof a chemically reactive substance which tends to fluidify and to render said material plastic, when hot,—which comprises mixing with the briquets of said material, others of like nature, but containing a lower content of said substance, heating said mixed briquets and reacting thereon with a gaseous reagent.

5. The method of chemically reacting upon briqueted material which includes as constituents thereof chemically reactive substances one of which tends to fluidify and to render said material plastic, when hot,—which comprises establishing a column of said briquets of said material, surrounded in part at least by a column of briquets of like nature but containing a lower content of said fluidifying substance, causing said briquet columns to descend together through a heat zone, and reacting upon said substances, while hot, with a gaseous reagent.

6. The method of chemically reacting upon briqueted material which includes as constituents thereof a catalyzer and chemically reactive substances, one of which tends to fluidify and to render said material plastic at the temperature of the reaction,—which comprises establishing a column of briquets of said material, surrounded in part at least by a column of briquets of like nature but containing a lower content of said fluidifying substance, causing said briquet columns to descend together through a heat zone, and reacting with a gaseous reagent upon said substance, while hot, and by means of said catalyzer.

7. The method of fixing nitrogen which comprises establishing a column of briquets which include as constituents thereof carbon, a catalyzer for rendering said carbon reactive, and a substance which supplies the base of a cyanogen compound to be formed and which tends to increase the plasticity of said briquets as the reaction temperature is approached, surrounding said column, in part at least, with a retort-protecting column of briquets of a like nature but having a lower content of said base supplying substance, causing said briquet columns to descend together into a zone heated to said reaction temperature, and reacting with free nitrogen upon the briquets in said first column, at least,—to form said cyanogen compound.

8. The method of fixing nitrogen which comprises placing in contact two species of briquets, one of said species including as

constituents thereof, carbon, a solvent for said carbon in finely divided condition, to render said carbon reactive, and a substance which supplies the base of a cyanogen compound to be formed, the other of said species including similar constituents but with a reduced content of said base supplying substance, heating said briquets of both species, while in contact with each other, to a reaction temperature, and reacting upon said briquets with free nitrogen while they are in motion through the heat zone of a retort to form said cyanogen compound, said briquets having the reduced content of base supplying substance, beneficially co-acting with those having the higher content of said substance, by absorbing the fused excess of said substance which may exude from the briquets first above mentioned, when in said zone, whereby to aid in preventing choking of said retort.

9. The method of fixing nitrogen which comprises placing in eontact two species of briquets, one of said species including as constituents thereof, carbon, iron in finely divided condition, and an alkaline substance which supplies the base of a cyanogen compound to be formed, the other of said species including similar constituents but with a reduced content of said alkaline substance, heating said briquets of both species, while in contact with each other, to a reaction temperature sufficient to at least partially fluidify said alkaline substance, the briquets having the lower content of said substance acting, in part, to absorb excess fluid matter present, and reacting upon briquets of both species with free nitrogen, while said briquets are in movement through a retort to form said cyanogen compound, said absorbently acting briquets co-acting with those having the higher content of said alkaline substance to substantially prevent choking of said retort by excessive fluidification of said substance.

10. The method of fixing nitrogen which comprises effecting a cyanogen compound forming reaction in the heat zone of a retort, by passing free nitrogen thereinto while substantially simultaneously delivering to said heat zone concentric columns of briquets, the briquets forming the inner of said columns being, for the most part, relatively rich in a liquefiable material which supplies the base of said cyanogen compound, while the briquets of the outer of said columns are relatively poor in said material, the briquets of both columns further containing carbon in reactive form to participate in said reaction.

11. The method of fixing nitrogen which comprises effecting a cyanogen compound forming reaction in a retort, by heating the walls of said retort, passing free nitrogen into contact with a charge in said retort comprising two portions, one of said portions being highly chemically reactive with said nitrogen and containing carbon, a metallic and heat conductive solvent for said carbon in finely divided form, and a salt which supplies the base of a cyanogen compound to be formed, said salt when in the solid phase being a relatively poor conductor of heat, the other of said portions of said charge having a relatively smaller content of said salt per unit of volume and separating the first mentioned portion from the walls of said retort.

12. The method of fixing nitrogen in a retort to form a cyanogen compound,—which comprises forming in said retort a charge containing carbon, a catalyzer and a substance which yields the base of said cyanogen compound, and which charge is materially less reactive in the portions thereof which contact with the walls of said retort, whereby to form a lower percentage of said compound in said portions, heating said charge to the reaction temperature, treating it with free nitrogen, chilling the reactive mass with its unequally disposed content of said cyanogen compound, effecting a downward movement of said charge through said retort, and breaking up the caked charge preparatory to the separation of said compound therefrom.

13. The method of effecting a chemical reaction in a charge in course of movement through a retort, to prevent adherence of said charge to the walls of said retort, which comprises, forming the materials of the charge into briquets, delivering said briquets to said retort together with an auxiliary charge of retort shielding material, feeding said briquets through the retort together with said auxiliary charge and with the latter interposed between the briquets aforesaid and the walls of said retort with which said briquets would otherwise contact, and effecting the desired reaction through the intermediacy of a gaseous reagent and heat sufficient to render said briquets plastic while leaving open interstices therebetween to permit of the passage of said gaseous reagent.

14. The method of effecting a chemical reaction in a charge in course of movement through a retort, to prevent adherence of said charge to the walls of said retort, which comprises, forming the materials of the charge into briquets, delivering said briquets to said retort together with an auxiliary charge of briqueted retort shielding material, feeding said briquets through the retort together with said auxiliary charge and with the latter interposed between the briquets aforesaid and the walls of said retort with which said briquets would otherwise contact, and effecting the desired reaction through the intermediacy of a gaseous reagent and heat sufficient to render said briquets plastic

while leaving open interstices therebetween to permit of the passage of said gaseous reagent.

15. The method of effecting a chemical reaction in a charge in course of movement through a retort, to prevent adherence of said charge to the walls of said retort, which comprises, forming the materials of the charge into briquets which tend to become plastic when heated to the reaction temperature, at least one of said materials being liquefiable as said temperature is approached, delivering said briquets to said retort together with an auxiliary charge of retort shielding material which is capable of absorbing excess liquid which may exude from the briquets in contact therewith, feeding said briquets through the retort together with said auxiliary charge and with the latter interposed between the briquets aforesaid and the walls of said retort with which said briquets would otherwise contact, and effecting the desired reaction through the intermediacy of a gaseous reagent and heat sufficient to render said briquets plastic while leaving open the interstices therebetween to permit of the passage of said gaseous reagent.

16. The method of effecting by heat a chemical reaction in a briqueted charge which comprises as a constituent thereof a substance which tends to liquefy as the reaction temperature is approached and which method includes contacting with the briqueted charge aforesaid auxiliary briquets including material which also participates in the reaction, but which auxiliary briquets are absorptive of said liquefiable subtance under the conditions of and during said reaction.

In testimony whereof I have affixed my signature, in the presence of two witnesses.

FRANK D. LINDQUIST.

Witnesses:

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