PATENT SPECIFICATION

646,557

Date of Application and filing Complete Specification: June 30, 1948.

No. 17511/48.

Application made in United States of America on Sept. 19, 1947.

Complete Specification Published Nov. 22, 1950.

3491

Index at acceptance:—Classes 1(i), F3a1a; and 55(i), B(4f: 11: 13), K(1: 5b).

COMPLETE SPECIFICATION

Improvements in or relating to Fluidised Solid Systems

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the treatment of subdivided solids. More particularly, the invention pertains to a process of contacting subdivided solids with upflowing gases in an enlarged contacting chamber at a controlled gas flow rate adapted to maintain the subdivided solids in the form of a highly turbulent ebullient mass resembling a boiling liquid.

Prior to the present invention, subdivided solids have been contacted with gases by passing the latter upwardly through an enlarged contacting zone containing a body of the subdivided solids and controlling the superficial gas velocity in such a manner as to maintain the solids in a quasi-liquid or fluidized state within the contacting zone. This quasi-liquid fluidized state involves a rapid circulation of the subdivided solids in all conceivable directions throughout the fluidized bed.

The advantages of processes using this type of fluidized solids are great in number and importance. For example, the contact between gases and solids, as well as between individual solid particles, is considerably improved as compared with other types of operation. A substantially uniform temperature may be maintained throughout a fluidized bed of subdivided solids because of the rapid circulation and high turbulence of the solids within the bed which result in an extremely efficient transfer of heat from particle to particle and between different sections of the bed. For the same reasons heat may be added to, or extracted from a fluidized solids bed with the greatest of ease and speed.

Fluid operations of the character described above have been employed for many processes including reduction and oxidation reactions, polymerization processes, the carbonization or gasification of carbonaceous solids, such as coal or the like, and a large number of other exothermic and endothermic reactions. More specifically, successful use of the fluid solids technique has been made in various petroleum oil refining processes, such as catalytic cracking, reforming, hydrogenating and similar operations, as well as in the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen. However, while the application of subdivided solids in the form of fluidized beds has found extensive uses, there are certain inherent limitations in this technique which have prevented its adaptation in some fields and limited its efficiency in others.

One of the more serious limitations of the fluid solids technique results from the fact that proper fluidization is bound to a definite particle size or particle size distribution for any given superficial velocity or range of superficial velocity of the fluidizing gas. For example, some materials may be properly fluidized at a superficial gas velocity of, say, about 0.1 to 3 feet per second and a particle size distribution ranging from about 30 to 200 microns. Particles considerably larger than the size range indicated will tend to settle out of the fluidized bed and particles considerably smaller than the indicated range will be carried to and beyond the top of the bed by the fluidizing gas, thus, destroying the particle size distribution desirable for proper fluidization at the prevailing gas velocity. Neither the unduly large settled particles nor the unduly small entrained particles may derive the full benefit from the advantageous characteristics of the fluidized bed. This situation becomes particularly troublesome when it is desired to form fluidized solids beds of materials which are naturally occurring or artificially produced in the form of subdivided particles whose size spreads over a wide range.

For example, many types of waste coal are obtained in the course of conventional coal mining processes in the form of masses composed of particles varying in size from a few microns to as much as 5, 10 or more millimeters. When masses of this type are treated in fluid carbonization or gasification units with fluidizing gases or gasifying media, such as steam, carbon dioxide, oxygen-containing gases, or the like, the superficial velocity of the fluidizing gas is usually controlled at about 1.0 to 3 feet per second at which proper fluidization of the bulk of the coal particles having particle size distributions within the approximate range of from about $^1/_{10}$ to 5 millimeters may be accomplished. However, under these conditions coal particles having a particle size of substantially more than 5 millimeters, say, up to about 10 to 15 millimeters settle out of the fluidized bed and coal particles considerably smaller than $^1/_{10}$ of a millimeter, say, of about 10 to 150 microns are blown out of the fluidized bed by the fluidizing gas. In addition, when fluidization is continued over a substantial length of time, a tendency develops toward a separation of particles having sizes within the upper originally fluidizable brackets of, say, about 2 to 5 millimeters from particles having sizes within the lower originally fluidizable brackets of about $^1/_{10}$ to 1 millimeter. As a result, substantial proportions of the coal feed, which may amount to as much as 10—30%, are lost either completely or to the desired treatment at optimum conditions. In addition, the superficial gas velocity of the fluidizing gas must be continuously checked and readjusted in order to compensate for the continuous shift in particle size distribution.

Similar difficulties arise in various catalytic processes involving a significant change of catalyst particle size during the catalytic reaction. An outstanding example for such processes is the synthesis of hydrocarbons from carbon monoxide and hydrogen employing fluidized iron-type catalysts at temperatures of about 500°—700° F. and pressures of about 5—50 atmospheres. It has been found by experiment that iron-type synthesis catalysts at these conditions have a strong tendency to carbonize, that is to form catalyst deposits of free carbon or coke-like materials. In fluid operation, carbonization leads to a rapid disintegration of the catalyst resulting in an equally rapid expansion and the ultimate loss of the catalyst bed in the form of catalyst fines entrained in the gaseous reaction products. It has been suggested to alleviate these difficulties by continuously or intermittently feeding fresh or regenerated coarse catalyst to the reaction zone in order to establish a particle size distribution desirable for proper fluidization. However, the above mentioned tendency of the particles of different size to classify, is not avoided in this manner.

The present invention overcomes the aforementioned difficulties and affords various additional avantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the accompanying drawing.

It is the principal object of the present invention to provide improved means for maintaining proper fluidization conditions within a fluidized bed of subdivided solids having particle sizes spreading over a wide range.

A more specific object of the present invention is to provide means for maintaining a desirable particle size distribution within a fluidized bed of subdivided solids having particle sizes spread over a wide range.

Other and more specific objects and advantages of the invention will appear hereinafter.

In accordance with the present invention, these objects and advantages may be accomplished by classifying the subdivided solids into two or more fractions of different particle size ranges before feeding them to the fluidized bed and then feeding the fraction containing the largest size particles to the upper portion of the bed and the fraction containing the smallest size particles to the lower portion of the bed. By this means, the small particles tending to rise upwardly through the fluidized bed encounter an excess of coarse particles and the large particles tending to sink to the bottom of the fluidized bed encounter an excess of small particles in the respective directions of classification so as to establish the particle size distribution adequate for proper fluidization within the center as well as within the top and bottom portions of the fluidized mass. In this manner, classification of particles varying greatly in size within the fluidized bed as well as an undesired removal of small and large particles from the fluidized bed may be substantially reduced or completely eliminated.

More specifically, in process involving the continuous or intermittent feed to a fluidized solids bed, of a subdivided solids charge varying in particle size over a wide range, the charge, in accordance with the present invention, is divided into at least 2 fractions which differ greatly in average particle size. A fraction comprising predominantly particles of the lowest size ranges is fed to a bottom portion of the fluidized bed while a fraction comprising predominantly particles of the highest size ranges is fed to an upper portion of the fluidized bed. Fractions composed predominantly of particles of intermediate size or having substantially the composition of the unfractionated charge material may be fed to intermediate sections of the bed, if desired. This procedure is particularly suitable for the treatment of carbonaceous solids such as coal, lignite, peat, oil shale, tar sands, coke, oil coke, cellulosic materials including lignin, etc., which are obtained from natural or artificial sources or specifically prepared for the purpose in the form of subdivided masses, the particle size of which spreads over wide ranges.

When applied to processes involving a change of particle size during the treatment of solids in a fluidized bed, the objects of the invention may be accomplished by feeding the solid undergoing treatment either in a relatively small particle size to a lower portion of the fluid solids bed or in a relatively large particle size to an upper portion of the fluid solids bed depending on whether the change of particle size taking place with the bed is of the type of disintegration or enlargement. An example for this application of the invention is the catalytic synthesis of hydrocarbon from carbon monoxide and hydrogen over iron catalysts, mentioned above. When catalyst disintegration begins adversely to affect fluidization conditions, fresh or regenerated catalyst of a particle size, substantially larger than the fines formed by disintegration, is charged to the upper portions of the fluidized bed in proportions adequate to maintain a suitable particle size distribution throughout the bed.

It will be appreciated that the absolute and relative amounts of subdivided particles of relatively large and relatively small particle size to be supplied to fluidized solids beds in accordance with the invention will vary widely as a function mainly of the character of the solids involved, particularly their specific gravity, and the character and velocity of the gases used for fluidization and/or reaction. It may be stated, however, quite generally, that proper fluidization may be obtained when the proportion of solid particles fully entrainable in the fluidizing gas at the prevailing superficial gas velocity amounts to about 30% to 50% by weight of the fluidized bed, the proportion of particles having a strong settling tendency at the prevailing superficial gas velocity amounts to about 0% to 30% by weight of the fluidized bed, and the proportion of particles of intermediate size amounts to about 20% to 70% by weight of the fluidized bed. The supply of solids fractions of extermely large or extremely small particle size, in the manner described above, should be so controlled that the particle size distribution throughout the fluidized bed is maintained with these ranges.

Having set forth its objects and general nature, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawing which is a schematical illustration of a system suitable for carrying out a preferred embodiment of the invention.

Referring now in detail to the drawing, the system illustrated therein essentially comprises solids feeding equipment (1), (5), and a conventional fluid solids reactor (30), the functions and cooperation of which will be presently explained using the carbonization of subdivided coal as an example. However, it should be understood that other subdivided solids may be treated in a substantially analogous manner.

In operation, feed hopper (1) contains a coal charge which may be subdivided waste coal having a particle size of less than 3/8 of an inch. Large amounts of coal waste of the character are obtained in the conventional processing of coal at the mines. These coal wastes may have a particle size distribution about as follows:—

3/8" to 4 mesh per linear inch	25%
4 to 14 ,, ,, ,, ,,	45%
14 to 48 ,, ,, ,, ,,	19%
48 to 100 ,, ,, ,, ,,	4%
Minus 100 ,, ,, ,, ,,	7%

A portion of about 20% to 60% of the total coal feed desired to be supplied to reactor (30) may be withdrawn from feed hopper (1) and passed by any suitable conveying means such as a screw conveyor, lock hopper, or a standpipe (3), provided with aeration taps (7) and slide valve (9) to reactor 30. If desired, the coal in hopper (1) may be preheated with gases from the process supplied through line (11), to temperatures of about 200° to 600° F. which lie below the carbonization, plastic and ignition temperatures of the coal. If no coal preheating is desired, a fluidizing gas, such as steam, flue gas, air, etc., may be introduced through line (11) to facilitate the flow of the coal particles.

A similar fluidizing gas may be injected, in small amounts through taps (7) into standpipe (3) to maintain the fluid character of the solids column therein.

The fluidized coal is forced under the pseudo-hydrostatic pressure of standpipe (3), at a rate controlled by slide valve (9), into reaction (30 wherein it forms above distributing grid (13) a dense turbulent mass of coal particles fludized by the gaseous or vaporous carbonization products and a gas injected through line (15) below grid (13). Superficial gas velocites of about 0.3 to 4 feet per second within reactor (30) are generally suitable for this purpose. The carbonization temperature in reactor (30) may be selected exclusively with a view to the type and quantity of gaseous or vaporous carbonization products desired and may vary within the wide limits of about 800° to 2000° F. The lower temperatures within said range are conductive to the formation of relatively large quantities of low temperature tar and light oils while at the higher temperatures more coal gas and hydrogenation products are formed.

The heat required to maintain the desired carbonization temperature m: supplied in any conventional manner, for instance indirectly or as sensible heat of the gas introduced through line (15), or by an exothermic reaction within reactor (30), such as a limited combustion of coal constituents, or by the circulation of externally heated char. Superheated steam, hot flue or product gases, or the like are preferred heating gases in the case of low temperature carbonization. When the carbonization is conducted above temperatures of about 1000° F. air and/or oxygen preheated to about 600° to 800° F. may be used in amounts sufficient to generate, by combustion, the heat required for carbonization. About 0.3 to 1.0 pounds of air per pound of coal is normally adequate for this purpose, the exact porportion depending on the character of the coal, the degree of preheat and the temperature desired.

Gaseous or vaporous carbonization products are withdrawn overhead from level (L_{30}) and passed through a conventional gas-solids separator (18) provided with a solids return line (20) leading, in accordance with invention, to a lower portion of the fluidized bed within reactor (30). In order to reduce entrainment of solid particles in the product gases and vapors to a desirable minimum, the top section of reactor (30) may be of enlarged cross-section as indicated at (32) so as to bring about a significant reduction in superficial gas velocity. However, entrainment of coal fines may not be completely avoided in this manner. A substantial proportion of the coal fines entrained in the gaseous or vaporous carbonization products are separated in separator (18) and returned through line (20) to the bottom portion of reactor (30) to aid in the maintenance of a proper particle size distribution in accordance with the invention. Separator (18) may also be arranged in series with some conventional cooling means outside reactor (30), if the high temperatures of reactor (30) make this appear more advisable. Vaporous and gaseous carbonization products, now substantially free of entrained coal particles, may be removed through line (22) and passed to a conventional product recovery system (not shown). Substantially "dry" coke may be withdrawn downwardly from carbonizer (30) through a withdrawal well (24) and line (26) for any desired use.

At the conditions of temperature and gas velocity specified above and when using a large diameter, relatively shallow fluidized bed, say having a depth equal to its diameter, or less, a coal particle size distribution suitable for proper fluidization within reactor (30) may, for example, be about as follows:—

	Weight %
1.5 to 5 millimeters	0.1 to 1
0.5 to 1.5 "	20 to 25
200 to 500 microns	50 to 60
100 to 200 "	5 to 15
50 to 100 "	5 to 10
<50 "	2 to 5

In conventional operation, the fluidized coal mass in reactor (30) will tend to classify the particles having a particle size of less than about 200 microns concentrating in the upper portion of the bed and the particles having a particle size larger than 1 millimeter concentrating in the lower portion of the bed depending on the gas velocity employed. This classification leads to serious fluidization troubles resulting in irregularities of the temperature throughout the bed and the different treating intensity within different sections of the bed. A considerable improvement is afforded by the recirculation of coal fines of less than about 200 microns size entrained in the product vapors and gases and separated in separator (18), to a lower portion of the fluidized bed through line (20). The amount of coal fines so recirculated may be about 100 to 10000 weight per cent. of the total coal fed to reactor (30), depending on the fines concentration and feed rate of the original coal feed.

The higher rates of solids flow through the cyclone and down to the bottom of the bed may be facilitated by extending the inlet to the cyclone, which may be a pipe (19), downwardly to within a short distance, say about 2 to 6 feet, from the top of the bed. The reasons for this effect are twofold. It is known that the efficiency of cyclone separators increases to a certain extent as the solids load of the cyclone inreases from very low levels. In addition, it has been found that the concentration of solids entrainment per cubic foot of gas decreases as the gas moves away from the upper level of the fluidized bed. For example, when using a solid material having a density of about 1.0 at a superficial linear gas velocity of about 1.4 feet per second, the solids entrainment of the gas at a distance of 1 foot above the level may be about 0.1 pound per cubic foot while at 10 feet above the level it may drop to about 0.003 pound per cubic foot.

However, there may still remain a classification of relatively large and relatively small particles, which are not removed with the carbonization products or recycled to the lower portions of the fluidized bed through line (20). In order to eliminate fluidization troubles which may result from this further classification, the invention provides for a separate feed of relatively coarse and relatively fine coal particles to the fluidized bed in opposite directions. For this purpose, a proportion of about 40% to 80% of the total coal charge to be supplied to reactor (30) is withdrawn from feed hopper (1) and passed through line (4) to a conventional classification means, such as an elutriation system (5) wherein the coal may be classified into two or more fractions of different avearge particle size. An elutriation gas may be supplied to the bottom of elutriator (5) through line (6). Other conventional classification means, such as suitable sieving means, may be used.

A coal fraction comprising predominantly particles having a particle size smaller than 200 microns may be taken overhead from elutriator (5) and passed through line (8) to a bottom portion of reactor (30), if desired via fluidizing gas feed line (15) and grid (13). In continuous operation, this fraction of coal particles may amount to about 5% to 50% by weight of the coal supplied to elutriator (5).

Another coal fraction comprising predominantly coal particles larger than 0.5 millimeters may be withdrawn from the bottom of elutriator (5) and passed through line (10) to the top of reactor (30). This fraction may amount to about 50% to 95% by weight of the coal charged to elutriator (5). If desired, a third fraction of intermediate particle size may be withdrawn from elutriator (5) through line (12) to be united with the coal charged through line (8).

The product drawn off through line (26) may be classified in a suitable conventional device such as an elutriator or sieve (40) and at least a portion of the fines returned through lines (42) and (8) to the fluid bed, thereby keeping the concentration of the fines in the reactor at a high level. This high concentration of fines greatly improves the fluidity of the bed. The retention of the fines within the system in this manner causes the particle size distribution within the reactor to have little resemblance to the particle size distribution of the feed. In certain cases it may also be desirable to return at least a portion of the coarse solid product separated in classifier (40), through lines (44) and (10) to reactor (30).

It will be readily appreciated from the above description of the drawing that the recirculation of coal fines and particularly the split feed of coal fractions of widely differing average particle size, in accordance with the present invention, counteract efficiently the natural classification tendencies of the fluidized bed permit the maintenance of proper fluidization conditions without careful control and readjustment of the superficial gas velocity.

While reactor (30) and its operation have been described with reference to the carbonization of coal, it will be understood that other carbonizable solids, such as oil shale or cellulosic materials, may be treated substantially as described. The system may also be used for the gasification of carbonaceous solids with gasifying media, such as steam and/or carbon dioxide, by supplying the gasifying medium through line (15) and maintaining a gasification temperature of, say, about 1500° to 2000° F. within reactor (30.) The invention, as described with reference to the drawing, may be applied to other processes involving the use of fluidized solids, such as catalytic reactions, in a generally analogous manner, catalyst or other solids used in the process being supplied in suitable particle size ranges through lines (8), (9), and/or (10) as required by the classification tendency of the solids mass maintained within reactor (30).

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within the scope of the invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for treating finely divided solids with gases by maintaining the solids in the form of a turbulent fluidized bed wherein the solids are classified into two or more fractions of different particle size ranges before being fed to the fluidized bed, the fraction containing the largest size particles being fed to the upper portion of the bed and the fraction containing the smallest size particles being fed to the lower portion of the bed.

2. A process as claimed in Claim 1, wherein there are fractions of intermediate size which are fed to intermediate points of the bed.

3. A process as claimed in Claim 1 or Claim 2, wherein the classified fractions fed to the bed are provided at least in part by withdrawing and classifying a mixed fraction from the bed.

4. A process according to any of the preceding claims, wherein a solids fraction of relatively small particle size is separated from the gases leaving the top of the fluidized bed, and fed to the lower portion of said bed.

5. A process according to any of the preceding claims, wherein the treatment is carbonization or gasification of carbonaceous solids, or a catalytic reaction such as the synthesis of hydrocarbons from CO and H_2 in presence of a fluidized iron-type catalyst.

Dated this 29th day of June, 1948.

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