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(54) **Process for upgrading low-grade fuel fines.**

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Process for upgrading low-grade fuel fines

The invention relates to a process for dewatering and decarboxylating water- and carboxyl groups-containing fines of low grade fuel, in which process the fines are shaped into coherent bodies and the coherent bodies are consecutively heated to a temperature of 150—375°C in the presence of the water originally present in the said fines, at a pressure which is higher than the vapour pressure of the water and the selected temperature and the heated bodies are separated from the water.

Solid fuel which contains more than 10% by weight, and more particularly more than 40% by weight of bound and/or unbound water (herein referred to as low-grade fuel) can suitably be subjected to thermal upgrading. This fuel is designated as low-grade because its weak or crumbly consistency gives it poor handleability and because the calorific value lies too far below that of normally used fuels such as hard coal or oil. Examples of such fuel are young coal (such as brown coal), peat, lignite, wood and carbon-containing waste (such as compost).

Young coal, for example, generally contains 40—70% by weight of water and peat contains 80—90% by weight. The water in said fuels occurs in a number of forms, namely as inherent or absorbed water, as a constituent in compound organic substances, as chemically bound water (for example water of crystallization) and as potentially present water, i.e. water that forms from chemically bound oxygen and hydrogen during upgrading of the fuel.

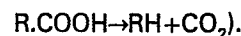
It is desirable to remove these types of water down to desired percentages and to separate them from the fuel, so as to raise the calorific value and to improve handleability. As a result of such treatment the fuel becomes less expensive to transport and its combustion properties are improved.

There are various ways of upgrading low-grade fuel, the most commonly used route being thermal upgrading. Examples of the various possibilities of achieving thermal upgrading include:

- The fuel can be dried (heating at atmospheric pressure at a temperature below 150°C, as a result of which the inherent water and the absorbed water is driven off and evaporated. This requires a relatively large amount of energy (heat of evaporation) and in most cases only produces a partial reduction of the water content of the fuel. In general, the water driven off will in the course of time be reabsorbed.
- The fuel can be subjected to such heating (suitably between 150 and 250°C) that a thermal upgrading takes place as a result of which chemically bound water is eliminated from the fuel and cannot be reabsorbed. This

thermal upgrading can be carried out under conditions in which the water to be removed evaporates (and this requires additional energy, in the form of heat of evaporation) or at such a pressure that the water remains liquid (so that a physical separation between a solid and a liquid phase becomes necessary).

- The fuel can be subjected to a treatment under more drastic conditions, under which organic substances such as acids, salts and esters are partly decomposed, such as by decarboxylation (separation of carbon dioxide). An organic substance (for example R.COOH) comprising an oxygen-containing group (for example a carboxyl group, i.e. COOH) can split off carbon dioxide while the hydrogen is becoming attached to the remaining carbon chain (for example:



This decomposition occurs at higher temperatures—in particular above 350°C—and is accompanied by a drastic structural change of the fuel. Decarboxylation, for example, causes fuel to become hydrophobic instead of hydrophilic, since the decarboxylation causes the polar oxygen-containing groups, which gave the fuel its hydrophilic character, to disappear.

An advantage of thermal upgrading in the presence of water (at a pressure higher than the water vapour pressure at the selected temperature) is that the formation of gas from the fuel (largely as a result of decarboxylation) already begins at 300°C, whereas under dry conditions (at a pressure lower than the water vapour pressure at the selected temperature) the formation of gas is fairly insignificant below 400°C.

In the past a number of proposals have been made envisaging an economically acceptable upgrading, and the Applicant has also proposed a process of the type mentioned in the preamble (see U.K. patent specification No. 1,471,949). In said process, which is of the slurry type, finely divided fuel is mixed with water into a pumpable slurry, and the slurry is heated at high pressure until upgrading occurs. Besides a number of advantages, said slurry process has the inherent drawback that the added quantity of water also has to be heated. Nevertheless, it has attracted wide interest from various quarters.

The present invention does not relate to the above-mentioned slurry process, but to a fixed-bed process which has been known for some time and in which the fuel, not in a pumpable slurry but essentially without additional water, is heated in a fixed bed under such conditions

that the driven-off water remains liquid. In this description, fixed bed-type processes include all processes in which a charge of solid fuel or a continuous stream of solid fuel is heated without the charge first having been converted into a pumpable slurry in water. Such processes may, for example, make use of a fixed bed, a moving bed or a fluidized bed.

An example of such a fixed-bed process is the Fleissner process, which essentially comprises the heating in a vessel of a quantity of fuel (see US patent specification No. 1,632,829 and Industrial and Engineering Chemistry, December 1930 (Vol. 22, No. 12, pp. 1347—1360)). The fuel is present in a fixed bed and is heated by passing saturated steam into the vessel, which steam partially condenses. The condensed steam and the water originating from the fuel percolate downwards through the fixed bed and are drained off at the bottom of the vessel. Said process is used on a considerable scale in practice. The invention relates to such a process, in which on the one hand liquid water is indeed present during the heating, but on the other hand, there is so little water that the charge to be heated is in the solid state.

In the "fixed-bed" processes of the Fleissner type, the fuel in the reactor in which the heating takes place must have as uniform as possible a particle size, which size is situated between certain limits. The upper limit is imposed by the requirement that the through-heat time must be sufficiently short, i.e. that the interior of the largest particles must be capable of being heated to the required temperature sufficiently fast to arrive at an economic process. The lower limit is imposed by the requirement that the smallest particles must not be washed out of the bed and by the fact that the proportion of inherent moisture increases with the percentage of small fuel particles (drainage from the bed deteriorates).

Certain fuels become available with too small a particle size, and they are not suitable for the Fleissner process. Other fuels contain a fraction, often considerable, with too large particles. Reduction (for example by grinding or crushing) always yields, in addition to a usable fraction, a fraction fines with too small particles which, hitherto, could not be utilized in the fixed bed-type process. It will be clear that these fines represent a loss, since they collect a considerably lower return than upgraded fuel.

A process of the type described in the beginning is mentioned in German patent specification 899,493. According to this known process peat is brought into forms and these forms are pressed to bodies. These bodies are brought into an autoclave in which they are heated to a temperature of 150—180°C. After heating, water is pressed off and the water remaining in the bodies is evaporated at sub-atmospheric pressure at a temperature above 100°C.

It is an object of the present invention to provide a process which yields dewatered and decarboxylated bodies of reduced size and having a very low water content and a very high strength.

Accordingly, the invention provides a process for upgrading fines of low grade fuel, in which process the fines are shaped into coherent bodies and the coherent bodies are consecutively heated to a temperature of 150—375°C in the presence of the water originally present in the said fines, at a pressure which is higher than the vapour pressure of the water at the selected temperature and the heated bodies are separated from the water, characterized in that the said fines have a particle size of less than 25 mm and that the said heated and separated bodies are kept at a temperature and pressure at which the water vaporizes and decarboxylation takes place, thus producing coherent bodies having a reduced content of water and of carboxyl groups.

The decarboxylated bodies obtained by the process according to the invention have a very low water content, a very high calorific value and, surprisingly, are of a considerably reduced size, have a high strength and have good dusting properties.

A very important advantage of the process according to the invention is that the separation of the upgraded fuel and the driven-off water is much simpler and cheaper, draining off being sufficient, and that the upgraded end product is obtained in convenient form and does not dust.

It has been found that the coherent bodies do not lose their initial strength during thermal upgrading and mostly even become considerably stronger. A possible explanation of this is that during the upgrading treatment some tar is formed, which might act as the binder. Of course, the bodies must possess a certain minimum "green" strength before thermal upgrading, in order that they can be passed without disintegrating to the apparatus in which they are subjected to the thermal upgrading treatment.

In practice, it has been found that the requirement of a certain minimum "green" strength can be met in a number of ways. The bodies may, for example, be obtained by extruding, by briquetting, by pressing (tablet making) and by compaction (ramming).

A very attractive method in which the shaping of the bodies can be combined with their supply to the space in which the upgrading treatment takes place, consists of supplying the fines to the upgrading space via an extrusion press or via a solids pump for overcoming high pressure.

The pressure which is applied for the purpose of shaping the bodies depends inter alia on the type of fuel, but it is usually between 0.1 and 25 kN/cm² and preferably between 1 and 15 kN/cm².

Although the application of a higher pressure will be correspondingly more expensive, it often yields the advantage of a greater strength and possibly partial dewatering when the bodies are shaped.

According to the invention, it is preferred to shape bodies having a largest dimension between 10 and 150 mm. On the one hand, such bodies give a sufficiently rapid upgrading and, on the other, they present no problem when separating the formed water from the bodies. It is preferred that during the heating of the bodies no fines are present having a particle size of less than 5 mm and preferably less than 10 mm.

In this connection it is noted that it will be clear that in all cases the bodies will be larger than the particles of which they are composed, so that the lower limit of 10 mm only applies to bodies made of particles having a smaller size.

If the "green" strength of the bodies is not satisfactory, according to the invention a binder can be added to the fines before the bodies are shaped. Examples of such binders are bitumen, residual petroleum fractions, and coal tar.

A principle known per se is advantageously applied to the present invention, namely that after the heating of the bodies and removal of the liquid water, the pressure in the upgrading space is reduced and/or the temperature is raised so that steam forms, thereby promoting the decarboxylation and facilitating the separation of fuel and water. During this second heating period under the changed conditions, the upgrading treatment is continued.

The invention will now be elucidated with reference to a specific example of a process according to the invention.

Example

A quantity of Victoria brown coal (an Australian brown coal having a water content of 53.9% by weight and a calorific value of 12.89 kJ (3078 cal/g)) was compacted at a pressure of 5.0 kN/cm² to form cushion-shaped tablets having a largest diameter of 11.4 mm.

A quantity of 533.8 g of tablets was heated at a temperature of 250°C for 60 min. at a pressure of 45 bar; during heating the tablets remained in contact with the separating water, which remained liquid (the water vapour pressure at 250°C is approx. 40 bar). The formed water was subsequently drained off.

Next the tablets were heated for 60 min. at 360°C at a pressure of 40 bar, during which treatment all the present water and all the forming separating water was in the vapour state (the water vapour pressure at 360°C is approx. 190 bar).

During both treatments the tablets remained intact, but considerable, crimping occurred: after the treatment the tablets were reduced to only 37% of their original volumes (the largest tablet dimension was now 8.2 mm).

Upgrading may therefore be said to have

taken place with regard to transportability (the fuel takes up considerably less space). The product has also been upgraded with regard to its combustion properties, since the calorific value of the fuel after the treatment was 31.82 kJ (7600 cal/g) (which is more than double the original value).

The following mass balance can be given for this experiment:

The tablets originally consisted of 256 g dry coal and 298 g water. After completion of the treatment there remained 207.3 g of end product, 17.75 l of gas was formed (principally CO₂)—which corresponds to a consumption of approx. 35 g=13.5% of the dry coal of the starting product, and approx. 5.5% of the dry coal of the starting product was converted into tar. The end product therefore contained 19% by weight of dry coal less than the starting product.

From this mass balance the following energy balance can be calculated:

The starting product, namely 553.8 g, had a calorific capacity of 553.8×12.89 kJ (3078 cal)=7138 kJ (1705 kcal).

The end product, namely 207.3 g, had a calorific capacity of 207.3×31.82 kJ (600 cal)=6594 kJ (1575 kcal).

The end product therefore still represented 92.1% of the calorific capacity of the starting product, concentrated into 37% of the original volume and into 37.4% of the original weight. Upgrading may therefore most certainly be said to have taken place.

The water content of the treated tablets was approx. 1% by weight.

In order to obtain an idea of the strength of the tablets in the various stages, the loads at which the tablets began to burst under a press were determined:

- the "green" strength of the untreated tablets was 4.0 N;
- the strength of the tablets after the treatment at 250°C was 7.5 N; and
- the strength of the tablets after treatment at 360°C was 29.8 N.

This demonstrates clearly that the strength of the tablets increases as a result of the upgrading treatment, which can be a great advantage in subsequent processing. Incidentally, the strength of lumps of the same brown coal (untreated) was 4.2 N.

In order to obtain an idea of the dusting properties of the treated brown coal, the tablets were subjected to a drop shatter test (modified ASTM D 440). In this, the elements to be tested are dropped a number of times in a conditioned manner and after the test the weight percentage of the fraction of small particles in the residues is analysed:

- of tablets heated only to 250°C, 33.0% by weight shattered into particles smaller than 2 mm;

- of tablets additionally heated at 360°C, only 6.3% by weight shattered into particles smaller than 2 mm, and
- of lumps of brown coal of comparable dimensions which had been thermally dried, 84.0% by weight shattered into particles smaller than 2 mm.

This shows clearly that upgrading may also be said to have taken place with regard to the dusting properties and handleability.

Comparative experiment

A quantity of Morwell brown coal (an Australian brown coal having a water content of 61.2% by weight and a calorific value of 10.89 kJ (2600 cal/g)) was compacted at a pressure of 5.0 kN/cm² to form uniform tablets (the same dimensions as in Example 1). The tablets were then heated at 340°C at a pressure of 156 bar for 1 min. (the vapour pressure of water at 340°C is approx. 149 bar) in the presence of some inherent moisture.

During this treatment there was a crimping of 40% and approx. 12% of the dry coal was lost during the treatment.

The end product had a water content of 34.6% by weight and a calorific value of 20.77 kJ (4960 cal).

Here again, upgrading may therefore be said to have taken place, since the volume was decreased by 40% and the calorific value was more than doubled.

Incidentally, the water content of the brown coal is still considerable and capable of further improvement.

In a drop shatter test, 1.9% by weight of the upgraded tablets shattered into a fraction smaller than 1.18 mm, while of upgraded brown coal lumps (particle size 7.5—12 mm) a quantity of 6.9% by weight shattered into a fraction smaller than 1.18 mm.

This shows that even an upgrading treatment of short duration produces strong tablets and a reduction in water content.

Claim

A process for upgrading fines of low grade fuel, in which process the fines are shaped into coherent bodies and the coherent bodies are consecutively heated to a temperature of 150—375°C in the presence of the water originally present in the said fines, at a pressure

which is higher than the vapour pressure of the water at the selected temperature and the heated bodies are separated from the water, characterized in that the said fines have a particle size of less than 25 mm and that the said heated and separated bodies are kept at a temperature and a pressure at which the water vaporizes and decarboxylation takes place, thus producing coherent bodies having a reduced content of water and of carboxyl groups.

Revendication

Un procédé pour améliorer la qualité de particules fines de combustible de qualité médiocre, selon lequel les particules fines sont mises sous la forme de corps ayant de la cohésion et les corps ayant de la cohésion sont consécutivement chauffés à une température de 150—375°C en présence de l'eau initialement présente dans les particules fines, à une pression supérieure à la pression de vapeur de l'eau à la température choisie, et les corps chauffés sont séparés de l'eau, caractérisé en ce que les particules fines ont une grosseur de particules de moins de 25 mm et que les corps chauffés et séparés sont maintenus à une température et une pression auxquelles l'eau se vaporise et une décarboxylation se produit, donnant ainsi des corps ayant de la cohésion et ayant une teneur réduite en eau et en groupes carboxyle.

Patentanspruch

Verfahren zur Aufbereitung von Feinteilen von minderwertigem Brennstoff, in welchem Verfahren die Feinteile zu kohärenten Körpern geformt und die kohärenten Körper anschließend in Gegenwart des ursprünglich in den genannten Feinteilen vorliegenden Wassers bei einem Druck, der über dem Dampfdruck des Wassers bei der gewählten Temperatur liegt, auf eine Temperatur von 150 bis 375°C erhitzt werden und die erhitzten Körper von dem Wasser abgetrennt werden, dadurch gekennzeichnet, daß die genannten Feinteile eine Teilchengröße von weniger als 25 mm aufweisen und daß die genannten erhitzten und abgetrennten Körper bei einer Temperatur und einem Druck gehalten werden, bei welchen das Wasser verdampft und eine Decarboxylierung stattfindet, wodurch kohärente Körper mit einem verminderten Gehalt an Wasser und an Carboxylgruppen gebildet werden.