(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 821 461 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.01.2015 Bulletin 2015/02

(21) Application number: **13755738.5**

(22) Date of filing: **28.02.2013**

(51) Int Cl.:
C10B 53/08 $^{(2006.01)}$ ***C10B 57/04*** $^{(2006.01)}$
C10L 5/04 $^{(2006.01)}$

(86) International application number:
PCT/JP2013/055519

(87) International publication number:
WO 2013/129607 (06.09.2013 Gazette 2013/36)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **29.02.2012 JP 2012044219**

(71) Applicant: **Kabushiki Kaisha Kobe Seiko Sho (Kobe Steel, Ltd.)**
Kobe-shi, Hyogo 651-8585 (JP)

(72) Inventors:
- **HAMAGUCHI Maki**
  Takasago-chi, Hyogo 676-8670 (JP)
- **OKUYAMA, Noriyuki**
  Takasago-chi, Hyogo 676-8670 (JP)
- **SAKAI, Koji**
  Takasago-chi, Hyogo 676-8670 (JP)
- **TANAKA, Takeharu**
  Nishi-ku, Kobe-shi, Hyogo 651-2271 (JP)
- **OKA, Takanori**
  Nishi-ku, Kobe-shi, Hyogo 651-2271 (JP)
- **SHISHIDO, Takahiro**
  Takasago-chi, Hyogo 676-8670 (JP)
- **ISHIDA, Kazuhide**
  Amagasaki-shi, Hyogo 660-0095 (JP)
- **KOTANI, Atsushi**
  Amagasaki-shi, Hyogo 660-0095 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) COAL BLEND BRIQUETTE AND PROCESS FOR PRODUCING SAME, AND COKE AND PROCESS FOR PRODUCING SAME

(57) A coal blend briquette which comprises a coal blend obtained by mixing both ash-free coal that comprises solvent-soluble components of coal and residue coal obtained by removing the solvent-soluble components from the coal with pulverized coal. The coal blend comprises 3 wt% or more of the ash-free coal, 8 wt% or less of the residue coal, and the pulverized coal as the remainder.

EP 2 821 461 A1

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a coal blend briquette including ash-free coal obtained by extraction treatment of coal with a solvent and residue coal which is a by-product thereof, and a process for producing the same, and in particular, relates to a coal blend which serves as a raw material for coke, and coke produced using the coal blend.

Background Art

[0002] Coke used in blast furnace ironmaking is required to have various properties, e.g., a certain level of mechanical strength such that coke is not easily crushed in the blast furnace, reactivity, an apparent density, and the size and distribution of lumps necessary to ensure gas permeability in blast furnace. As the raw material for coke satisfying such requirements, usually, hard coking coal, which is referred to as "coking coal", is used, which has a caking property, fluidity, or degree of coalification in a certain range, and high quality, and which is expensive coal compared with coal generally used as fuel for boilers. In recent years, under limited resources and rising costs, there has been an attempt to use inexpensive, low-rank coal as the raw material for coke. For example, various technological developments have been made for blending a large amount of low-rank coal with hard coking coal.

[0003] Furthermore, coal may be modified in order to effectively use resources and used as modified coal in some cases. In particular, recently, from the standpoint of being used as fuel with high efficiency, so-called "ash-free coal" (Hyper-coal) has been actively developed. The ash-free coal, which is obtained by removing most of the ash from coal, does not substantially contain ash (target: 200 ppm by mass or less), and structurally has a wide molecular weight distribution ranging from a component with a relatively low molecular weight having two or three fused aromatic rings to a component with a high molecular weight having about five or six fused aromatic rings. Therefore, ash-free coal has a high fluidity under heating. Some coal, such as coking coal, has thermoplasticity at a high temperature of about 400°C, whereas the ash-free coal generally melts at 200°C to 300°C (has softening and melting properties) regardless of the grade of raw coal. Accordingly, taking advantage of such properties, application development of binders for coke making has been advanced (for example, refer to Patent Literature 1). Furthermore, in recent years, an attempt has been made to produce a carbon material using the ash-free coal as a raw material.

[0004] Ash-free coal is produced by a method in which, by subjecting coal to extraction with a solvent having a high affinity for the coal at a high temperature, ash that is not dissolved in the solvent settles as a residue, and the solvent is removed from an extract (liquid portion) separated as a supernatant (for example, refer to Patent Literatures 2 to 4). On the other hand, from the remainder (non-liquid portion) from which the extract has been separated, the solvent is recovered by distillation or an evaporation method (for example, refer to Patent Literature 3), thereby, a residue composed of components that are insoluble in the solvent, such as un-resolved coal components and ash (mineral matter in coal), is produced as a by-product.

Citation List

Patent Literature

[0005]

PTL 1: Japanese Unexamined Patent Application Publication No. 2008-174592
PTL 2: Japanese Patent No. 3198305
PTL 3: Japanese Patent No. 4061351
PTL 4: Japanese Patent No. 4708463

Summary of Invention

Technical Problem

[0006] This by-product is referred to as "residue coal" and contains a large amount of ash. However, moisture is removed in the production process of ash-free coal, and residue coal has a sufficient calorific value. Therefore, residue coal can be used as a fuel for various applications. Furthermore, residue coal is derived from steam coal which is not usually used as a raw material for coke. Consequently, if residue coal can be used as a raw material for coke, it is believed that coke can be produced more inexpensively.

[0007] However, since residue coal is a coal component that remains after ash-free coal, which is a caking component, has been separated from coal, residue coal lacks in fluidity and caking property. It has been found that in the case where residue coal is used as a raw material for coke, even if a small amount of residue coal is used, the strength of coke decreases markedly.

[0008] The present invention has been achieved in view of the problems described above. It is an object of the present invention, in order to more effectively use residue coal which is a by-product of ash-free coal production, to produce a formed material having excellent handleability and convenience using a coal blend into which residue coal is mixed, and to provide coke having sufficient strength obtained by subjecting the formed material, as a raw material for coke, to carbonization even though the formed material contains residue coal having a low fluidity and a low coking ability, and a process for producing the same.

Solution to Problem

[0009] The present invention provides a coal blend briquette, coke, a process for producing a coal blend briquette, and a process for producing coke as described below.

(1) A coal blend briquette including a coal blend obtained by mixing ash-free coal containing solvent-soluble components of coal and residue coal obtained by removing the solvent-soluble components from the coal with pulverized coal, characterized in that the coal blend includes 3% by weight or more of the ash-free coal, 8% by weight or less of the residue coal, and the pulverized coal as the remainder.
(2) The coal blend briquette according to (1), characterized in that 90% or more of particles of the pulverized coal have a diameter of 2 mm or less.
(3) The coal blend briquette according to (2), characterized in that more than 60% of particles of the pulverized coal have a diameter of 1 mm or less.

[0010] By specifying the blending of ash-free coal and residue coal as described above, it becomes possible to strengthen the cohesion of coal and the like which are unlikely to be held together as a formed material, and the coal, the ash-free coal, and the residue coal are bonded together strongly by forming. Therefore, even though the residue coal is included, it is possible to produce a coal blend briquette for forming coke having sufficient strength.

(4) The coal blend briquette according to any one of (1) to (3), characterized in that the pulverized coal has a maximum fluidity MF value (log (ddpm)) of 0.2 to 2.0 and an average maximum reflectance Ro value of 0.8 to 1.1.

[0011] By specifying predetermined properties for the coal in such a manner, even though coal is unsuitable as a raw material for coke, it is possible to use the coal for producing a coal blend briquette that is subjected to carbonization to produce coke having sufficient strength.

(5) Coke characterized by being produced by subjecting a coal mixture containing the coal blend briquette according to (4) to carbonization.

[0012] By using a coal briquette having a predetermined composition as described above, it is possible to obtain coke which has sufficient and uniform strength even though residue coal is included, with low raw material costs.

(6) A process for producing a coal blend briquette characterized by including an ash-free coal production step in which, by subjecting coal to extraction with a solvent, an extract is separated from a residue, and the solvent is removed from the extract, thereby obtaining ash-free coal containing solvent-soluble components of the coal; a residue coal production step in which, by removing the solvent from the residue separated in the ash-free coal production step, residue coal is produced; a coal pulverization step in which coal is pulverized into pulverized coal; a mixing step in which the ash-free coal and the residue coal are mixed with the pulverized coal to obtain a coal blend including 3% by weight or more of the ash-free coal and 8% by weight or less of the residue coal; and a forming step in which the coal blend is formed into a coal blend briquette.
(7) The process for producing a coal blend briquette according to (6), characterized in that, in the forming step, the temperature of the coal blend is 80°C to 200°C.

[0013] In such a procedure, by pulverizing coal into pulverized coal, the pulverized coal can be suitably mixed with the ash-free coal and the like, and cohesion is strengthened during forming. Furthermore, by specifying the blending of the ash-free coal and the residue coal, it is possible to produce a coal blend briquette that serves as a raw material for coke having sufficient strength. Moreover, by setting the temperature of the coal blend at a predetermined value during forming, the strength of the coal blend briquette is improved, and the surface layer thereof becomes unlikely to be detached or peeled off. Furthermore, since the coal, the ash-free coal, and the residue coal are bonded together more strongly, the coal blend briquette serves as a suitable raw material for coke even though containing the residue coal.

(8) A process for producing coke including a step of subjecting a coal mixture containing a coal blend briquette produced by the process for producing a coal blend briquette according to (6) or (7) to carbonization.

[0014] Since the coal blend has already been formed into a coal blend briquette as described above, it is possible to produce coke that can be used for producing pig iron.

Advantageous Effects of Invention

[0015] In accordance with the coal blend briquette of the present invention, it is possible to obtain a fuel or a raw material for coke that is suitable for storage and transportation. In accordance with the coke of the present invention, sufficient strength can be achieved at low raw material costs using residue coal. Furthermore, in accordance with the process for producing a coal blend briquette and the process for producing coke of the present invention, since residue coal can be effectively used, economic efficiency is improved in the production of ash-free coal.

Brief Description of Drawings

[0016] [Fig. 1] Fig. 1 is a schematic view showing a modified-coal production apparatus for producing residue coal to be used as a raw material for a coal blend briquette according to the present invention.

Description of Embodiments

[0017] A coal blend briquette and a process for producing the same according to the present invention will be described in detail below.

[Coal blend briquette]

[0018] A coal blend briquette according to the present invention is obtained by mixing ash-free coal and residue coal with coal to produce a coal blend and forming the coal blend into lumps having a predetermined solid shape, and is used as a coal blend for a fuel or a raw material for coke as in the case of each of coal, ash-free coal, and the like alone. The shape and size of the coal blend briquette are not particularly specified, and are designed according to intended use. Ash-free coal, residue coal, and coal, which are raw materials for the coal blend briquette, will be described below.

(Ash-free coal: 3% by weight or more)

[0019] Ash-free coal is modified coal obtained by removing ash and insoluble coal components as much as possible from coal, does not substantially contain ash, and contains components having a high fluidity and a high coking ability. Ash-free coal is produced by a method in which, by subjecting coal to extraction with a solvent having a high affinity for the coal, an extract from which insoluble components, such as ash, are separated is obtained, and the solvent is removed from the extract by an evaporation method or the like. Consequently, the ash-free coal contains large amounts of organic substances which are soluble in the solvent and which have softening and melting properties among coal components. Furthermore, the ash-free coal is dewatered in a state of mixture (slurry) of coal and the solvent before extraction and separation, and therefore, the moisture is decreased to about 0.2% to 3% by mass. Accordingly, the ash-free coal has a high volatile content, excellent thermal fluidity, and a high coking ability. Thus, even when mixed with low-rank coal, such as soft coking coal or non-coking coal, and residue coal, the mixture can be heated and formed to produce a coal blend briquette which has a certain degree of strength, in which the occurrence of dust can be suppressed, and which is suitable for storage and the like. Furthermore, by imparting a coking ability to the low-rank coal during carbonization, coke having high strength can be produced. In order to provide sufficient strength when coke is produced, the content of the ash-free coal (excluding moisture) in the coal blend briquette is set at 3% by weight or more, and is further adjusted according to the fluidity of coal to be blended. The upper limit of the content of the ash-free coal is not particularly limited. However, when the content of the ash-free coal is excessively high, strength is rather decreased when coke is produced. Therefore, the content of the ash-free coal is preferably set at 10% by weight or less. Furthermore, in order to increase the strength of the coal blend briquette and coke, the ash-free coal is preferably in a pulverized form with a size as small as possible, and specifically, the diameter (maximum length) thereof is preferably 1 mm or less. In the present invention, regarding raw coal for obtaining the ash-free coal, quality does not matter. The details of the process for producing ash-free coal will be described later.

(Residue coal: 8% by weight or less)

[0020] Residue coal is a by-product occurring in the process of producing ash-free coal from coal. As described above, ash-free coal is produced by extracting solvent-soluble components from coal. On the other hand, by sufficiently removing the solvent from the insoluble components separated as a residue, residue coal is obtained. Consequently, since solvent-soluble organic substances having softening and melting properties are removed as ash-free coal from raw coal, the residue coal has low softening and melting properties. Furthermore, ash that is insoluble in the solvent is concentrated from raw coal, and the ash concentration is high at about 10% to 20% by mass. However, the residue coal contains carbon (C) as a main component as in raw coal. Furthermore, as in the ash-free coal, the residue coal is dewatered in a state of mixture (slurry) of coal and the solvent before extraction and separation, and therefore, the moisture is decreased to about 0.2% to 3% by mass. The residue coal has a sufficient calorific value. Since the residue coal has a low fluidity and no coking ability, a high content of the residue coal decreases strength when coke is produced. Thus, the content of the residue coal (excluding moisture) in the coal blend briquette is set at 8% by weight or less, and is adjusted according to the degree of coalification and fluidity of coal to be blended and the amount of the ash-free coal to be blended. Preferably, the content of the residue coal is 1% by weight or more. Furthermore, in order to increase the strength of the coal blend briquette and coke, the residue coal is preferably in a pulverized form with a size as small as possible, and specifically, the diameter (maximum length) thereof is preferably 1 mm or less. Note that the ash in coal refers to the inorganic residue when coal is incinerated by heating at 815°C, and includes silicic acid, alumina, iron oxide, lime, magnesium oxide, alkali metal oxides, and the like. In the present invention, regarding raw coal for obtaining the residue coal, quality does not matter as in the ash-free coal. The details of the process for producing residue coal will be described later as part of the process for producing ash-free coal. Furthermore, the ash-free coal and the residue coal may not be produced from the same raw coal or using the same production apparatus and the same method.

(Coal)

[0021] The type (grade, quality) of coal is selected according to intended use of the coal blend briquette. In particular, when a coal blend as a raw material for coke is produced, preferably, the coal has a maximum fluidity MF value (log (ddpm)) of 0.2 to 2.0 and an average maximum reflectance Ro value of 0.8 to 1.1. Coal with an MF value of less than 0.2 and an Ro value of less than 0.8 is not suitable for producing coke because the quality is too low, or the amount of such coal must be extremely decreased, and cost reduction is not achieved. On the other hand, coal with an MF value of more than 2.0 and an Ro value of more than 1.1 can be used alone for producing coke, resulting in an increase in raw material costs. That is, by using coal with medium-low degree of coalification and medium-low fluidity, which is generally considered to be difficult to use as a raw material for coke, among various types of bituminous coal, the raw material cost can be reduced. Furthermore, two or more different types of coal may be used within the ranges of the degree of coalification and fluidity. The coal can be included in the coal blend briquette in an amount of 80% by weight or more, or 85% by weight or more, on the basis of dry coal. Although dried coal may be produced by air drying or the like, coal in the state of containing moisture may be mixed with the ash-free coal and the residue coal and subjected to forming.

[0022] The coal is preferably in a pulverized form, as in the ash-free coal and the residue coal. Specifically, preferably, 90% or more of particles of the coal have a diameter of 2 mm or less, and more preferably, more than 60% of particles of the coal have a diameter of 1 mm or less. In this description, the particle diameter refers to the maximum length of the particle. The expression "90% or more of particles have a diameter of 2 mm or less" means that "90% or more of the particles of coal pass through a sieve with an opening of 2 mm". In the coal blend briquette according to the present invention, as the particle size of each of the coal, the ash-free coal, and the residue coal is decreased, the strength of the coal blend briquette can be increased, and furthermore, the strength of coke can be increased when coke is produced.

[0023] The coal blend briquette according to the present invention preferably contains a very small amount of water. Water serves as a binder for causing particles of the ash-free coal, the residue coal, and the coal to adhere to each other, forming lumps, and thus the strength of the coal blend briquette is improved. The water is not particularly limited, and water that is generally used, such as tap water, can be used. Although a liquid other than water may be used for forming, water is inexpensive and easily available, water adheres to coal itself, and coal is impregnated with water in an amount of about 2% to 8% by mass. In the coal blend briquette, the total amount of water contained in the coal, the ash-free coal, and the residue coal is preferably adjusted to 0.5% to 13% by mass by adding water if there is a deficiency of water. Since the amount of water in the coal blend, i.e., before forming, remains substantially the same after the coal blend is formed into the coal blend briquette, the amount of water can be adjusted at the time of mixing the coal and the like. Such water is not particularly limited, and water that is generally used, such as tap water, can be used. In the coal blend briquette, an amount of water of less than 0.5% by mass is insufficient for holding together the coal, the ash-free coal, and the residue coal during forming. On the other hand, when the amount of water exceeds 13% by mass, water films are formed on surfaces of particles of each of the coal, the ash-free coal, and the residue coal, which makes the particles unlikely to adhere to each other. Furthermore, the amount of water is preferably 4% to 9% by mass.

[Process for producing coal blend briquette]

[0024] A process for producing a coal blend briquette according to the present invention includes an ash-free coal production step in which ash-free coal is produced from coal, a residue coal production step in which residue coal is produced from coal, a coal pulverization step in which coal is pulverized into pulverized coal, a mixing step in which the ash-free coal and the residue coal are mixed with the coal to obtain a coal blend, and a forming step in which the coal blend is formed into a coal blend briquette. The individual steps will be described below.

(Ash-free coal production step, residue coal production step)

[0025] In the ash-free coal production step, coal is subjected to extraction with a solvent, and the solvent is removed from an extract separated from a residue to produce ash-free coal. In the residue coal production step, by removing the solvent from a slurry of the residue, residue coal is produced. That is, residue coal is a by-product occurring in the process of producing ash-free coal from coal. Accordingly, in this embodiment, the ash-free coal production step and the residue coal production step are described as one step. Furthermore, as the residue coal, residue coal which is not obtained as a by-product in the production of ash-free coal may be used as long as it has the same components, and the ash-free coal and the residue coal may not be produced in the same step. As the method of producing ash-free coal, for example, the method described in any one of Patent Literatures 2 to 4 may be employed. Description will be made below with reference to an example of a modified-coal production apparatus shown in Fig. 1, in which ash-free coal and residue coal can be obtained.

[0026] As shown in Fig. 1, a modified-coal production apparatus 10 includes a solvent storage tank 1, a slurry preparation tank 2 equipped with a stirrer, a preheater 3, an extraction tank 4 equipped with a stirrer, a gravity settling tank 5, a solid-content concentrated liquid receiver 6, and a supernatant receiver 7, and further includes pumps and a distillation means, a cooling mechanism, and the like (not shown) which will be described later. A method of producing ash-free coal and residue coal using the modified-coal production apparatus 10 will be described as the ash-free coal production step and the residue coal production step.

[0027] First, predetermined amounts of coal (raw coal) and a solvent, which is supplied by a pump from the solvent storage tank 1, are supplied to the slurry preparation tank 2. In the slurry preparation tank 2, the coal and the solvent are mixed with the stirrer provided to prepare a slurry. At this time, preferably, the moisture of the coal is removed by a dewatering means (not shown). A predetermined amount of the slurry is heated by the preheater 3 and further stirred for a predetermined time in the extraction tank 4. Thereby, bonds between molecules constituting the coal are loosened to cause mild pyrolysis, and extraction proceeds. The extracted solvent (extract) in which solvent-soluble components are dissolved and components that are insoluble in the solvent (solid content and residue), in a separated state, are supplied to the gravity settling tank 5.

[0028] As the method for isolating and taking out an extract and a residue, various filtration methods and centrifugation methods are known. In the production of ash-free coal, it is preferable to use a gravity settling method in which continuous handling of a fluid is possible and which is suitable for treatment of a large amount at low costs. That is, in the gravity settling tank 5, the extract is taken out as a supernatant and supplied, as necessary, through a filter unit, to the supernatant receiver 7. In the supernatant receiver 7, the solvent is removed from the extract, and ash-free coal is produced. On the other hand, the portion containing the residue (solid-content concentrated liquid) settled on the bottom of the gravity settling tank 5 is discharged to the solid-content concentrated liquid receiver 6. The solvent is removed from the solid-content concentrated liquid in the solid-content concentrated liquid receiver 6, and residue coal is produced.

[0029] In the solid-content concentrated liquid receiver 6 and the supernatant receiver 7, the solvent can be removed from the extract or the solid-content concentrated liquid by distillation or an evaporation method, such as a spray dry method. The solute (ash-free coal) and the solid content (residue coal) obtained by removing the solvent are in the form of powder particles with a diameter of about 0.2 to 1.0 mm, or in some cases, secondary particles with a diameter of up to about 50 mm in which the powder particles serving as primary particles are aggregated may be mixed therewith. On the other hand, the solvent (recovered solvent) removed in each of the solid-content concentrated liquid receiver 6 and the supernatant receiver 7 is recovered and may be regenerated as necessary and reused by being supplied to the slurry preparation tank 2 or the solvent storage tank 1. Conditions and the like in the individual operations will be described below.

[0030] Coal used as a raw material for each of ash-free coal and residue coal may be of any type (grade, quality, brand), and may not necessarily be of the same type as that of coal to be mixed in the coal blend briquette. Accordingly, bituminous coal having a high extraction rate (ash-free coal recovery rate) may be used, or less expensive low-quality coal (sub-bituminous coal or brown coal) may be used. Furthermore, in order to facilitate extraction and increase the yield of ash-free coal, the coal is preferably pulverized into particles with a size as small as possible before being fed into the modified-coal production apparatus 10 (slurry preparation tank 2), and the particle diameter (maximum length) thereof is preferably 1 mm or less.

[0031] The solvent has a high affinity for coal, i.e., dissolves coal. Examples of such a solvent include monocyclic aromatic compounds, such as benzene, toluene, and xylene; and polar solvents, such as N-methylpyrrolidone (NMP) and pyridine. However, in the production of ash-free coal (and residue coal), use of a non-hydrogen donor solvent (aromatic solvent) mainly composed of a bicyclic aromatic compound is preferable. Accordingly, in the residue coal production step in this embodiment, a case where an aromatic solvent is used as the solvent will be described.

[0032] An aromatic solvent, which is a non-hydrogen donor solvent, is a coal derivative obtained mainly by purifying a carbonization product of coal and is a solvent mainly composed of a bicyclic aromatic compound. Such an aromatic solvent is relatively stable even under the extraction conditions described above, and has a high affinity for coal. Therefore, the percentage of soluble components of coal extracted in such a solvent (extraction rate) is sufficiently high. As a result, the yield of ash-free coal is high, and at the same time, it is possible to obtain, as a by-product, residue coal in which soluble components minimally remain. Furthermore, the aromatic solvent can be easily recovered from the extract and the like by a distillation method or the like. In addition, the recovered solvent can be directly recycled and reused (refer to Fig. 1). Examples of the main component of the aromatic solvent include bicyclic aromatic compounds, such as naphthalene, methylnaphthalene, dimethylnaphthalene, and trimethylnaphthalene. Examples of other components include naphthalenes, anthracenes, and fluorenes having an aliphatic side chain, and alkylbenzenes having a biphenyl or long-chain aliphatic side chain.

[0033] On the other hand, a hydrogen donor solvent can achieve a high extraction rate regardless of the type of coal, and therefore, the yield of ash-free coal can be increased. Examples of the hydrogen donor solvent include partially hydrogenated aromatic compounds, such as tetralin and tetrahydroquinoline, and hydrogenated coal liquid. However, the hydrogen donor solvent is generally more expensive than the aromatic solvent, and when the hydrogen donor solvent is used for extraction, most of its hydrogen-donating capability is lost. Therefore, the hydrogen donor solvent cannot be reused without being regenerated (hydrogen-treated) after recovery, resulting in an increase in costs. Consequently, the solvent is appropriately selected in consideration of the type of coal and the design of raw material for intended use. For example, a hydrogen donor solvent may be used for coal having a low extraction rate with an aromatic solvent. Furthermore, for example, by using an aromatic solvent and a hydrogen donor solvent in combination, the yield of ash-free coal can be increased while controlling costs (refer to Patent Literature 4).

[0034] The amount of the coal mixed with the solvent is preferably in the range of 10% to 50% by mass, more preferably in the range of 20% to 35% by mass, relative to the total mass of the coal and the solvent, on the basis of dry coal, although depending on the type of raw coal. When the amount of the coal is less than 10% by mass, the amount of coal components extracted is small relative to the solvent, and thus productivity is low. On the other hand, when the amount of the coal exceeds the equivalent amount of the solvent, i.e., 50% by mass, the viscosity of the prepared slurry increases, fluidity decreases, and movement between treatment systems (tanks) and separation between the extract and the residue may become difficult in some cases.

[0035] By heating the slurry to a high temperature, bonds between molecules constituting the coal are loosened to cause mild pyrolysis, and extraction proceeds. When the slurry temperature is lower than 300°C, bonds between molecules constituting the coal are insufficiently weakened, and extraction does not proceed sufficiently. On the other hand, when the slurry temperature exceeds 450°C, the pyrolytic reaction of the coal becomes very active to cause recombination of pyrolytic radicals generated. Accordingly, the extraction rate is unlikely to be increased, and the coal is unlikely to be modified. Consequently, the heating temperature of the slurry is preferably in the range of 300°C to 450°C, and more preferably 300°C to 400°C.

[0036] If the solvent is volatilized and is not kept in a liquid phase, extraction cannot be performed. Therefore, during the heating (preheating) and extraction of the slurry, the pressure is set higher than the vapor pressure of the solvent at the heating temperature such that the solvent is not volatilized at the heating temperature. On the other hand, when the pressure is excessively high, an expensive instrument having a high hermetic property and the like is required as the modified-coal production apparatus 10, and the operation cost increases. Specifically, the pressure is preferably in the range of 1.0 to 2.0 MPa, although it depends on the temperature in the extraction and the vapor pressure of the solvent. Furthermore, since the extraction is performed at high temperatures, there is a possibility of ignition when the solvent and coal components, in particular, solvent-soluble components, come into contact with oxygen. Therefore, the heating (preheating) and extraction of the slurry are preferably performed in an inert gas atmosphere, such as nitrogen.

[0037] A criterion of the extraction time (time within the range of the heating temperature of the slurry) is a time until reaching the solution equilibrium. However, realization thereof decreases productivity. Consequently, it is preferable to finish the extraction when the rise in the extraction rate apparently stops, or becomes fairly mild. The preferable extraction time is usually about 10 to 60 minutes, although it varies depending on conditions, such as the particle size of the coal and the type of solvent. When the extraction time is less than 10 minutes, the extraction may proceed insufficiently in many cases. On the other hand, even when the extraction time exceeds 60 minutes, the extraction is unlikely to proceed further, resulting in poor productivity.

(Coal pulverization step)

[0038] In the coal pulverization step, coal to be mixed in the coal blend briquette is pulverized into particles by a usual method. Furthermore, regarding the ash-free coal and the residue coal, in the case where coarse secondary particles are mixed therein as described above, they may be pulverized in the same manner. Alternatively, the ash-free coal and the residue coal may be mixed with the coal at the blending ratio described above, and the resulting mixture may be pulverized.

(Mixing step)

[0039] In the mixing step, the ash-free coal, the residue coal, the coal, and, as necessary, water are mixed to obtain a mixture (coal blend). The blending of the ash-free coal, the residue coal, and the coal, and the water content are as described above in the description of the coal blend briquette. In particular, the amount of water is adjusted by supplying a deficient amount in view of the amounts of water in the coal, the ash-free coal, and the residue coal as described above. For example, the ash-free coal, the residue coal, and the coal pulverized in advance are fed through a hopper into a known mixer, and stirring is performed while adding water thereto by a spray or the like. Thereby, secondary particles of the ash-free coal and the residue coal are easily pulverized, and even immediately after the ash-free coal and the residue coal are produced in the ash-free coal production step and the residue coal production step, i.e., even immediately after being heated to a temperature exceeding 200°C, they are moderately cooled. In the case where such ash-free coal and residue coal are subjected to moisture adjustment, water is added taking into consideration the amount of vaporization in the subsequent forming step.

(Forming step)

[0040] In the forming step, the coal blend is formed into lumps having a predetermined solid shape to produce a coal blend briquette. The forming of the coal blend can be performed, for example, by compression forming using a forming machine or by double-roll briquetting, which is also used in forming a carbon material, such as ash-free coal. The pressure applied to the coal blend for forming is not particularly specified and may be set according to a forming machine or the like.

[0041] At a certain temperature or higher, the fluidity of the ash-free coal facilitates forming of the coal blend, the strength is further improved, and it is possible to obtain a coal blend briquette suitable as a raw material for coke in which the coal, the ash-free coal, and the residue coal are strongly bonded together. Specifically, the temperature of the coal blend is preferably 80°C or higher, and more preferably in the range of 100°C to 150°C. This temperature is a temperature measured at the time when the forming mold is filled with the coal blend. Consequently, the coal blend or the coal and the like before being mixed may be heated by a heater or the like in advance such that the temperature during forming is 80°C or higher and then charged into the mold for forming. For example, heating may be performed simultaneously with mixing of the coal blend or adjustment of moisture, or heating may be performed while performing forming. On the other hand, an increase in the heating temperature raises costs, and even if heating is performed to a temperature higher than 200°C, a particular improvement effect of formability, strength, or the like is not obtained. Therefore, preferably, the heating temperature of the coal blend is set at 200°C or lower.

[0042] Coke and a process for producing the same according to the present invention will be described in detail below.

[Coke]

[0043] Coke according to the present invention is produced by subjecting a coal mixture obtained by mixing the coal blend briquette according to the present invention with another coal used as a raw material for coke to carbonization under the general conditions as will be described later. The content of the coal blend briquette according to the present invention in the coal mixture is preferably 10% to 30% by mass. Furthermore, examples of the coal used as a raw material for coke include hard coking coal, semi-hard coking coal, soft coking coal, and non-coking or slightly coking coal, which are generally used as a raw material for coke. As in the case where coke is produced using these coals alone, the coal used as a raw material for coke is pulverized, for example, such that 80% or more of particles of the coal have a diameter of 3 mm or less. As described above, the coal blend briquette according to the present invention is formed into a desired shape and has certain strength. Therefore, by subjecting the coal blend briquette together with the coal used as a raw material for coke to carbonization, the resulting coke holds the shape. Furthermore, it is not necessary to set the size and shape of the coal blend briquette to be the same as those of the coal used as a raw material for coke. Depending on the size, the coal blend briquette with the formed shape may be mixed with the coal used as a raw material for coke and subjected to carbonization. However, in the case where the coal blend briquette is considerably large compared with the (pulverized) coal used as a raw material for coke, problems, such as segregation on the wall portion of the coke oven due to a difference in particle flowability between the coal blend briquette and the coal used as a raw material for coke, are likely to occur. Therefore, the coal blend briquette is preferably pulverized to substantially the same size as that of the coal used as a raw material for coke. As described above, in the coal blend briquette, the coal, the ash-free coal, and the residue coal are bonded together strongly by forming, and the bonds are held even after being pulverized. Thus, the effect of mixing the coal blend briquette according to the present invention is not affected. The coke obtained by carbonization can be directly fed into a blast furnace for producing pig iron.

[Process for producing coke]

[0044] In the present invention, the conditions for carbonization are not particularly limited, and usual carbonization conditions in the coke production using a coke oven can be employed. For example, the coal mixture is charged into a chamber oven, in which about 30 tons can be charged through a charging hole, in the amount of about 10% to 50% of the capacity, and carbonization is performed. The carbonization is performed at a temperature of preferably 950°C or higher, more preferably 1,000°C or higher, and preferably 1,200°C or lower, more preferably 1,050°C or lower, for a time of preferably 8 hours or more, more preferably 10 hours or more, and preferably 24 hours or less, more preferably 20 hours or less.

EXAMPLES

[0045] The coal blend briquette and coke and processes for producing the same according to the present invention will be specifically described on the basis of examples and comparative examples.

[Production of coke]

(Production of ash-free coal and residue coal)

[0046] First, ash-free coal and residue coal were produced by the method described below. Using bituminous coal produced in Australia as raw coal, the raw coal (in terms of dried coal) and a solvent (1-methylnaphthalene (manufactured by Nippon Steel Chemical Co., Ltd.)) in four times (20 kg) the volume of the raw coal were mixed to prepare a slurry. The slurry was subjected to extraction treatment in a batch-type autoclave with an inner volume of 30 L, at 370°C for one hour in a state in which the pressure was increased to 1.2 MPa by introducing nitrogen. The slurry was separated into a supernatant and a solid-content concentrated liquid in a gravity settling tank maintaining the same temperature and the same pressure. By separating and recovering the solvent from the solid-content concentrated liquid by distillation, residue coal was obtained. On the other hand, by separating and recovering the solvent from the supernatant by distillation, ash-free coal was obtained. The moisture content of each of the resulting ash-free coal and residue coal was 1.5% by mass. 1 Kg of each of the ash-free coal and the residue coal was pulverized such that the particle diameter (maximum length) was 1 mm or less.

(Mixing and forming)

[0047] As coal to be mixed into a coal blend, bituminous coal produced in Australia with a moisture content of 6.7% by mass (a maximum fluidity MF value (log (ddpm)) of 0.5 and an average maximum reflectance Ro value of 1.01) was pulverized such that the particle diameter was 1 mm or less. The ash-free coal and the residue coal were mixed with the coal at the blending ratio (%) shown in Table 1, and water was further added thereto in an amount of 0.5% by mass relative to the total mass. By mixing with a V mixer for 10 minutes, a mixture (coal blend) was prepared. Note that the moisture content of bituminous coal is the value measured in accordance with Coal JIS (JIS M8812).

[0048] Next, 6 g of the mixture was placed in each of molds with a diameter of 20 mm, and while heating at 120°C under an applied pressure of 2 tons/cm^2, columnar tablets were formed. Thereby, a coal blend briquette was obtained.

[0049] The tablets of the coal blend briquette were placed side by side in a retort made of steel. The retort was placed in an electric furnace of a both-side heating type, and the coal blend briquette was subjected to carbonization under a nitrogen stream. In the carbonization, the temperature was raised at 3°C/min, and heating was performed at 1,000°C for 20 minutes. Then, the retort was taken out of the electric furnace, and it was left to cool naturally. Furthermore, as an evaluation reference, a coke sample (No. 8) was produced using a coal blend briquette which did not contain the residue coal. The following evaluations were performed for each coke thus obtained.

[Evaluation]

(Compression test)

[0050] A compression test was performed as an indicator of strength. A compressive load was applied to the coke in a direction perpendicular to the axis of the columnar shape (in the radial direction), and the load required to cause a fracture was measured. The measured load, which is defined as the crushing load, is shown in Table 1. The strength acceptability criterion was set to be 100 kg or more in terms of crushing load.

(Abrasion test)

[0051] An abrasion test was performed as an indicator of suppression of dust occurrence. First, 20 coke tablets were placed in a cylindrical container with a diameter of 250 mm, and rotated at 30 RPM for 10 minutes. Then, the coke taken out of the cylindrical container was screened using a sieve with an opening of 5.66 mm, and the portion passed through the sieve was weighed. The weight ratio (%) of the portion (powder) passed through the sieve to the entire coke was calculated as an incidence of powder, which is shown in Table 1. The acceptability criterion for suppression of dust occurrence was set to be 10% or less in terms of incidence of powder.

[Table 1]

Sample		Composition (%)			Evaluation	
Classification	No.	Ash-free coal	Residue coal	Coal	Crushing load (kg)	Incidence of powder (%)
Example	1	5	5	90	168	2.3
Comparative Example	2	0*	10*	90	13	29.6
Comparative Example	3	0.5*	8	91.5	41	18.3
Comparative Example	4	5	10*	85	66	16.1
Example	5	3	3	94	105	6.1
Comparative Example	6	2*	2	96	79	11.3
Example	7	10	8	82	165	4.8
Reference Example	8	10	0	90	223	1.2

* indicates out of the range of the present invention.
The underlined value indicates failure.

[0052] As shown in Table 1, Sample Nos. 1, 5, and 7 are examples which satisfy the ranges of the present invention, in which the strength is sufficient as the raw material for coke, although lower than that of Sample No. 8 which does not contain the residue coal. In contrast, in Sample Nos. 2, 3, and 6, since the content of the ash-free coal is insufficient, the strength is low, and in Sample No. 2 which does not contain the ash-free coal, the strength is particularly low. Furthermore, in Sample No. 4, since the content of the residue coal is excessively high, the strength is low.

[0053] While the present invention has been described in detail with reference to embodiments and examples, the gist of the present invention is not limited to the above description, and the scope of rights should be construed widely on the basis of the claims. In the present invention, various modifications and changes are possible on the basis of the above description.

[0054] This application claims the benefit of Japanese Patent Application No. 2012-044219 filed in the Japan Patent Office on February 29, 2012, the entire contents of this application being incorporated herein by reference.

Industrial Applicability

[0055] In accordance with the coal blend briquette of the present invention, it is possible to obtain a fuel or a raw material for coke that is suitable for storage and transportation. In accordance with the coke of the present invention, sufficient strength can be achieved at low raw material costs using residue coal. Furthermore, in accordance with the process for producing a coal blend briquette and the process for producing coke of the present invention, since residue coal can be effectively used, economic efficiency is improved in the production of ash-free coal.

Reference Signs List

[0056]

10	modified-coal production apparatus
1	solvent storage tank
2	slurry preparation tank
3	preheater
4	extraction tank
5	gravity settling tank
6	solid-content concentrated liquid receiver
7	supernatant receiver

Claims

1. A coal blend briquette comprising a coal blend including:

   ash-free coal containing solvent-soluble components of coal;
   residue coal obtained by removing the solvent-soluble components from the coal; and
   pulverized coal,
   characterized in that the coal blend includes 3% by weight or more of the ash-free coal, 8% by weight or less of the residue coal, and the pulverized coal as the remainder.

2. The coal blend briquette according to Claim 1, **characterized in that** 90% or more of particles of the pulverized coal have a diameter of 2 mm or less.

3. The coal blend briquette according to Claim 2, **characterized in that** more than 60% of particles of the pulverized coal have a diameter of 1 mm or less.

4. The coal blend briquette according to Claim 1, **characterized in that** the pulverized coal has a maximum fluidity MF value (log (ddpm)) of 0.2 to 2.0 and an average maximum reflectance Ro value of 0.8 to 1.1.

5. Coke **characterized by** being produced by subjecting a coal mixture containing the coal blend briquette according to Claim 4 to carbonization.

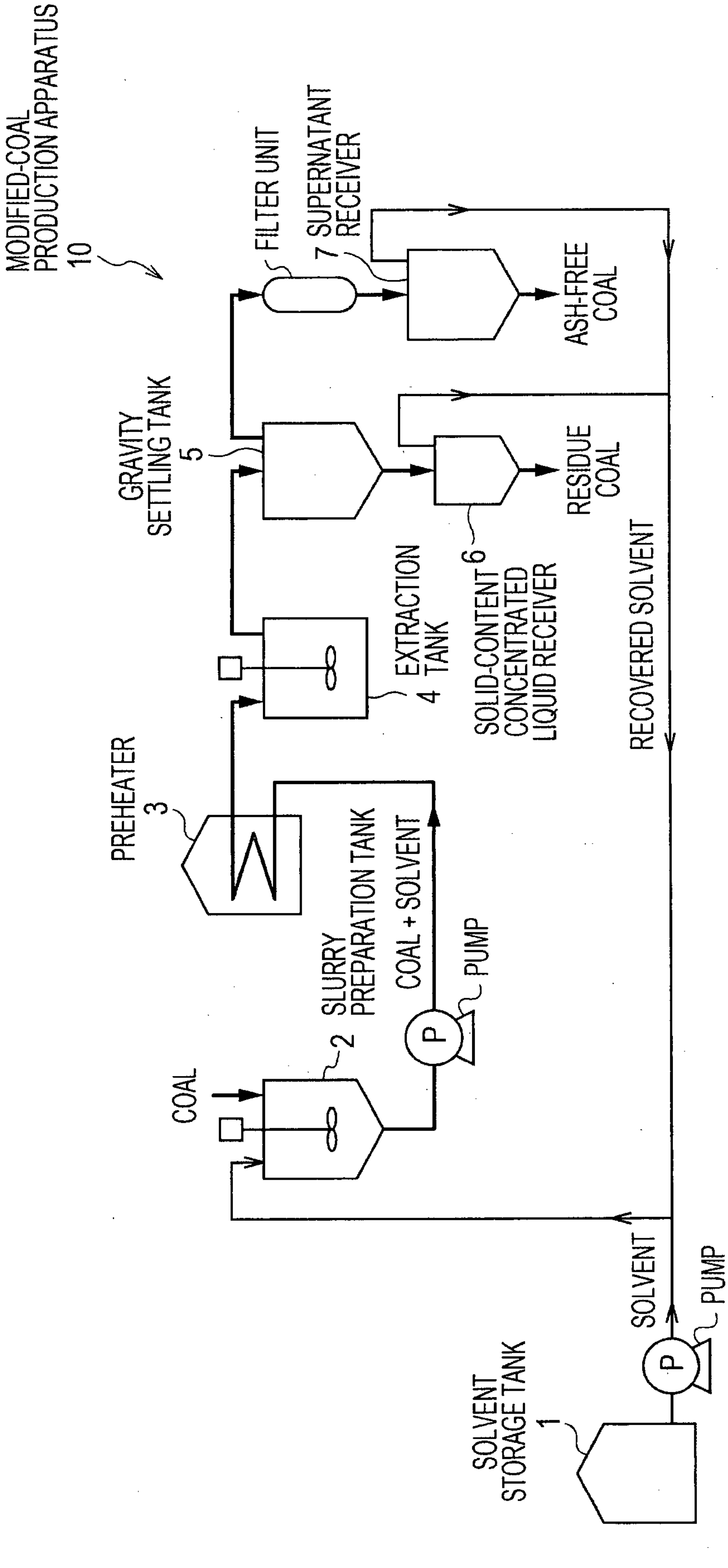
6. A process for producing a coal blend briquette **characterized by** comprising:

   an ash-free coal production step in which, by subjecting coal to extraction with a solvent, an extract is separated from a residue, and the solvent is removed from the extract, thereby obtaining ash-free coal containing solvent-soluble components of the coal;
   a residue coal production step in which, by removing the solvent from the residue separated in the ash-free coal production step, residue coal is produced;
   a coal pulverization step in which coal is pulverized into pulverized coal;
   a mixing step in which the ash-free coal and the residue coal are mixed with the pulverized coal to obtain a coal blend including 3% by weight or more of the ash-free coal and 8% by weight or less of the residue coal; and
   a forming step in which the coal blend is formed into a coal blend briquette.

7. The process for producing a coal blend briquette according to Claim 6, **characterized in that**, in the forming step, the temperature of the coal blend is 80°C to 200°C.

8. A process for producing coke comprising a step of subjecting a coal mixture containing a coal blend briquette produced by the process for producing a coal blend briquette according to Claim 6 to carbonization.

FIG. 1


MODIFIED-COAL PRODUCTION APPARATUS
10
SOLVENT STORAGE TANK
1
PUMP
P
SOLVENT
COAL
2
SLURRY PREPARATION TANK
PUMP
P
COAL + SOLVENT
PREHEATER
3
EXTRACTION TANK
4
GRAVITY SETTLING TANK
5
SOLID-CONTENT CONCENTRATED LIQUID RECEIVER
6
RESIDUE COAL
FILTER UNIT
7
SUPERNATANT RECEIVER
ASH-FREE COAL
RECOVERED SOLVENT

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/055519

A. CLASSIFICATION OF SUBJECT MATTER
C10B53/08(2006.01)i, *C10B57/04*(2006.01)i, *C10L5/04*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10B53/08, C10B57/04, C10L5/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2012-31235 A (Kobe Steel, Ltd.), 16 February 2012 (16.02.2012), examples; fig. 6 to 8 (Family: none)	1-5 6-8
Y	JP 2006-70182 A (Kobe Steel, Ltd.), 16 March 2006 (16.03.2006), entire text (Family: none)	6-8
A	WO 2007/069469 A1 (Kobe Steel, Ltd.), 21 June 2007 (21.06.2007), & JP 2007-161955 A & KR 10-2008-0067382 A & CN 101365775 A	1-8

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 28 March, 2013 (28.03.13)	Date of mailing of the international search report 09 April, 2013 (09.04.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2008174592 A **[0005]**
- JP 3198305 B **[0005]**
- JP 4061351 B **[0005]**
- JP 4708463 B **[0005]**
- JP 2012044219 A **[0054]**