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(54) **Title**: PROCESS FOR PRODUCTION OF FUELS AND CHEMICALS FROM BIOMASS FEEDSTOCKS

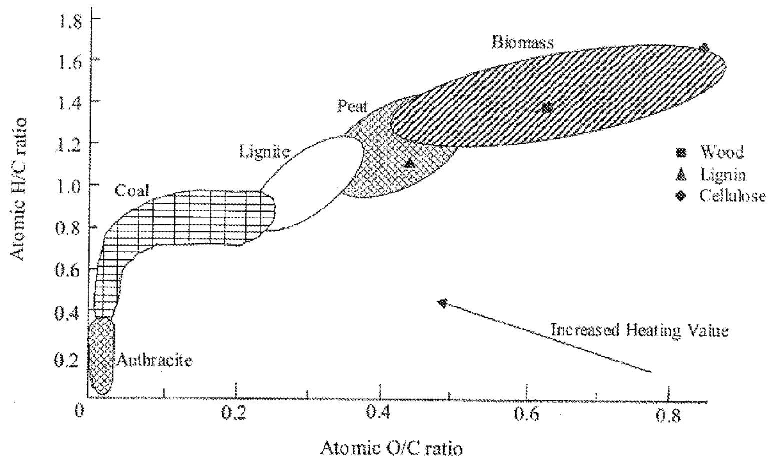

Figure 1

(57) **Abstract**: A process for the production of fuels and chemicals from biomass feedstock is provided. The process includes (a) drying the biomass feedstock using heated dry carbon monoxide gas; (b) devolatilizing the feedstock by reductive torrefaction with heated dry carbon monoxide gas; (c) pulverizing the feedstock; and (d) pyrolyzing the feedstock by reductive pyrolysis with high pressure or high temperature carbon monoxide gas. An integrated system for producing fuels and chemicals from biomass feedstock is also provided.

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PROCESS FOR PRODUCTION OF FUELS AND CHEMICALS FROM BIOMASS FEEDSTOCKS

[0001] The present application claims priority to U.S. Patent Application No. 61/608,734, filed March 9, 2012, entitled *Process for Production of Fuels and Chemicals From Biomass Feedstocks*, the disclosures of which are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

[0002] The present invention relates generally to the production of fuels and chemicals from biomass feedstocks, and more particularly to thermochemical processing of biomass feedstocks to produce fuels and chemicals.

BACKGROUND

[0003] A feedstock is defined as any renewable, biological material that can be used directly as a fuel, or converted to another form of fuel or energy product. Biomass feedstocks are the plant and algal materials used to derive fuels like ethanol, butanol, biodiesel, and other hydrocarbon fuels. Examples of biomass feedstocks include crop residues such as corn stover and sugarcane bagasse, energy grass crops, forestry residues, short-rotation forest crops, by-product glycerol from biodiesel production, municipal solid waste, manures, pulp and paper residues, and spoils from demolition and disaster recovery operations.

[0004] The increasing costs associated with oil, coal and natural gas has made using biomass feedstocks to produce energy a promising alternative. A Van Krevelen diagram is shown in FIG.1 and compares the hydrogen index versus the oxygen index for various products including wood, lignin and cellulose. The diagram cross plots the hydrogen: carbon as a function of the oxygen:carbon atomic ratio of carbon compounds. The region on this diagram shows the general path from the high oxygen biomass feedstocks to lower oxygen fuels produced in nature and by prior art. The present invention breaks away from this region of the van Krevelen diagram by reducing oxygen with lower losses of carbon and hydrogen fuel values.

[0005] Supertorrefied wood and other biomass feedstocks produced by reductive torrefaction by the present invention are expected to find exemplary use in achieving mandated renewable fuel co-burning in coal-fired power generation.

[0006] There are two primary platforms that are currently under investigation for the production of fuels and chemicals from biomass feedstocks: thermochemical and biochemical. While neither one of these platforms has progressed to demonstrate commercial viability, the present invention is primarily focused on using the thermochemical platform.

[0007] It should be noted that a significant contribution to the slow progress of the biochemical platform is the lack of an effective pretreatment step that delivers treated feedstock suitable for enzymatic and cellular biochemical steps to process. The present invention, however, offers effective thermochemical pretreatment options to accelerate progress in this platform as well.

[0008] The primary process categories under investigation within the thermochemical platform are gasification, pyrolysis, and direct liquefaction. One classification of gasification methods is based on the agent employed to treat the feedstock. The most elementary gasifier is the air-blown type, with downdraft, updraft, sidedraft, stratified, bubbling- and circulating-fluid bed, entrained-flow, etc., types investigated. Oxygen-blown and steam-blown are the next most commonly discussed types. Air-blown gasifiers suffer from low fuel value of gas produced, low quality of gas produced, including contamination with water, ash, feedstock fines, tars, and CO2. Effective gas-cleaning technology has yet to emerge to resolve these issues, despite extensive research into water scrubbing, oil scrubbing, thermal cracking, catalytic cracking, dry filtration, and wet electrostatic filtration methods.

[0009] Oxygen- and steam-blown systems offer higher fuel value, but have similar gas quality issues, and additionally require significant investment in auxiliary systems to provide the agent employed. More exotic dual and plasma gasification approaches have not yet demonstrated economic operation of their more capital-intensive systems.

[0010] None of these approaches to gasification rates as “good” in more than one or two of these criteria: feedstock tolerance, syngas quality, development status, scale-up potential, and costs.

[0011] Pyrolysis systems are broadly classified into carbonization, conventional, fast, flash, ultra, vacuum, hydro-, and methano-pyrolysis. Like gasification, pyrolysis converts a feedstock containing gas, liquid, and solid matter to products consisting of gas, liquid, and solid matter. In the most promising of these, fast pyrolysis, liquids are the primary products. However, as produced, these liquids do not find a ready market as fuels or chemicals. Oxygen content, viscosity, and storage stability are among the weaknesses of bio-oils produced by fast pyrolysis in finding a ready market. One limitation in pyrolysis processes in the current art is that liquids produced rely on gases produced to move them out of the reactive zone before being converted to char.

[0012] Supercritical fluid processes employing methane, carbon dioxide, and water as SCF medium are well known to those skilled in the art. However, these processes have not found commercial use in biomass processing. Furthermore, gas expanded liquids for processing are a more recent development and their use in biomass is not currently known. Despite its occurrence as a product of all thermochemical processes for biomass feedstocks, the use of carbon monoxide as a treatment agent does not appear to have been suggested in the extensive prior art, other than its use as a component in synthesis gas or fuel gas.

[0013] The use of carbon monoxide as a reducing agent for solid reagents used for chemical looping has been described in the art. Despite its advantages over hydrogen for removal of oxygen from oxygenated biomass and its thermochemical derivatives, its utility does not appear to have been recognized.

[0014] The use of added gas in pyrolysis to provide additional carrier capacity for liquids produced beyond that of the gases produced increases liquid yield, particularly during initial and final stages of pyrolysis where evolved gas flowrate is low. As is recognized by those skilled in the art, gasification occurs at an equivalence ratio of approximately 0.25, and pyrolysis for positive equivalence ratios below this. The present invention represents thermochemical treatment at negative equivalence ratios. This produces movement along a direction on the van Krevelen diagram toward the desirable regions of lower oxygen content, without sacrificing either carbon or hydrogen content. The result of this is deoxygenation of biomass feedstocks to higher caloric value fuels.

[0015] The presently disclosed process which uses carbon monoxide gas or liquid, or liquid expanded with carbon monoxide to process biomass feedstock for fuel production is directed to overcoming one or more shortcomings in the currently available methods.

SUMMARY

[0016] In accordance with some embodiments of the present invention, a process for producing fuels and chemicals from biomass feedstock is provided. The process includes (a) drying the biomass feedstock using heated dry carbon monoxide gas; (b) devolatilizing the feedstock by reductive torrefaction with heated dry carbon monoxide gas; (c) pulverizing the feedstock; and (d) pyrolyzing the feedstock by reductive pyrolysis with high pressure or high temperature carbon monoxide gas.

[0017] In another aspect of the present invention, an integrated system for producing fuel and chemicals from a biomass feedstock is provided. The system includes a fixed bed; a source of heated dry carbon monoxide gas for drying the feedstock; a source of heated dry carbon monoxide gas for devolatilizing the feedstock; a means for pulverizing the feedstock and a source of high pressure or high temperature carbon monoxide gas for pyrolyzing the feedstock by reductive pyrolysis.

[0018] In another aspect of the present invention, a means for producing fuel and chemicals is provided. The means includes (a) drying the biomass feedstock using heated dry carbon monoxide gas; (b) devolatilizing the feedstock by reductive torrefaction with heated dry carbon monoxide gas; (c) pulverizing the feedstock; and (d) pyrolyzing the feedstock by reductive pyrolysis with high pressure or high temperature carbon monoxide gas.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 presents a Van Krevelen diagram and compares the hydrogen index versus the oxygen index for various biomass feedstock products including wood, lignin and cellulose.

[0020] There has thus been outlined, rather broadly, certain embodiments of the invention in order that the detailed description thereof herein may be better understood, and in order that the present contribution to the art may be better appreciated. There are, of course, additional embodiments of the invention that will be described below and which will form the subject matter of the claims appended hereto.

[0021] In this respect, before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. The invention is capable of aspects in addition to those described and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein, as well as the abstract, are for the purpose of description and should not be regarded as limiting.

[0022] As such, those skilled in the art will appreciate that the conception upon which this disclosure is based may readily be utilized as a basis for the designing of other structures, methods and systems for carrying out the several purposes of the invention. It is important, therefore, that the claims be regarded as including such equivalent constructions insofar as they do not depart from the spirit and scope of the invention.

DETAILED DESCRIPTION

[0023] The present invention relates to a method for processing biomass feedstock for fuel production. In some embodiments, the biomass feedstock is dried using a portion of carbon monoxide gas, super critical carbon monoxide or liquid expanded with carbon monoxide. It should be understood that all references to carbon monoxide herein may refer to carbon monoxide being either solo or in mixtures with e.g., fuel gases, hydrogen, water, carbon dioxide etc., as might be present in gas from gasification or reforming natural gas, coal bed methane or biogas.

[0024] It is preferable to dry the biomass feedstock during processing because the water content will lower the energy content of the feedstock. Dried feedstock can be further processed, pulverized for combustion fuel use, or densified for storage or transport. Wet carbon monoxide can alternatively be dried and recycled to continue to dry feedstock, stored to dry feedstock at a later time, or shifted to produce hydrogen in a water gas shift reactor.

[0025] In another embodiment of the invention, carbon monoxide gas, supercritical carbon monoxide, or liquid expanded with carbon monoxide is used to reductively devolatilize dried biomass feedstock. Devolatilized feedstock, similar to torrefied feedstock, can be further processed, pulverized for combustion fuel use, or densified for storage or transport. Carbon dioxide produced by removal of oxygen from feedstock and its oxygenated decomposition products can be separated and used to convert carbon in feedstock char residues to generate carbon monoxide for use in drying or devolatilization of feedstock.

[0026] In yet another embodiment of the invention, carbon monoxide gas, supercritical carbon monoxide, or liquid expanded with carbon monoxide is used to reductively gasify devolatilized biomass feedstock. Gas and liquids produced in reducing environment offered by carbon monoxide are low in oxygen content and thereby compatible with conventional gas and liquid fuels, as is known in the art for hydrogen treatment to upgrade pyrolysis oils. Feedstock gasification residues, char of desired characteristics, can be further processed, pulverized for combustion fuel use, or densified for storage or transport. Carbon dioxide produced by removal of oxygen from feedstock and its oxygenated decomposition products can be separated and used to convert carbon in feedstock char residues to generate carbon monoxide for use in drying, devolatilization, or gasification of feedstock.

[0027] In yet another embodiment of the invention, carbon monoxide gas, supercritical carbon monoxide, or liquid expanded with carbon monoxide is used to reductively pyrolyze devolatilized biomass feedstock. Gas and liquids produced in reducing environment offered by carbon monoxide are low in oxygen content and thereby compatible with conventional gas and liquid fuels, as is known in the art for hydrogen treatment to upgrade pyrolysis oils. Feedstock gasification residues, char of desired characteristics, can be further processed, pulverized for combustion fuel use, or densified for storage or transport. Carbon dioxide produced by removal of oxygen from feedstock and its oxygenated decomposition products can be separated and used to convert carbon in feedstock char residues to generate carbon monoxide for use in drying, devolatilization, gasification, or pyrolysis of feedstock.

[0028] In yet another embodiment of the invention, carbon monoxide gas, supercritical carbon monoxide, or liquid expanded with carbon monoxide is used to reductively liquefy devolatilized biomass feedstock. Gas and liquids produced in reducing environment offered by carbon monoxide are low in oxygen content and thereby compatible with conventional gas and liquid fuels, as is known in the art for hydrogen treatment to upgrade pyrolysis oils. Feedstock gasification residues, char of desired characteristics, can be further processed, pulverized for combustion fuel use, or densified for storage or transport carbon dioxide produced by removal of oxygen from feedstock and its oxygenated decomposition products can be separated and used to convert carbon in feedstock char residues to generate carbon monoxide for use in drying, devolatilization, gasification, pyrolysis, or liquefaction of feedstock.

[0029] In yet another embodiment of the invention, near critical carbon monoxide gas, supercritical carbon monoxide, or liquid expanded with carbon monoxide is used to extract or extractively convert feedstock polymers, oligomeric decomposition products, and monomeric products of depolymerization of feedstock polymers. Transport of cellulosic decomposition products such as levoglucosan from reactive char matrix allows production of sugars in high yield.

[0030] The processes recited in the above embodiments are accomplished thermally, without the use of a catalyst. Alternatively, the process may be accomplished catalytically, with the use of a catalyst of homogeneous or heterogeneous type.

[0031] In some embodiments of the present invention, the process is carried out in fixed bed mode with a batch of feedstock solids. For example, the following batch process may be performed:

Step	Action
1	Open reactor top.
2	Charge bale.
3	Close reactor.
4	Purge reactor with exhaust gas.
5	Purge reactor with fuel gas. Divert to dump burner on gas heater on defined criteria.

Step	Action
6	Flow hot gas through reactor to hot gas handling system. Divert from wet fuel gas dump burner on gas heater on defined criteria.
7	Purge reactor with exhaust gas. Divert from dump burner on gas heater on defined criteria.
8	Purge reactor with air.
9	Open reactor bottom.
10	Discharge reactor contents to product extruder.
11	Close reactor bottom.

[0032] In yet another embodiment according to the present invention, the process steps may be carried out using a cascade reactor in a continuous flow process as described in U.S. Patent No. 3,801,469, the disclosure of which is fully incorporated herein. In other embodiments, the process may be carried out, in part using an aggressive convective dryer. In yet other embodiments of the present invention, the process may be carried out in a containment vessel having for example, superquadratic geometry as described in U.S. Patent Application Serial No. 13/774,600 entitled “Containment Vessel and Scale-Up Method for Chemical Processes,” the disclosures of which are hereby incorporated by reference in their entirety.

[0033] In some embodiments according to the present invention, there is an integrated system in which biomass feedstock is dried with hot, dry carbon monoxide gas, then devolatilized by reductive torrefaction with hot, dry carbon monoxide gas, then pulverized, then converted to methane, naptha- and diesel-range liquid fuels, and char by reductive pyrolysis with high pressure or high temperature carbon monoxide gas. Any char that is produced is used as adsorbant in purification of liquids and gases produced by reductive pyrolysis reaction, then oxidatively converted to ash and carbon monoxide by treatment with high temperature or high pressure carbon dioxide in a chemical looping conversion reaction accomplished without the addition of foreign oxygen-carrying agents.

[0034] Carbon monoxide generated beyond that needed for feedstock drying, torrefaction, and conversion is used to generate heat and electricity for process use or external sale. Wet carbon monoxide produced in drying and devolatilization/torrefaction is shifted to carbon dioxide and hydrogen, for process use or external sale. Gases and liquids produced in reductive pyrolysis are separated and purified for sale as hydrocarbon-compatible fuels, pipeline quality gas, and low calorific value fuel gas to generate heat and electricity for process use or external sale. Low calorific value gas streams produced in startup, shutdown, purging, and similar auxiliary operations is combusted to control emissions and recover heat. Ash produced in char oxidation is fortified with missing elements and pelletized for sale as fertilizer.

[0035] The advantages of the present invention include, without limitation, simple, flexible, direct conversion of biomass feedstocks to desirable hydrocarbon fuel analogues, including pipeline quality natural gas, clean syngas, gasoline, diesel fuel, aviation fuel, milspec fuels, fuel oils, lubricants, etc., using materials native to the process as transformation agent. Further advantages include reduced yields of undesired co-products; reduced processing temperatures, allowing construction from less costly alloys, especially for high halide containing feedstocks; reduced production of polycyclic aromatic hydrocarbons, dioxins, other refractory organic compounds, and high viscosity by-products.

[0036] Additional features, advantages, and aspects of the disclosure may be set forth or apparent from consideration of the following detailed description, drawings, and claims. Moreover, it is to be understood that both the foregoing summary of the disclosure and the following detailed description are exemplary and intended to provide further explanation without limiting the scope of the disclosure as claimed.

CLAIMS

What is claimed is:

1. A process for producing fuels and chemicals from biomass feedstock comprising the steps of:

(a) drying the biomass feedstock using heated dry carbon monoxide gas;

(b) devolatilizing the feedstock by reductive torrefaction with heated dry carbon monoxide gas;

(c) pulverizing the feedstock; and

(d) pyrolyzing the feedstock by reductive pyrolysis with high pressure or high temperature carbon monoxide gas.

2. The process of claim 1 wherein the carbon monoxide gas used in the drying step is super critical carbon monoxide gas or liquid expanded with carbon monoxide gas.

3. The process of claim 1 wherein the wet carbon monoxide gas produced from the drying step is dried and used again in the drying step.

4. The process of claim 1 further comprising the step of reducing and gasifying the devolatized biomass feedstock using carbon monoxide gas wherein the reducing and gasifying step occurs after the devolatilizing step and before the pulverizing step.

5. The process of claim 1 further comprising the step of reductively pyrolyzing the feedstock using carbon monoxide gas.

6. The process of claim 1 further comprising the step of reductively liquefying devolatized biomass feedstock using carbon monoxide gas.

7. The process of claim 1 wherein a heterogeneous or homogeneous catalyst is used.

8. The process of claim 1 wherein a fixed bed reactor is used to carry out the process steps in a batch process.

9. The process of claim 1 wherein the process is carried out in a continuous flow process.

10. The process of claim 1 wherein the feedstock is converted to one of the group consisting of: methane, naptha and diesel range liquid fuels.

11. An integrated system for producing fuel or chemicals from biomass feedstock comprising:

a fixed bed reactor;

a source of heated dry carbon monoxide gas for drying the feedstock;

a source of heated dry carbon monoxide gas for devolatilizing the feedstock;

a means for pulverizing the feedstock;

a source of high pressure or high temperature carbon monoxide gas for pyrolyzing the feedstock by reductive pyrolysis.

12. The system of claim 11 wherein the carbon monoxide gas used to dry the feedstock is super critical carbon monoxide gas or liquid expanded with carbon monoxide gas.

13. The system of claim 11 wherein wet carbon monoxide gas produced from drying the feedstock is dried and used again to dry the feedstock.

14. The system of claim 11 further comprising the step of reducing and gasifying the devolatized biomass feedstock using carbon monoxide gas wherein the reducing and gasifying step occurs after the devolatilizing step and before the pulverizing step.

15. The system of claim 11 further wherein the feedstock is reductively pyrolizing the feedstock using carbon monoxide gas.

16. The system of claim 10 wherein the devolatized biomass feedstock is reductively liquefied using carbon monoxide gas.

17. The system of claim 10 wherein a heterogeneous or homogeneous catalyst is used.

18. The system of claim 10 wherein the feedstock is converted to one of the group consisting of: methane, naptha and diesel range liquid fuels.

19. The system of claim 10 wherein the fuel and chemicals are produced in batch process.

20. A means for producing fuels and chemicals from biomass feedstock comprising the steps of:

(a) drying the biomass feedstock using heated dry carbon monoxide gas;

(b) devolatilizing the feedstock by reductive torrefaction with heated dry carbon monoxide gas;

(c) pulverizing the feedstock; and

(d) pyrolyzing the feedstock by reductive pyrrolsis with high pressure or high temperature carbon monoxide gas.

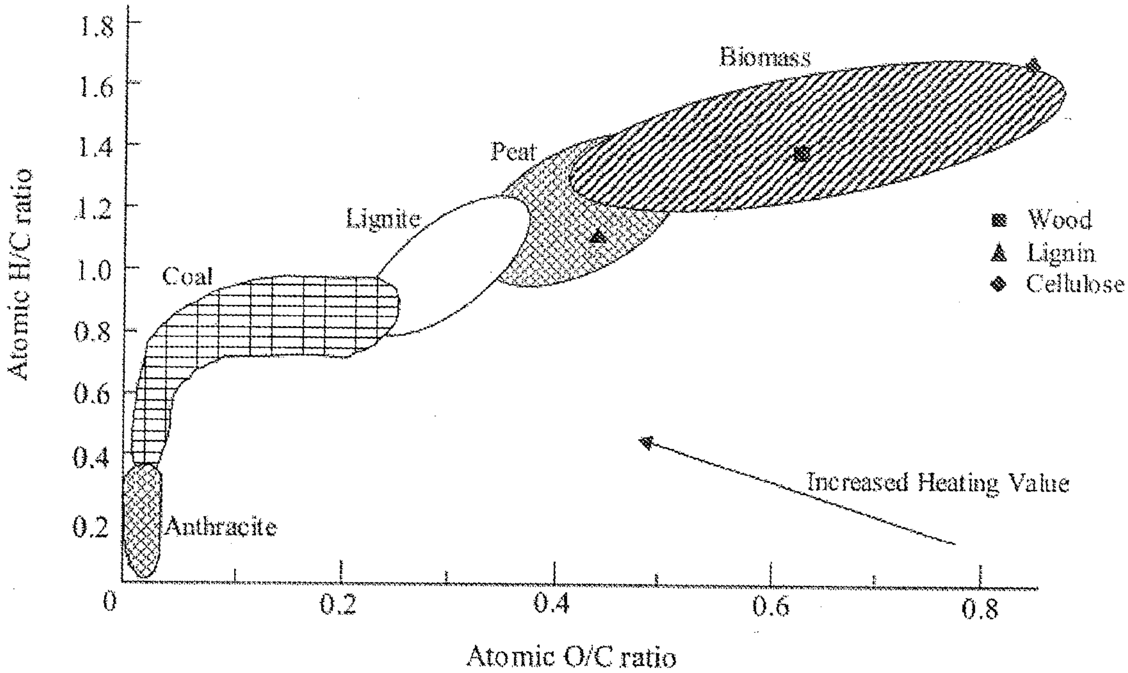
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
Atomic H/C ratio
Atomic O/C ratio
Biomass
Peat
Lignite
Coal
Anthracite
Wood
Lignin
Cellulose
Increased Heating Value

Figure 1

INTERNATIONAL SEARCH REPORT

International application No. PCT/US13/30218

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 1/00; C10G 1/10 (2013.01)

USPC - 585/240; 208/49; 252/373

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)

IPC(8): C07C 1/00; C10G 1/10 (2013.01)
USPC: 208/15, 46, 49; 110/101R, 104R, 106; 252/373, 372

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

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

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); Google Scholar; DialogPRO; Google; dry, dried, desiccate, carbon monoxide, 'CO,' syngas, biomass, trash, landfill, waste, feedstock, feed, pyrolysis, pyrolyze, torrefaction, devolatize, 'reducing gas,' environment, atmosphere, crush, pulverize, grind, superfluidic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4313011 A (WEIL, TA et al.), January 26, 1982; column 3, lines 35-37; column 4, lines 20-48; column 5, lines 63-68; column 6, lines 22-24; column 6, lines 45-53; column 8, lines 36-49;	1, 5, 6, 8-11, 15, 16, 18-20 ----- 2-4, 7, 12-14, 17
Y	US 3634533 A (FRILETTE, VJ), January 11, 1972; column 4, lines 25-46; column 4, lines 57-67 to column 5, lines 1-3	2, 3, 12, 13
Y	WO 2009/079127 A2 (MANZER, L et al.), June 25, 2009; paragraphs [0058]-[0060]	4, 7, 14, 17
A	US 2010/0251614 A1 (JI, KS), October 7, 2010; entire document	1-20
A	US 2005/0095183 A1 (REHMAT, AG et al.), May 5, 2005; entire document	1-20
A	US 4497637 A (PURDY, KR et al.), February 5, 1985; entire document	1-20

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

* 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	Date of mailing of the international search report
19 April 2013 (19.04.2013)	06 MAY 2013

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774