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(54) **Title:** CELLULOSE ESTER COMPOSITIONS DERIVED FROM POST-CONSUMER TIRE CONTENT SYNGAS

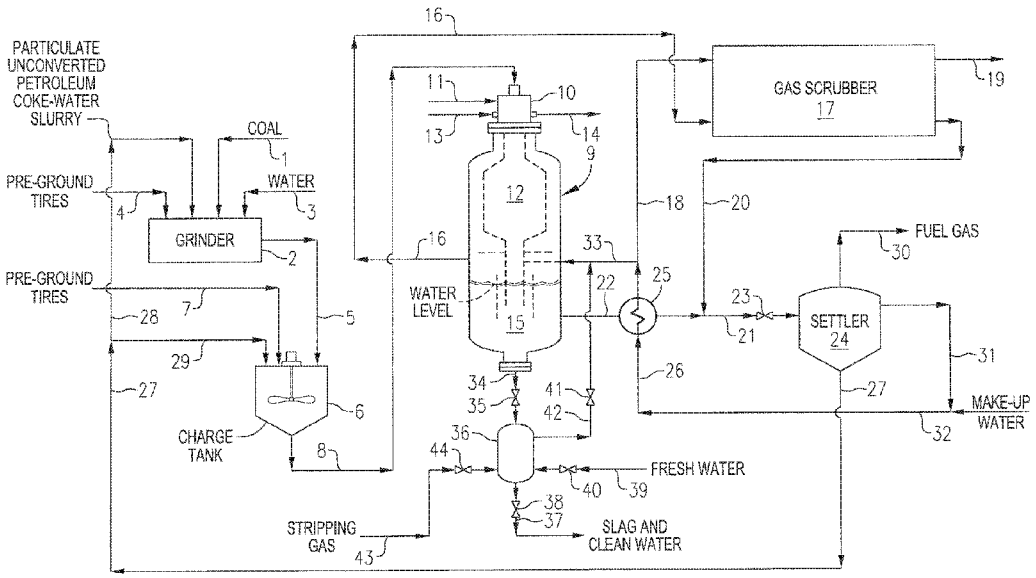


FIG. 1

(57) **Abstract:** A process for preparing a cellulose ester and a cellulose ester composition comprising at least one cellulose ester having at least one substituent on an anhydroglucose unit (AU) derived from post-consumer tire content syngas are provided.

[Continued on next page]

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CELLULOSE ESTER COMPOSITIONS DERIVED FROM POST-CONSUMER TIRE CONTENT SYNGAS

BACKGROUND OF THE INVENTION

[0001] There is a well-known global issue with waste disposal, particularly of large volume consumer products such as plastics, tires, textiles and other polymers that are not considered biodegradable within acceptable temporal limits. There is a public desire to incorporate these types of wastes into new products through recycling, reuse, or otherwise reducing the amount of waste in circulation or in landfills.

[0002] It would be beneficial to provide products having significant amounts of renewable, recycled, re-used and/or biodegradable content.

SUMMARY OF THE INVENTION

[0003] Cellulose ester is a renewable material in that the back bone of the molecule is cellulose. However, the organic acid groups attached to the cellulose backbone that make it an ester and affect the properties of the material are generally made from fossil fuels (e.g., oil, natural gas, coal). The present invention offers a way to include both renewable and recycled content in cellulose esters by providing cellulose esters that are made from cellulose and organic compounds, e.g., acids, derived from recycled, reused or other environmentally favored raw material.

[0004] In one aspect, the invention is directed to a process for preparing a cellulose ester comprising: (1) preparing a post-consumer tire content syngas in a synthesis gas operation by gasifying a feedstock containing a solid fossil fuel source and at least some content of post-consumer tires; (2) using the post-consumer tire content syngas as a feedstock in a reaction scheme to produce at least one cellulose reactant for preparing a cellulose ester; and (3) reacting said at least one cellulose reactant to prepare at least one cellulose ester.

[0005] In another aspect, the invention is directed to use of post-consumer tire content syngas to produce at least one cellulose reactant. In embodiments, the invention is directed to use of post-consumer tire content syngas to produce at least one cellulose ester.

[0006] In another aspect, a cellulose ester composition is provided comprising at least one cellulose ester (e.g., prepared according to one or more of the processes described herein) having at least one substituent on an anhydroglucose unit (AU) derived from post-consumer tire content syngas.

[0007] In an aspect, an article is provided that comprises the cellulose ester composition. In embodiments, the article is a textile fabric. In embodiments, the article is biodegradable and/or compositable. In embodiments, the article is a molded article comprising the cellulose ester. In an embodiment, the molded article is made from a thermoplastic composition comprising the cellulose ester. In an embodiment, the cellulose ester is in the form of a moldable thermoplastic resin.

[0008] In embodiments, a staple fiber is provided comprising the cellulose ester composition, wherein the cellulose ester composition comprises cellulose acetate.

[0009] In another aspect, the invention is directed to an integrated process for preparing a cellulose ester which comprises the processing steps of: (1) preparing a post-consumer tire content syngas in a synthesis gas operation utilizing a feedstock that contains a solid fossil fuel source and at least some content of post-consumer tires; (2) preparing at least one chemical intermediate from said syngas; (3) reacting said chemical intermediate in a reaction scheme to prepare at least one cellulose reactant for preparing a cellulose ester, and/or selecting said chemical intermediate to be at least one cellulose reactant for preparing a cellulose ester; and (4) reacting said at least one cellulose reactant to prepare said cellulose ester; wherein said cellulose ester comprises at least one substituent on an anhydroglucose unit (AGU) derived from post-consumer tire content syngas.

[0010] In embodiments, the processing steps (1) to (4) are carried out in a system that is in fluid and/or gaseous communication.

[0011] In embodiments, the post-consumer tire content syngas can be provided by a process for the production of syngas comprising:

a. charging an oxidant and a feedstock composition comprising post-consumer tires and a solid fossil fuel, to a gasification zone within a gasifier;

b. gasifying the feedstock composition together with the oxidant in a gasification zone to produce a syngas composition; and

c. discharging at least a portion of the syngas composition from the gasifier;

wherein the gasifier is an entrained flow gasifier.

[0012] In embodiments, the post-consumer tire content syngas can be provided by a process for the production of syngas comprising:

a. charging an oxidant and a feedstock slurry composition comprising post-consumer tires and a solid fossil fuel and water, to a gasification zone within a gasifier;

b. gasifying the feedstock composition together with the oxidant in a gasification zone to produce a syngas composition; and

c. discharging at least a portion of the syngas composition from the gasifier.

[0013] In embodiments, the post-consumer tire content syngas can be provided by a process for the production of syngas comprising:

a. charging an oxidant and a feedstock composition comprising post-consumer tires and a solid fossil fuel, to a gasification zone within a gasifier;

b. gasifying the feedstock composition together with the oxidant in a gasification zone to produce a syngas composition; and

c. discharging at least a portion of the syngas composition from the gasifier,

wherein at least one of the following conditions is present:

(i) gasification within the gasification zone is conducted at a temperature of at least 1000℃, or

(ii) the pressure within the gasification zone greater than 2.7 MPa, or

(iii) the feedstock composition is a slurry, or

(iv) no steam is introduced to the gasifier that flows into the gasification zone, or

(v) the tires are pre-ground such that at least 90% of the particles have a particle size of less than 2 mm, or

(vi) the tar yield is less than 4 wt.%, or

(vii) the gasifier contains no membrane wall in the gasification zone, or

(viii) a combination of two or more of the above conditions.

[0014] In embodiments, the post-consumer tire content syngas can be produced from a feedstock slurry composition comprising a post-consumer tires, a solid fossil fuel, and water, wherein the post-consumer tires are pre-ground to a particle size of less than 2 mm, the solid fossil fuel in the feedstock composition has a particle size of less than 2 mm, the solids content in the slurry is at least 62 wt.% (or at least 65 wt.%, or at least 68 wt.%, or at least 69 wt.%, or at least 70 wt.%), the amount of pre-ground tires present in the feedstock stream slurry composition is 0.1 wt.% to 25 wt.% based on the weight of all solids (or 0.5 wt.% to 10 wt.%), and the water is at least 20 wt.% based on the weight of the feedstock slurry composition, and wherein either:

a. the slurry is stable as determined by having an initial viscosity of 100,000 cP or less at 5 minutes, or 10 minutes, or 15 minutes, or 20 minutes, or 25 minutes, or even for 30 minutes using a Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm, measured at ambient conditions; or

b. the slurry is pumpable as determined by having a viscosity of less than 30,000 cP, or 25,000 cP or less, or not more than 23,000 cP, or not more than 20,000 cP, or not more than 18,000 cP, or not more than 15,000 cP, or not more than 13,000 cP, after mixing to obtain a homogeneous distribution of solids throughout the slurry and using a Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm, measured at ambient conditions , or

c. both.

[0015] In embodiments, the post-consumer tire content syngas can comprise a syngas composition discharged from a gasifier and obtained by gasifying a feedstock stream comprising post-consumer waste tires and solid fossil fuel, wherein said syngas stream contains no tar or less than 4 wt.% (or less than 3 wt.%, or not more than 2 wt.%, or not more than 1 wt.%, or not more than 0.5 wt.%, or not more than 0.2 wt.%, or not more than 0.1 wt.%, or not more than 0.08 wt.%, or not more than 0.05 wt.%, or not more than 0.02 wt.%, or not more than 0.01 wt.%, or nor more than 0.005 wt.%) tar, based on the weight of all condensable solids in the syngas composition.

[0016] In embodiments, the post-consumer tire content syngas can comprise a syngas composition stream produced by gasifying in a gasifier a feedstock comprising solid fossil fuel and post-consumer tires (Mixed Feed) having a compositional variability that is 5% or less measured over a time period that is the lesser of 12 days or feeding the Mixed Feed to the gasifier, said syngas compositional variability is measured and satisfied against at least one of the following gaseous compounds (in moles):

a. CO amount, or
b. H_2 amount, or
c. CO2 amount, or
d. CH4 amount, or
e. H2S amount, or
f. COS amount, or
g. H_2 + CO amount, or its molar ratio in sequence (e.g. H2:CO ratio), or
h. H2 + CO + CO2 amount, or its molar ratio in sequence, or
i. H2 + CO + CH4 amount, or its molar ratio in sequence, or
j. H2 + CO + CO2 + CH4 amount, or its molar ratio in sequence, or
k. H2S + COS amount, or its molar ratio in sequence, or
l. H2 + CO + CO_2 + CH_4 + H_2S + COS.

[0017] In embodiments, the post-consumer tire content syngas can comprise a syngas composition stream having a switching variability that is negative, zero, or not more than 15%, wherein the switching frequency is at least is at least 1x/2 years and the switching variability is determined by the following equation:

$$\%SV = \frac{V_m - V_{ff}}{V_{ff}} \times 100$$

where %SW is percent syngas switching variability on one or more measured ingredients in the syngas composition; and

V_m is the syngas compositional variability of a gaseous compound(s) using a mixed stream containing post-consumer tires and the fossil fuel; and

V_{ff} is the syngas compositional variability of the same gaseous compound(s) using a fossil fuel only stream, and where the solids concentration is the same in both cases, the fossil fuel is the same in both cases, and the feedstocks are gasified under the same conditions, other than temperature fluctuations which may autogeneously differ as a result of having tires in the feedstock, and the

variabilities are measured and satisfied against at least one of the following gaseous compounds (in moles):

a. CO amount, or
b. H_2 amount, or
c. CO2 amount, or
d. CH4 amount, or
e. H2S amount, or
f. COS amount, or
g. H2 + CO amount, or its molar ratio in sequence (e.g. H2:CO ratio), or
h. H2 + CO + CO2 amount, or its molar ratio in sequence, or
i. H2 + CO + CH4 amount, or its molar ratio in sequence, or
j. H2 + CO + CO2 + CH4 amount, or its molar ratio in sequence, or
k. H2S + COS amount, or its molar ratio in sequence, or
l. H2 + CO + CO2 + CH_4 + H_2S + COS.

[0018] In embodiments, the process for the production of syngas can comprise:

a. charging an oxidant and a feedstock composition comprising post-consumer tires and a solid fossil fuel to a gasification zone within an entrained flow gasifier;
b. gasifying the feedstock composition together with the oxidant in said gasification zone to produce said syngas composition; and
c. discharging at least a portion of said syngas composition from said gasifier;

wherein said post-consumer tires are added to said solid fossil fuel at a feed point comprising a solid fossil fuel belt feeding a grinder after the solid fossil fuel is loaded on the belt, a solid fossil fuel belt feeding a grinder before the solid fossil fuel is loaded onto the belt, or a solid fossil fuel slurry storage tank containing a slurry of said solid fossil fuel ground to a size as the size fed to the gasification zone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Figure 1 is a schematic plant design for combining tires and solid fossil fuel as a feedstock to a gasification process to produce syngas.

[0020] Figure 2 is another example of a plant design for gasifying a feedstock of tires and solid fossil fuel to produce a syngas stream that is scrubbed.

[0021] Figure 3 is a cross section view of a gasifier injector.

[0022] Figure 4 is a more detailed view of the nozzle section of a gasifier injector.

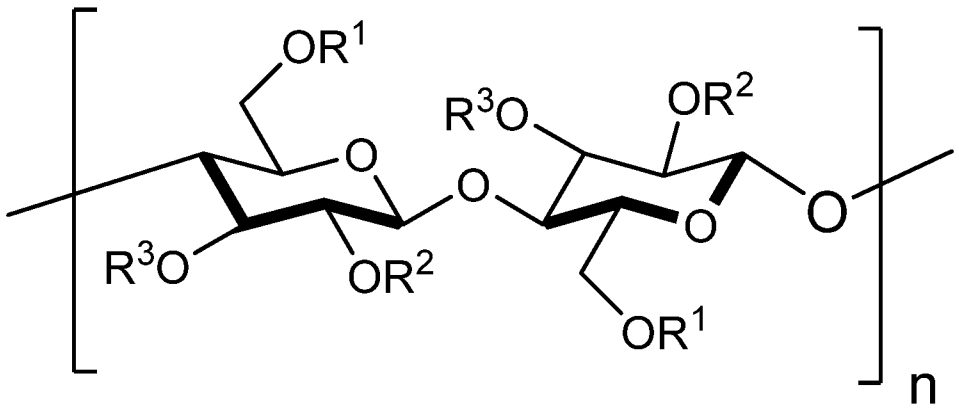
[0023] Figure 5 is a detailed view of the locations for adding post-consumer tires to a solid fossil fuel.

DETAILED DESCRIPTION OF THE INVENTION

Cellulose Esters

[0024] In one embodiment of the invention, a cellulose ester composition is provided comprising at least one cellulose ester having at least one substituent on an anhydroglucose unit (AU) derived from post-consumer tire content syngas.

[0025] In embodiments, the cellulose ester utilized in this invention can be any that is known in the art. Cellulose esters that can be used for the present invention generally comprise repeating units of the structure:



wherein R^1, R^2, and R^3 are selected independently from the group consisting of hydrogen or straight chain alkanoyl having from 2 to 10 carbon atoms. For cellulose esters, the substitution level is usually express in terms of degree of substitution (DS), which is the average number of non-OH substitutents per anhydroglucose unit (AGU). Generally, conventional cellulose contains three hydroxyl groups in each AGU unit that can be substituted; therefore, DS can have a value between zero and three. However, low molecular weight cellulose mixed esters can have a total degree of substitution slightly above 3 due to end group contributions. Native cellulose is a large polysaccharide with a degree of polymerization from 250 – 5,000 even after pulping and purification, and thus the assumption that the maximum DS is 3.0 is approximately correct. However, as the degree of polymerization is lowered, as in low molecular weight cellulose mixed esters, the end groups of the polysaccharide backbone become relatively more significant, thereby resulting in a DS that can range in excess of 3.0. Low molecular weight cellulose mixed esters are discussed in more detail subsequently in this disclosure. Because DS is a statistical mean value, a value of 1 does not assure that every AGU has a single substitutent. In some cases, there can be unsubstituted anhydroglucose units, some with two and some with three substitutents, and typically the value will be a non-integer. Total DS is defined as the average number of all of substituents per anhydroglucose unit. The degree of substitution per AGU can also refer to a particular substitutent, such as, for example, hydroxyl, acetyl, butyryl, or propionyl.

[0026] In embodiments, the cellulose ester utilized can be a cellulose triester or a secondary cellulose ester. Examples of cellulose triesters include, but are not limited to, cellulose triacetate, cellulose tripropionate, or cellulose tributyrate. Examples of secondary cellulose esters include cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate.

[0027] In one embodiment of the invention, the cellulose ester can be chosen from cellulose acetate (CA), cellulose propionate (CP), cellulose butyrate (CB), cellulose acetate propionate (CAP), cellulose acetate butyrate

(CAB), cellulose propionate butyrate (CPB), and the like, or combinations thereof. Examples of such cellulose esters are described in U.S. Pat. Nos. 1,698,049; 1,683,347; 1,880,808; 1,880,560; 1,984,147, 2,129,052; and 3,617,201, incorporated herein by reference in their entirety to the extent that they do not contradict the statements herein.

[0028] In embodiments of the invention, the cellulose esters have at least 2 anhydroglucose rings and can have between at least 50 and up to 5,000 anhydroglucose rings. The number of anhydroglucose units per molecule is defined as the degree of polymerization (DP) of the cellulose ester. In embodiments, n is in a range from 20 to 2,500, or 25 to 2,000, or 25 to 1,000, or 50 to 500, or 50 to 250. In embodiments, cellulose esters can have an inherent viscosity (IV) of about 0.2 to about 3.0 deciliters/gram, or about 0.5 to about 1.8, or about 1 to about 1.5, as measured at a temperature of 25°C for a 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane. Examples of cellulose esters include, but are not limited to, cellulose acetate, cellulose diacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), cellulose propionate butyrate, and the like. In embodiments, cellulose esters useful herein can have a DS/AGU of about 2 to about 2.99, and the substituting ester can comprise acetyl, propionyl, butyryl, or any combinations of these. In another embodiment of the invention, the total DS/AGU ranges from about 2 to about 2.99 and the DS/AGU of acetyl ranges from about 0 to 2.2, with the remainder of the ester groups comprising propionyl, butyryl or combinations thereof.

[0029] Cellulose esters can be produced by any method known in the art. Examples of processes for producing cellulose esters are taught in Kirk-Othmer, Encyclopedia of Chemical Technology, 5th Edition, Vol. 5, Wiley-Interscience, New York (2004), pp. 394-444. Cellulose, the starting material for producing cellulose esters, can be obtained in different grades and sources such as from cotton linters, softwood pulp, hardwood pulp, corn fiber and other agricultural sources, and bacterial cellulose, among others.

[0030] One method of producing cellulose esters is esterification of the cellulose by mixing cellulose with the appropriate organic acids, acid anhydrides, and catalysts. Cellulose is then converted to a cellulose triester. Ester hydrolysis is then performed by adding a water-acid mixture to the cellulose triester, which can then be filtered to remove any gel particles or fibers. Water is then added to the mixture to precipitate the cellulose ester. The cellulose ester can then be washed with water to remove reaction by-products followed by dewatering and drying.

[0031] The cellulose triesters to be hydrolyzed can have three substitutents selected independently from alkanoyls having from 2 to 10 carbon atoms. Examples of cellulose triesters include cellulose triacetate, cellulose tripropionate, and cellulose tributyrate or mixed triesters of cellulose such as cellulose acetate propionate, and cellulose acetate butyrate. These cellulose esters can be prepared by a number of methods known to those skilled in the art. For example, cellulose esters can be prepared by heterogeneous acylation of cellulose in a mixture of carboxylic acid and anhydride in the presence of a catalyst such as H_2SO_4. Cellulose triesters can also be prepared by the homogeneous acylation of cellulose dissolved in an appropriate solvent such as LiCl/DMAc or LiCl/NMP.

[0032] Those skilled in the art will understand that the commercial term of cellulose triesters also encompasses cellulose esters that are not completely substituted with acyl groups. For example, cellulose triacetate commercially available from Eastman Chemical Company, Kingsport, TN, U.S.A., typically has a DS from about 2.85 to about 2.99.

[0033] After esterification of the cellulose to the triester, part of the acyl substitutents can be removed by hydrolysis or by alcoholysis to give a secondary cellulose ester. As noted previously, depending on the particular method employed, the distribution of the acyl substituents can be random or non-random. Secondary cellulose esters can also be prepared directly with no hydrolysis by using a limiting amount of acylating reagent. This process is particularly useful when the reaction is conducted in a solvent that will

dissolve cellulose. All of these methods yield cellulose esters that are useful in this invention.

[0034] In one embodiment, the secondary cellulose esters useful in the present invention have an absolute weight average molecular weight (Mw) from about 5,000 to about 400,000 as measured by gel permeation chromatography (GPC) according to ASTM D6474. The following method is used to calculate the absolute weight average molecular weight values (Mw) for CE. The solvent is THF stabilized with BHT Preservative. The instrumentation for the THF/cellulose ester procedure consists of the following Agilent 1200 series components: degasser, isocratic pump, auto-sampler, column oven, UV/Vis detector and a refractive index detector. The test temperature is 30°C and flow rate is 1.0 ml/min. A sample solution of 25 mg cellulose ester in 10 ml THF with BHT preservative and 10 µl toluene flow rate marker is made. The injection volume is 50 µl. The column set is Polymer Laboratories 5 µm PLgel, Guard + Mixed C + Oligopore. The detection is by refractive index. The calibrants are monodisperse polystyrene standards, Mw=580 to 3,220,000 from Polymer Laboratories. The universal calibration parameters are as follows: PS (K=0.0001280 and a=0.7120) and CE (K=0.00007572 and a=0.8424). The universal calibration parameters above were determined by light scattering and viscometery to yield the correct weight average molecular weights. In a further embodiment, the Mw is from about 15,000 to about 300,000. In yet further embodiments, the Mw ranges from about 10,000 to about 250,000; from about 15000 to 200000; from about 20,000 to about 150,000; from about 50,000 to about 150,000, or from about 70,000 to about 120,000.

[0035] The most common commercial secondary cellulose esters are prepared by initial acid catalyzed heterogeneous acylation of cellulose to form the cellulose triester. After a homogeneous solution in the corresponding carboxylic acid of the cellulose triester is obtained, the cellulose triester is then subjected to hydrolysis until the desired degree of substitution is

obtained. After isolation, a random secondary cellulose ester is obtained. That is, the relative degree of substitution (RDS) at each hydroxyl is roughly equal.

[0036] The cellulose esters useful in the present invention can be prepared using techniques known in the art, and can be chosen from various types of cellulose esters, such as for example the cellulose esters that can be obtained from Eastman Chemical Company, Kingsport, TN, U.S.A., e.g., Eastman™ Cellulose Acetate Propionate CAP 482-20, Eastman™ Cellulose Acetate Propionate CAP 141-20, Eastman™ Cellulose Acetate Butyrate CAB 381-20, Cellulose Acetate Butyrate CAB 171-15 and Eastman™ Cellulose Acetate CA 398-30.

[0037] In embodiments, the cellulose esters can contain chemical functionality and are described herein as either derivatized, modified, or functionalized cellulose esters. Functionalized cellulose esters can be produced by reacting the free hydroxyl groups of cellulose esters with a bifunctional reactant that has one linking group for grafting to the cellulose ester and one functional group to provide a new chemical group to the cellulose ester. Examples of such bifunctional reactants include succinic anhydride which links through an ester bond and provides acid functionality; mercaptosilanes which links through alkoxysilane bonds and provides mercapto functionality; and isocyanotoethyl methacrylate which links through a urethane bond and gives methacrylate functionality.

[0038] In one embodiment of the invention, functionalized cellulose esters are produced by reacting the free hydroxyl groups of the cellulose esters with a bifunctional reactant producing a cellulose ester with at least one functional group selected from the group consisting of unsaturation (double bonds), carboxylic acids, acetoacetate, acetoacetate imide, mercapto, melamine, and long alkyl chains.

[0039] Bifunctional reactants to produce cellulose esters containing unsaturation (double bonds) functionality are described in U.S. Patents 4,839,230, 5,741,901, 5,871,573, 5,981,738, 4,147,603, 4,758,645, and 4,861,629; all of which are incorporated by reference to the extent they do not

contradict the statements herein. In one embodiment, the cellulose esters containing unsaturation is produced by reacting a cellulose ester containing residual hydroxyl groups with an acrylic based compound and m-isopropyenyl-α,α'-dimethylbenzyl isocyanate. The grafted cellulose ester is a urethane-containing product having pendant (meth)acrylate and α-methylstyrene moieties. In another embodiment, the cellulose esters containing unsaturation is produced by reacting maleic anhydride and a cellulose ester in the presence of an alkaline earth metal or ammonium salt of a lower alkyl monocarboxylic acid catalyst, and at least one saturated monocarboxylic acid have 2 to 4 carbon atoms. In another embodiment, the cellulose esters containing unsaturation is produced from the reaction product of (a) at least one cellulosic polymer having isocyanate reactive hydroxyl functionality, and (b) at least one hydroxyl reactive poly(alpha,beta ethyleneically unsaturated) isocyanate.

[0040] Bifunctional reactants to produce cellulose esters containing carboxylic acid functionality are described in U.S. Patents 5,384,163, 5,723,151, and 4,758,645; all of which are incorporated by reference to the extent they do not contradict the statements herein. In one embodiment, the cellulose esters containing carboxylic acid functionality are produced by reacting a cellulose ester and a mono- or di-ester of maleic or furmaric acid, thereby obtaining a cellulose derivative having double bond functionality. In another embodiment, the cellulose esters containing carboxylic acid functionality has a first and second residue, wherein the first residue is a residue of a cyclic dicarboxylic acid anhydride and the second residue is a residue of an oleophilic monocarboxylic acid and/or a residue of a hydrophilic monocarboxylic acid. In yet another embodiment, the cellulose esters containing carboxylic acid functionality are cellulose acetate phthalates, which can be prepared by reacting cellulose acetate with phthalic anhydride.

[0041] Bifunctional reactants to produce cellulose esters containing acetoacetate functionality are described in U.S. Patent 5,292,877; which is incorporated by reference to the extent it does not contradict the statements

herein. In one embodiment, the cellulose esters containing acetoacetate functionality are produced by contacting: (i) cellulose; (ii) diketene, an alkyl acetoacetate, 2,2,6, trimethyl-4H 1,3-dioxin-4-one, or a mixture thereof, and (iii) a solubilizing amount of solvent system comprising lithium chloride plus a carboxamide selected from the group consisting of 1-methyl-2-pyrolidinone, N,N dimethylacetamide, or a mixture thereof.

[0042] Bifunctional reactants to produce cellulose esters containing acetoacetate imide functionality are described in U.S. Patent 6,369,214 which is incorporated by reference to the extent it does not contradict the statements herein. Cellulose esters containing acetoacetate imide functionality are the reaction product of a cellulose ester and at least one acetoacetyl group and an amine functional compound comprising at least one primary amine.

[0043] Bifunctional reactants to produce cellulose esters containing mercapto functionality are described in U.S. Patent 5,082,914; which is incorporated by reference to the extent it does not contradict the statements herein. In one embodiment of the invention, the cellulose ester is grafted with a silicon-containing thiol component which is either commercially available or can be prepared by procedures known in the art. Examples of silicon-containing thiol compounds include, but are not limited to, (3-mercaptopropyl)trimethoxysilane, (3-mercaptopropyl)-dimethyl-methoxysilane, (3-mercaptopropyl)dimethoxymethylsilane, (3-mercaptopropyl)dimethylchlorosilane, (3-mercaptopropyl)dimethylethoxysilane, (3-mercaptopropyl)diethyoxy-methylsilane, and (3-mercapto-propyl)triethoxysilane.

[0044] Bifunctional reactants to produce cellulose esters containing melamine functionality are described in U.S. Patent 5,182,379; which is incorporated by reference to the extent it does not contradict the statements herein. In one embodiment, the cellulose esters containing melamine functionality are prepared by reacting a cellulose ester with a melamine compound to form a grafted cellulose ester having melamine moieties grafted to the backbone of the anhydrogluclose rings of the cellulose ester. In one

embodiment, the melamine compound is selected from the group consisting of methylol ethers of melamine and aminoplast resins.

[0045] Bifunctional reactants to produce cellulose esters containing long alkyl chain functionality are described in U.S. Patent 5,750,677; which is incorporated by reference to the extent it does not contradict the statements herein. In one embodiment, the cellulose esters containing long alkyl chain functionality is produced by reaction of cellulose in a carboxamide diluents or a urea-based diluent with an acylating reagent using a titanium-containing specifies. Cellulose esters containing long alkyl chain functionality can be selected from the group consisting of cellulose acetate hexanoate, cellulose acetate nonanoate, cellulose acetate laurate, cellulose palmitate, cellulose acetate stearate, cellulose nonanoate, cellulose hexanoate, cellulose hexanoate propionate, and cellulose nonanoate propionate.

[0046] In embodiments of the invention, the cellulose esters can be prepared by converting cellulose to cellulose esters with reactants that are obtained from a post-consumer tire content syngas source. In embodiments, such reactants can be cellulose reactants that include organic acids and/or acid anhydrides used in the esterification or acylation reactions of the cellulose, e.g., as discussed herein.

[0047] By "post-consumer tire content syngas" is meant syngas obtained from a synthesis gas operation utilizing a feedstock that contains a solid fossil fuel source and at least some content of post-consumer tires, as described in the various embodiments more fully herein below. In embodiments, the post-consumer tire content syngas can be made in accordance with any of the processes for producing syngas described herein; can comprise, or consist of, any of the syngas compositions or syngas composition streams described herein; or can be made from any of the feedstock slurry compositions described herein.

[0048] In embodiments, the feedstock (for the synthesis gas operation) can be in the form of a combination of one or more particulated fossil fuel sources and particulated post-consumer tires. In one embodiment, the solid fossil fuel

source can include coal. In one embodiment, the feedstock is in the form of an aqueous slurry that comprises coal and post-consumer tires. In embodiments, the feedstock is fed to a gasifier along with an oxidizer gas, and the feedstock is converted to syngas, as described more fully herein.

[0049] In embodiments, the post-consumer tire content syngas is utilized to make at least one chemical intermediate in a reaction scheme to make a cellulose ester (CE intermediate). In embodiments, the post-consumer tire content syngas can be a component of feedstock (used to make at least one CE intermediate) that includes other sources of syngas, hydrogen, carbon monoxide, or combinations thereof. In one embodiment, the only source of syngas used to make the CE intermediates is the post-consumer tire content syngas.

[0050] In embodiments, the CE intermediates made using the post-consumer tire content syngas can be chosen from methanol, acetic acid, methyl acetate, acetic anhydride and combinations thereof. In embodiments, the CE intermediates can be a at least one reactant or at least one product in one or more of the following reactions: (1) syngas conversion to methanol; (2) syngas conversion to acetic acid; (3) methanol conversion to acetic acid, e.g., carbonylation of methanol to produce acetic acid; (4) producing methyl acetate from methanol and acetic acid; and (5) conversion of methyl acetate to acetic anhydride, e.g., carbonylation of methyl acetate and methanol to acetic acid and acetic anhydride.

[0051] In embodiments, post-consumer tire content syngas is used to produce at least one cellulose reactant. In embodiments, the post-consumer tire content syngas is used to produce at least one cellulose ester.

[0052] In embodiments, the post-consumer tire content syngas is utilized to make acetic anhydride. In embodiments, syngas that comprises post-consumer tire content syngas is first converted to methanol and this methanol is then used in a reaction scheme to make acetic anhydride. "PCTS acetic anhydride" refers to acetic anhydride that is derived from post-consumer tire content syngas. Derived from means that at least some of the feedstock

source material (that is used in any reaction scheme to make a CE intermediate) has some content of post-consumer tire content syngas.

[0053] In embodiments, the PCTS acetic anhydride is utilized as a CE intermediate reactant for the esterification of cellulose to prepare a cellulose ester, as discussed more fully above. In embodiments, the PCTS acetic acid is utilized as a reactant to prepare cellulose acetate or cellulose diacetate.

[0054] In embodiments, the PCTS acetic anhydride is utilized to make a biodegradable cellulose ester.

[0055] In one aspect, a cellulose ester composition is provided that comprises at least one cellulose ester having at least one substituent on an anhydroglucose unit (AGU) derived from post-consumer tire content syngas. In embodiments, the substituent is a combination of acetyl and propionyl functional groups. In embodiments, the substituent is a combination of acetyl and butyryl functional groups. In embodiments, the substituent is any combination of organic acid functional groups. In an embodiment, the at least one substituent is an acetyl functional group.

[0056] In embodiments, the cellulose ester is cellulose di-acetate (CDA). In an embodiment, the cellulose ester is cellulose tri-acetate (CTA).

[0057] In embodiments, the cellulose ester is prepared from a cellulose reactant that comprises acetic anhydride that is derived from post-consumer tire content syngas.

[0058] In embodiments, the post-consumer tire content syngas comprises gasification products from a gasification feedstock. In an embodiment, the gasification products are produced by a gasification process using a gasification feedstock that comprises post-consumer tires. In embodiments, the gasification feedstock comprises coal.

[0059] In embodiments, the gasification feedstock comprises a liquid slurry that comprises coal and post-consumer tires. In embodiments, the gasification process comprises gasifying said gasification feedstock in the presence of oxygen.

[0060] In one aspect, a cellulose ester composition is provided that comprises at least one cellulose ester having at least one substituent on an anhydroglucose unit (AGU) derived from one or more chemical intermediates, at least one of which is obtained at least in part from post-consumer tire content syngas.

[0061] In aspects, an article is provided that comprises the cellulose ester compositions, as described herein. In embodiments, the article is a textile fabric. In embodiments, the article is biodegradable and/or compositable. In embodiments, a staple fiber is provided that comprises a cellulose ester composition that comprises cellulose acetate, as described herein.

[0062] In embodiments, the cellulose ester is biodegradable. In embodiments, the cellulose ester is biodegradable and contains content derived from a renewable source, e.g., cellulose from wood or cotton linter, and content derived from a recycled material source, e.g., post-consumer tires. Thus, in embodiments, a thermoplastic material is provided that is biodegradable and contains both renewable and recycled content, i.e., made from renewable and recycled sources.

[0063] In one aspect, the invention is directed to a fiber comprising at least one cellulose ester, as described herein. In embodiments, sheets, webs or fabrics are provided that comprise such fibers. In embodiments, the sheets, webs or fabrics can be woven or non-woven. In embodiments, the sheets, webs or fabrics can be wet laid or dry laid.

[0064] In another aspect, the invention is directed to a spun yarn that comprises at least one cellulose ester, as described herein. In embodiments, fibers comprising at least one cellulose ester can be prepared by spinning fibers. The fibers can be spun as a continuous fiber or can be cut to a desired length.

[0065] In embodiments, the invention can include fibers, filaments, yarns and nonwoven fabrics as described in WO2018/160588 A1, published on September 7, 2018 (Applicant: Eastman Chemical Company), the contents of which is incorporated herein by reference, with the proviso that the fibers,

filaments, yarns or nonwoven fabrics comprise at least one cellulose ester having post-consumer tire content, as described more fully herein.

[0066] In another aspect, the invention is directed to a textile fabric comprising fibers that comprise at least one cellulose ester, as described herein. In embodiments, the textile fabric can be prepared from spun yarns comprising at least one cellulose ester, as described herein.

[0067] It has been found that slivers can be successfully formed from CA staple fibers and further processed successfully to spun yarns to make textile fabric. CA staple fibers may be environmentally-friendly, exhibit thermoplastic behavior, have a soft feel similar to that of cotton, and can be processed using both new and existing processing equipment.

[0068] As used herein, textile fabrics are materials made from spun yarn and that are either woven, knitted, crocheted, knotted, embroidered, braided/plaited, laced, or carpet piling. Textile fabrics can include geotextile fabrics, carpet pilings, and fabrics (which includes cloth). The geotextile fabrics as used in the context of a textile fabric herein are those that are woven or knitted. Examples of suitable types of textile fabrics formable from the inventive staple fibers can include, but are not limited to, clothing (undergarments, socks, hats, shirts, pants, dresses, scarves, gloves, etc.), bags, baskets, upholstered furnishings, window shades, towels, table cloths, bed coverings, flat surface coverings, in art work, filters, flags, backpacks, tents, handkerchiefs, rags, balloons, kites, sails, parachutes, automotive upholstery, protective clothing such as against heat for firefighters and welders, protective clothing for bullet armor or stab protection, medical textile fabrics such as implants, and agrotextile fabrics for crop protection. A CA staple fiber means a cellulose acetate staple fiber, and a “staple fiber” refers to a fiber cut from a continuous filament or tow band of continuous filaments. A carded sliver, spun yarn, or textile fabric “obtained from” a described element includes any number and type of intervening steps or process operations.

[0069] Staple fibers as described herein may be formed from one or more cellulose esters including, but not limited to, cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate formate, cellulose acetate propionate, cellulose acetate butyrate, cellulose propionate butyrate, and mixtures thereof. Although described herein with reference to "cellulose acetate," it should be understood that one or more of the above cellulose acid esters or mixed esters may also be used to form the fibers, nonwovens, and articles as described herein. Various types of cellulose esters are described, for example, in U.S. Patent Nos. 1,698,049; 1,683,347; 1,880,808; 1,880,560; 1,984,147, 2,129,052; and 3,617,201, each of which is incorporated herein by reference to the extent not inconsistent with the present disclosure. In some cases, other types of treated or regenerated cellulose (*e.g.*, viscose, rayon, or lyocell) may or may not be used in forming staple fibers as described herein.

[0070] When the staple fiber is formed from cellulose acetate, it may be formed from cellulose diacetate, cellulose triacetate, or mixtures thereof. The cellulose acetate (or other cellulose ester) useful in embodiments of the present invention can have a degree of substitution in the range of from 1.9 to 2.9. As used herein, the term "degree of substitution" or "DS" refers to the average number of acyl substituents per anhydroglucose ring of the cellulose polymer, wherein the maximum degree of substitution is 3.0, as described above. In some cases, the cellulose acetate used to form fibers as described herein may have an average degree of substitution of at least about 1.95, 2.0, 2.05, 2.1, 2.15, 2.2, 2.25, or 2.3 and/or not more than about 2.9, 2.85, 2.8, 2.75, 2.7, 2.65, 2.6, 2.55, 2.5, 2.45, 2.4, or 2.35, with greater than 90, 91, 92, 93, 94, 95, 96, 97, 98, or 99 percent of the cellulose acetate having a degree of substitution greater than 2.15, 2.2, or 2.25. In some cases, greater than 90 percent of the cellulose acetate can have a degree of substitution greater than 2.2, 2.25, 2.3, or 2.35. Typically, acetyl groups can make up at least about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 60 percent and/or not more than about 99, 95, 90, 85, 80, 75, or 70 percent of the total acyl substituents.

[0071] In embodiments, the cellulose acetate may have a weight-average molecular weight (M_w) of not more than 90,000, measured using gel permeation chromatography with N-methyl-2-pyrrolidone (NMP) as the solvent. In some cases, the cellulose acetate may have a molecular weight of at least about 10,000, at least about 20,000, 25,000, 30,000, 35,000, 40,000, or 45,000 and/or not more than about 100,000, 95,000, 90,000, 85,000, 80,000, 75,000, 70,000, 65,000, 60,000, or 50,000.

[0072] In an aspect, the invention is directed to a staple fiber formed from cellulose acetate, as described herein. In embodiments, the fiber is at least partially coated with at least one finish. In embodiments, the fiber has a denier per filament of less than about 3.0 and a crimp frequency of less than 22 crimps per inch (CPI). In embodiments, a plurality of the fibers exhibits a fiber-to-fiber staple pad coefficient of friction of not more than about 0.70.

[0073] In aspects of the invention, a carded sliver is provided comprising CA staple fibers that comprise cellulose acetate prepared according to the methods described herein. A carded sliver is a continuous bundle or strand of loose untwisted fibers that are aligned generally relatively parallel to each other. This alignment is conducted by subjecting the fibers to a carding process.

[0074] Optionally, the carded sliver can be combed, which may be a desirable operation on natural fibers for very fine yarns intended to make finer fabrics. In combining, fine tooth combs are applied to the sliver to further separate and remove fibers that are too short and further align the fibers parallel to each other.

[0075] The carded sliver can be the output of a carding machine that is not yet subjected to combing (if used) and drawing operations. In embodiments, the carded sliver desirably has a total denier of at least 10,000 or least 15,000, or at least 20,000, or at least 25,000, or at least 30,000, or at least 35,000, or at least 40,000, or at least 45,000, or at least 50,000. In general, the sliver total denier would not exceed 200,000, or not exceed 150,000, or not exceed 100,000, or not exceed 80,000, or not exceed 60,000, or not

exceed 50,000. For most applications, the sliver will have a total denier of 20,000 to 80,000, or 25,000 to 60,000 or 30,000 to 60,000. If one desires to convert the sliver denier to grains, a conversion factor of 60 grain sliver = 35,000 denier is used.

[0076] In embodiments, spun yarns are provided that are obtained from one or more carded slivers, where at least one of the carded slivers comprise CA staple fibers (as described herein). Slivers and spun yarns of the present invention may be formed according to any suitable process.

[0077] In embodiments, carded slivers, spun yarn, and textile fabrics can be blends of CA staple fibers with other fibers that are not CA staple fibers. The CA staple fibers may be present in a sliver or spun yarn or in an amount of at least 5, or at least 10, or at least 15, or at least 20, or at least 25, or at least 30, or at least 35, or at least 40, or at least 45 wt.% and up to 70 or up to 60, or up to 55, or up to 52, or up to 50, or up to 45, or up to 40, or up to 35, or up to 30, or up to 25, or up to 22, or up to 20 wt.%, based on the total weight of the blend. One or more of the other fibers may be present in an amount of at least about 5, or at least 10, or at least 15, or at least 20, or at least 25, or at least 30, or at least 35, or at least 40, or at least 45, or at least 50, or at least 55, or at least 60, or at least 65, or at least 70, or at least 75, or at least 80 weight percent. Compositions of specific blends can be determined according to AATCC TM20A-2014, No. 1. Examples of suitable ranges of the CA staple fibers in the sliver, spun yarn, or textile fabric include from 5 to 70, or 5 to 65, or 5 to 60, or 5 to 55, or 5 to 50, or 5 to 45, or 5 to 40 or 5 to 35, or 5 to 30, or 5 to 25, or 5 to 25, or 5 to 20, or 10 to 70, or 10 to 65, or 10 to 60, or 10 to 55, or 10 to 50, or 10 to 45, or 10 to 40 or 10 to 35, or 10 to 30, or 10 to 25, or 10 to 25, or 10 to 20, or 15 to 70, or 15 to 65, or 15 to 60, or 15 to 55, or 15 to 50, or 15 to 45, or 15 to 40 or 15 to 35, or 15 to 30, or 15 to 25, or 15 to 25, or 15 to 20, or 20 to 70, or 20 to 65, or 20 to 60, or 20 to 55, or 20 to 50, or 20 to 45, or 20 to 40 or 20 to 35, or 20 to 30, or 20 to 25 wt% based on the weight of all fibers in the sliver, spun yarn, or textile fabric.

[0078] Other types of fibers suitable for use in a blend with CA staple fibers can include natural and/or synthetic fibers including, but not limited to, cotton, rayon, viscose) or other types of regenerated cellulose such as Cupro, Tencel, Modal, and Lyocell cellulose, acetates such as polyvinylacetate, wool, glass, polyamides including nylon, polyesters such as polyethylene terephthalate (PET), polycyclohexylenedimethylene terephthalate (PCT) and other copolymers, olefinic polymers such as polypropylene and polyethylene, polycarbonates, poly sulfates, poly sulfones, polyethers, acrylics, acrylonitrile copolymers, polyvinylchloride (PVC), poly lactic acid, poly glycolic acid and combinations thereof.

[0079] In embodiments, the fibers (e.g., staple fibers), and yarns and nonwovens formed therefrom can be biodegradable, meaning that such fibers are expected to decompose under certain environmental conditions. The degree of degradation can be characterized by the weight loss of a sample over a given period of exposure to certain environmental conditions. In some cases, the material used to form the staple fibers, the fibers, or the nonwoven webs or articles produced from the fibers can exhibit a weight loss of at least about 5, 10, 15, or 20 percent after burial in soil for 60 days and/or a weight loss of at least about 15, 20, 25, 30, or 35 percent after 15 days of exposure to a typical municipal composter. However, the rate of degradation may vary depending on the particular end use of the fibers, as well as the composition of the remaining article, and the specific test. Exemplary test conditions are provided in U.S. Patent No. 5,970,988 and U.S. Patent No. 6,571,802.

[0080] In some embodiments, the cellulose ester fibers may be biodegradable fibers and such fibers may be used to form fibrous articles such as textiles, nonwoven fabrics, filters, and yarns. It has been found that cellulose ester fibers as described herein exhibit enhanced levels of environmental non-persistence, characterized by better-than-expected degradation under various environmental conditions. Fibers and fibrous articles described herein may meet or exceed passing standards set by

international test methods and authorities for industrial compostability, home compostability, and/or soil biodegradability.

[0081] To be considered "compostable," a material must meet the following four criteria: (1) the material must be biodegradable; (2) the material must be disintegrable; (3) the material must not contain more than a maximum amount of heavy metals; and (4) the material must not be ecotoxic. As used herein, the term "biodegradable" generally refers to the tendency of a material to chemically decompose under certain environmental conditions. Biodegradability is an intrinsic property of the material itself, and the material can exhibit different degrees of biodegradability, depending on the specific conditions to which it is exposed. The term "disintegrable" refers to the tendency of a material to physically decompose into smaller fragments when exposed to certain conditions. Disintegration depends both on the material itself, as well as the physical size and configuration of the article being tested. Ecotoxicity measures the impact of the material on plant life, and the heavy metal content of the material is determined according to the procedures laid out in the standard test method.

[0082] The cellulose ester fibers can exhibit a biodegradation of at least 70 percent in a period of not more than 50 days, when tested under aerobic composting conditions at ambient temperature (28 °C ± 2 °C) according to ISO 14855-1 (2012). In some cases, the cellulose ester fibers can exhibit a biodegradation of at least 70 percent in a period of not more than 49, 48, 47, 46, 45, 44, 43, 42, 41, 40, 39, 38, or 37 days when tested under these conditions, also called "home composting conditions." These conditions may not be aqueous or anaerobic. In some cases, the cellulose ester fibers can exhibit a total biodegradation of at least about 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, or 88 percent, when tested under according to ISO 14855-1 (2012) for a period of 50 days under home composting conditions. This may represent a relative biodegradation of at least about 95, 97, 99, 100, 101, 102, or 103 percent, when compared to cellulose subjected to identical test conditions.

[0083] To be considered "biodegradable," under home composting conditions according to the French norm NF T 51-800 and the Australian standard AS 5810, a material must exhibit a biodegradation of at least 90 percent in total (*e.g.,* as compared to the initial sample), or a biodegradation of at least 90 percent of the maximum degradation of a suitable reference material after a plateau has been reached for both the reference and test item. The maximum test duration for biodegradation under home compositing conditions is 1 year. The cellulose ester fibers as described herein may exhibit a biodegradation of at least 90 percent within not more than 1 year, measured according 14855-1 (2012) under home composting conditions. In some cases, the cellulose ester fibers may exhibit a biodegradation of at least about 91, 92, 93, 94, 95, 96, 97, 98, 99, or 99.5 percent within not more than 1 year, or the fibers may exhibit 100 percent biodegradation within not more than 1 year, measured according 14855-1 (2012) under home composting conditions.

[0084] Additionally, or in the alternative, the fibers described herein may exhibit a biodegradation of at least 90 percent within not more than about 350, 325, 300, 275, 250, 225, 220, 210, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, or 50 days, measured according 14855-1 (2012) under home composting conditions. In some cases, the fibers can be at least about 97, 98, 99, or 99.5 percent biodegradable within not more than about 70, 65, 60, or 50 days of testing according to ISO 14855-1 (2012) under home composting conditions. As a result, the cellulose ester fibers may be considered biodegradable according to, for example, French Standard NF T 51-800 and Australian Standard AS 5810 when tested under home composting conditions.

[0085] The cellulose ester fibers can exhibit a biodegradation of at least 60 percent in a period of not more than 45 days, when tested under aerobic composting conditions at a temperature of 58℃ (± 2℃) according to ISO 14855-1 (2012). In some cases, the fibers can exhibit a biodegradation of at least 60 percent in a period of not more than 44, 43, 42, 41, 40, 39, 38, 37,

36, 35, 34, 33, 32, 31, 30, 29, 28, or 27 days when tested under these conditions, also called "industrial composting conditions." These may not be aqueous or anaerobic conditions. In some cases, the fibers can exhibit a total biodegradation of at least about 65, 70, 75, 80, 85, 87, 88, 89, 90, 91, 92, 93, 94, or 95 percent, when tested under according to ISO 14855-1 (2012) for a period of 45 days under industrial composting conditions. This may represent a relative biodegradation of at least about 95, 97, 99, 100, 102, 105, 107, 110, 112, 115, 117, or 119 percent, when compared to cellulose fibers subjected to identical test conditions.

[0086] To be considered "biodegradable," under industrial composting conditions according to ASTM D6400 and ISO 17088, at least 90 percent of the organic carbon in the whole item (or for each constituent present in an amount of more than 1% by dry mass) must be converted to carbon dioxide by the end of the test period when compared to the control or in absolute. According to European standard ED 13432 (2000), a material must exhibit a biodegradation of at least 90 percent in total, or a biodegradation of at least 90 percent of the maximum degradation of a suitable reference material after a plateau has been reached for both the reference and test item. The maximum test duration for biodegradability under industrial compositing conditions is 180 days. The cellulose ester fibers described herein may exhibit a biodegradation of at least 90 percent within not more than 180 days, measured according 14855-1 (2012) under industrial composting conditions. In some cases, the cellulose ester fibers may exhibit a biodegradation of at least about 91, 92, 93, 94, 95, 96, 97, 98, 99, or 99.5 percent within not more than 180 days, or the fibers may exhibit 100 percent biodegradation within not more than 180 days, measured according 14855-1 (2012) under industrial composting conditions.

[0087] Additionally, or in the alternative, cellulose ester fibers described herein may exhibit a biodegradation of least 90 percent within not more than about 175, 170, 165, 160, 155, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, or 45 days, measured

according 14855-1 (2012) under industrial composting conditions. In some cases, the cellulose ester fibers can be at least about 97, 98, 99, or 99.5 percent biodegradable within not more than about 65, 60, 55, 50, or 45 days of testing according to ISO 14855-1 (2012) under industrial composting conditions. As a result, the cellulose ester fibers described herein may be considered biodegradable according ASTM D6400 and ISO 17088 when tested under industrial composting conditions.

[0088] The fibers or fibrous articles may exhibit a biodegradation in soil of at least 60 percent within not more than 130 days, measured according to ISO 17556 (2012) under aerobic conditions at ambient temperature. In some cases, the fibers can exhibit a biodegradation of at least 60 percent in a period of not more than 130, 120, 110, 100, 90, 80, or 75 days when tested under these conditions, also called "soil composting conditions." These may not be aqueous or anaerobic conditions. In some cases, the fibers can exhibit a total biodegradation of at least about 65, 70, 72, 75, 77, 80, 82, or 85 percent, when tested under according to ISO 17556 (2012) for a period of 195 days under soil composting conditions. This may represent a relative biodegradation of at least about 70, 75, 80, 85, 90, or 95 percent, when compared to cellulose fibers subjected to identical test conditions.

[0089] In order to be considered "biodegradable," under soil composting conditions according the OK biodegradable SOIL conformity mark of Vinçotte and the DIN Geprüft Biodegradable in soil certification scheme of DIN CERTCO, a material must exhibit a biodegradation of at least 90 percent in total (*e.g.,* as compared to the initial sample), or a biodegradation of at least 90 percent of the maximum degradation of a suitable reference material after a plateau has been reached for both the reference and test item. The maximum test duration for biodegradability under soil compositing conditions is 2 years. The cellulose ester fibers as described herein may exhibit a biodegradation of at least 90 percent within not more than 2 years, 1.75 years, 1 year, 9 months, or 6 months measured according ISO 17556 (2012) under soil composting conditions. In some cases, the cellulose ester fibers may

exhibit a biodegradation of at least about 91, 92, 93, 94, 95, 96, 97, 98, 99, or 99.5 percent within not more than 2 years, or the fibers may exhibit 100 percent biodegradation within not more than 2 years, measured according ISO 17556 (2012) under soil composting conditions.

[0090] Additionally, or in the alternative, cellulose ester fibers described herein may exhibit a biodegradation of at least 90 percent within not more than about 700, 650, 600, 550, 500, 450, 400, 350, 300, 275, 250, 240, 230, 220, 210, 200, or 195 days, measured according 17556 (2012) under soil composting conditions. In some cases, the cellulose ester fibers can be at least about 97, 98, 99, or 99.5 percent biodegradable within not more than about 225, 220, 215, 210, 205, 200, or 195 days of testing according to ISO 17556 (2012) under soil composting conditions. As a result, the cellulose ester fibers described herein may meet the requirements to receive The OK biodegradable SOIL conformity mark of Vinçotte and to meet the standards of the DIN Geprüft Biodegradable in soil certification scheme of DIN CERTCO.

[0091] In some embodiments, cellulose ester fibers (or fibrous articles) of the present invention may include less than 1, 0.75, 0.50, or 0.25 weight percent of components of unknown biodegradability. In some cases, the fibers or fibrous articles described herein may include no components of unknown biodegradability.

[0092] In addition to being biodegradable under industrial and/or home composting conditions, cellulose ester fibers or fibrous articles as described herein may also be compostable under home and/or industrial conditions. As described previously, a material is considered compostable if it meets or exceeds the requirements set forth in EN 13432 for biodegradability, ability to disintegrate, heavy metal content, and ecotoxicity. The cellulose ester fibers or fibrous articles described herein may exhibit sufficient compostability under home and/or industrial composting conditions to meet the requirements to receive the OK compost and OK compost HOME conformity marks from Vinçotte.

[0093] In some cases, the cellulose ester and fibers and fibrous articles described herein may have a volatile solids concentration, heavy metals and fluorine content that fulfill all of the requirements laid out by EN 13432 (2000). Additionally, the cellulose ester fibers may not cause a negative effect on compost quality (including chemical parameters and ecotoxicity tests).

[0094] In some cases, the cellulose ester fibers or fibrous articles can exhibit a disintegration of at least 90 percent within not more than 26 weeks, measured according to ISO 16929 (2013) under industrial composting conditions. In some cases, the fibers or fibrous articles may exhibit a disintegration of at least about 91, 92, 93, 94, 95, 96, 97, 98, 99, or 99.5 percent under industrial composting conditions within not more than 26 weeks, or the fibers or articles may be 100 percent disintegrated under industrial composting conditions within not more than 26 weeks. Alternatively, or in addition, the fibers or articles may exhibit a disintegration of at least 90 percent under industrial compositing conditions within not more than about 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, or 10 weeks, measured according to ISO 16929 (2013). In some cases, the cellulose ester fibers or fibrous articles described herein may be at least 97, 98, 99, or 99.5 percent disintegrated within not more than 12, 11, 10, 9, or 8 weeks under industrial composting conditions, measured according to ISO 16929 (2013).

[0095] In some cases, the cellulose ester fibers or fibrous articles can exhibit a disintegration of at least 90 percent within not more than 26 weeks, measured according to ISO 16929 (2013) under home composting conditions. In some cases, the fibers or fibrous articles may exhibit a disintegration of at least about 91, 92, 93, 94, 95, 96, 97, 98, 99, or 99.5 percent under home composting conditions within not more than 26 weeks, or the fibers or articles may be 100 percent disintegrated under home composting conditions within not more than 26 weeks. Alternatively, or in addition, the fibers or articles may exhibit a disintegration of at least 90 percent within not more than about 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, or 15 weeks under home composting conditions, measured according to ISO 16929 (2013). In some

cases, the cellulose ester fibers or fibrous articles described herein may be at least 97, 98, 99, or 99.5 percent disintegrated within not more than 20, 19, 18, 17, 16, 15, 14, 13, or 12 weeks, measured under home composting conditions according to ISO 16929 (2013).

[0096] In embodiments, cellulose acetate fibers are provided that comprise post-consumer tire content and are biodegradable and/or compostable. It is believed that the cellulose acetate fibers can achieve higher levels of biodegradability and/or compostability without use of additives that have traditionally been used to facilitate environmental non-persistence of similar fibers. Such additives can include, for example, photodegradation agents, biodegradation agents, decomposition accelerating agents, and various types of other additives. Despite being substantially free of these types of additives, in embodiments, the cellulose acetate fibers and articles can be provided that exhibit enhanced biodegradability and compostability when tested under industrial, home, and/or soil conditions, as discussed herein.

[0097] In some embodiments, the cellulose acetate fibers described herein may be substantially free of photodegradation agents. For example, the fibers may include not more than about 1, 0.75, 0.50, 0.25, 0.10, 0.05, 0.025, 0.01, 0.005, 0.0025, or 0.001 weight percent of photodegradation agent, based on the total weight of the fiber, or the fibers may include no photodegradation agents. Examples of such photodegradation agents include, but are not limited to, pigments which act as photooxidation catalysts and are optionally augmented by the presence of one or more metal salts, oxidizable promoters, and combinations thereof. Pigments can include coated or uncoated anatase or rutile titanium dioxide, which may be present alone or in combination with one or more of the augmenting components such as, for example, various types of metals. Other examples of photodegradation agents include benzoins, benzoin alkyl ethers, benzophenone and its derivatives, acetophenone and its derivatives, quinones, thioxanthones, phthalocyanine and other photosensitizers, ethylene-carbon monoxide copolymer, aromatic ketone-metal salt sensitizers, and combinations thereof.

[0098] In some embodiments, the cellulose acetate fibers described herein may be substantially free of biodegradation agents and/or decomposition agents. For example, the fibers may include not more than about 1, 0.75, 0.50, 0.25, 0.10, 0.05, 0.025, 0.01, 0.005, 0.0025, 0.0020, 0.0015, 0.001, 0.0005 weight percent of biodegradation agents and/or decomposition agents, based on the total weight of the fiber, or the fibers may include no biodegradation and/or decomposition agents. Examples of such biodegradation and decomposition agents include, but are not limited to, salts of oxygen acid of phosphorus, esters of oxygen acid of phosphorus or salts thereof, carbonic acids or salts thereof, oxygen acids of phosphorus, oxygen acids of sulfur, oxygen acids of nitrogen, partial esters or hydrogen salts of these oxygen acids, carbonic acid and its hydrogen salt, sulfonic acids, and carboxylic acids.

[0099] Other examples of such biodegradation and decomposition agents include an organic acid selected from the group consisting of oxo acids having 2 to 6 carbon atoms per molecule, saturated dicarboxylic acids having 2 to 6 carbon atoms per molecule, and lower alkyl esters of the oxo acids or the saturated dicarboxylic acids with alcohols having from 1 to 4 carbon atoms. Biodegradation agents may also comprise enzymes such as, for example, a lipase, a cellulase, an esterase, and combinations thereof. Other types of biodegradation and decomposition agents can include cellulose phosphate, starch phosphate, calcium secondary phosphate, calcium tertiary phosphate, calcium phosphate hydroxide, glycolic acid, lactic acid, citric acid, tartaric acid, malic acid, oxalic acid, malonic acid, succinic acid, succinic anhydride, glutaric acid, acetic acid, and combinations thereof.

[0100] Cellulose acetate fibers described herein may also be substantially free of several other types of additives that have been added to other fibers to encourage environmental non-persistence. Examples of these additives can include, but are not limited to, polyesters, including aliphatic and low molecular weight (e.g., less than 5000) polyesters, enzymes, microorganisms, water soluble polymers, modified cellulose acetate, water-dispersible

additives, nitrogen-containing compounds, hydroxy-functional compounds, oxygen-containing heterocyclic compounds, sulfur-containing heterocyclic compounds, anhydrides, monoepoxides, and combinations thereof. In some cases, the fibers described herein may include not more than about 0.5, 0.4, 0.3, 0.25, 0.1, 0.075, 0.05, 0.025, 0.01, 0.0075, 0.005, 0.0025, or 0.001 weight percent of these types of additives, or the cellulose acetate fibers may not include any of these types of additives.

[0101] In another aspect, durable articles are provided that comprise the cellulose esters, as described herein. In embodiments, the durable articles are made from moldable thermoplastic material comprising the cellulose esters, as described herein. In embodiments, the moldable thermoplastic material comprises cellulose esters chosen from cellulose acetate propionate, cellulose acetate butyrate, or combinations thereof.

[0102] In another aspect, an integrated process for preparing a cellulose ester is provide which comprises the processing steps of: (1) preparing a post-consumer tire content syngas in a synthesis gas operation utilizing a feedstock that contains a solid fossil fuel source and at least some content of post-consumer tires; (2) preparing at least one chemical intermediate from said syngas; (3) reacting said chemical intermediate in a reaction scheme to prepare at least one cellulose reactant for preparing a cellulose ester, and/or selecting said chemical intermediate to be at least one cellulose reactant for preparing a cellulose ester; and (4) reacting said at least one cellulose reactant to prepare said cellulose ester; wherein said cellulose ester comprises at least one substituent on an anhydroglucose unit (AGU) derived from post-consumer tire content syngas.

[0103] In embodiments, the processing steps (1) to (4) are carried out in a system that is in fluid and/or gaseous communication (i.e., including the possibility of a combination of fluid and gaseous communication). It should be understood that the chemical intermediates, in one or more of the reaction schemes for producing cellulose esters starting from post-consumer tire

content syngas, may be temporarily stored in storage vessels and later reintroduced to the integrated process system.

[0104] In embodiments, the at least one chemical intermediate is chosen from methanol, methyl acetate, acetic anhydride, acetic acid, or combinations thereof. In embodiments, one chemical intermediate is methanol, and the methanol is used in a reaction scheme to make a second chemical intermediate that is acetic anhydride. In embodiments, the cellulose reactant is acetic anhydride.

Gasification Process

[0105] Unless otherwise stated, reference the weight of the feedstock stream includes all solids, and if present liquids, fed to the gasifier, and unless otherwise stated, does not include the weight of any gases in the feedstock stream as fed to the injector or gasifier.

[0106] For purposes of classifying materials in the feedstock stream, a fossil fuel used is coal, petcoke, or any other solid at 25°C and 1 atmosphere that is a byproduct from refining oil or petroleum. The fossil fuel portion of the feedstock stream is to be distinguished from post-consumer materials such as tires, even if those post-consumer materials are carbonaceous and derived from raw materials obtained from refining crude oil.

[0107] Post-consumer tires have presented a disposal problem because they are not biodegradable, they are vulcanized making their depolymerization impractical and economically unfeasible, and they contain steel wire. At lower temperatures, tires can incompletely combust to produce tarry products.

[0108] Generally, in a synthesis gas operation the feedstock stream comprised of finely particulated fossil fuel sources (e.g. coal, petcoke) and particulated rubber tires, and optionally water and other chemical additives, are injected along with an oxidizer gas into gasification reaction zone or chamber of a synthesis gas generator (gasifier). A hot gas stream is produced in the reaction zone, desirably refractory lined, at high temperature

and pressure generating a molten slag, ash, soot, and gases including hydrogen, carbon monoxide, carbon dioxide and can include other gases such as methane, hydrogen sulfide and nitrogen depending on the fuel source and reaction conditions. The hot gas stream is produced in the reaction zone is cooled using a syngas cooler or in a quench water bath at the base of the gasifier which also solidifies ash and slag and separates solids from the gases. The quench water bath also acts as a seal to maintain the internal temperature and pressure in the reactor while the slag, soot and ash are removed into a lock hopper. The cooled product gas stream removed from the gasifier (the raw syngas stream) is further treated with a scrubber to remove remaining solids, and then further treated to remove acid gas (e.g. hydrogen sulfide) after optionally further cooling and shifting the ratio of carbon monoxide to hydrogen.

[0109] The post-consumer tires employed in the feedstock stream are tires that (i) have been used at least once for its intended application for any duration of time regardless of wear, and (ii) scrap, and (iii) out of specification tires that have not been used. While the latter two categories are generally considered pre-consumer tires, they are deemed for purposes of this invention to be included as a "post-consumer tire" since such tires are not usable by the consumer, and are not biodegradable, and may find their way into the same supply stream as used tires. Suitable sources of post-consumer tires in category (i) include those used on passenger cars, light trucks (vans, pick-up trucks, light utility vehicles), heavy trucks and buses, and other such as bicycle, motor cycle, agriculture, air plane, construction, and mining.

[0110] In one embodiment, the pre-ground tires comprise an average of at least 70 wt.% truck and bus tires, based on the weight of the tires used in the feedstock stream and based over any three-day period. In another embodiment, the tires are at least 70 wt.% passenger car and light truck tires, based on the weight of the tires used in the feedstock stream.

[0111] The rubber tires, as a co-fuel in a feedstock stream, have the advantage of not requiring thermal treatment prior to their introduction into the gasification zone or their introduction to one or more components of a feedstock stream. Unlike wood or grain which typically requires a thermal treatment beyond drying such as torrefaction, the tires do not receive a thermal treatment (above their pyrolysis temperature or above 150 °C, or above 110 °C, or above 100 °C, or above 90 °C, or above 80 °C, or above 60 °C, or above 58 °C or above their nominal temperature at their ambient conditions), or are not torrefied, prior to their introduction into the gasification zone. Further, unlike many biomass feedstocks which reduce the cold gas efficiency of the reactor and generate higher amounts of CO_2 and water which reduce the gasifier efficiency, tires can be co-fed with other solid fossil fuels as they are more similar in composition while substantially maintaining the gasifier efficiency and cold gas efficiency. It is to be noted that the tires can be dried before their introduction into the feedstock stream, however, this would not be necessary in a slurry-based feedstock stream.

[0112] The process is flexible to permit the introduction of a wide range of tires. The composition of the tires is not particularly limited. The post-consumer will generally have two components: the elastomer and the cord. The cord can contain metal such as steel, or natural fibers such as cotton or silk, or synthetic fibers such as nylon and aramids. The elastomer is generally natural rubber or a synthetic rubber such as butadiene-based rubber, styrene-butadiene copolymer based rubber, or butyl rubbers optionally halogenated, nitride rubber, isoprene rubber, neoprene rubber polysulphide rubber, and mixtures thereof. Other common materials found in tires include carbon black and silica, antioxidants, antiozonants, and curing systems such as sulfur and zinc oxide used in vulcanizing the rubber. The total amount of carbon (free or fixed) in all materials added to the solid fossil fuel, or in the tires, is at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%. The total amount of material in the pre-ground tires, other than the cord and elastomer and carbon black, is

generally not more 7 wt.%, or not more than 6 wt.%, or not more than 5 wt.%, or not more than 4 wt.%, based on the weight of the tires.

[0113] In an embodiment, at least 50 wt.%, or at least 70 wt.%, or at least 80 wt.%, or at least 90 wt.% of the tires are vulcanized. In another embodiment, the pre-ground tires used in the feedstock stream have an average fixed carbon content of at least 60 wt.%, or at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, based on the weight of the pre-ground tires.

[0114] The pre-ground tires may have an average sulfur content of at least 0.1 wt.%, or at least 0.2 wt.%, or at least 0.5 wt.%, or at least 0.8 wt.%, or at least 1 wt.%, or at least 1.2 wt.%, or at least 1.4 wt.%, based on the weight of the pre-ground tires. The upper amount is not particularly limited, but generally will be lower than 5 wt.%, or up to 4 wt.%, or up to 3 wt.%, or up to 2.5 wt.%, or up to 2 wt.%, based on the weight of the pre-ground tires.

[0115] The pre-ground tires may have an average ash content of at least 1 wt.%, or at least 2 wt.%, or at least 3 wt.%, or at least 4 wt.%, and up to 15 wt.%, or up to 12 wt.%, or up to 10 wt.%, or up to 8 wt.%. The tire ash content is similar to the typical ash content of coal used for gasification which may range from 3-10 wt.%, more typically in the 4-7 wt.% range.

[0116] In another embodiment, the average content of minerals, metals and elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur, in the pre-ground tires is at least 0.5 wt.%, or at least 0.8 wt.%, or at least 1 wt.%, or at least 1.2 wt.%, or at least 1.5 wt.%, or at least 1.8 wt.%, or at least 2 wt.%, or at least 2.3 wt.%, or at least 2.5 wt.%, or at least 2.8 wt.%, or at least 3 wt.%, based on the weight of the pre-ground tires. The upper amount is not particularly limited, although an excessive amount of metals and minerals at high concentrations can result in excessive accumulation of solids in the quench zone of a gasifier that must be removed, and therefore, should generally not exceed 8 wt.%, or not exceed 7 wt.%, or not exceed 6 wt.%, or not exceed 5 wt.%, or not exceed 4.5 wt.%, or not exceed 4 wt.%, or not exceed 3.8 wt.%.

[0117] The post-consumer tires (hereinafter referred to as "tires" for convenience) charged to the gasifier have been treated by at least one granulation step to reduce the size of the tires from either their original form or from their form as shredded/chipped tires having an average size of 1/4 inch or more in their longest dimension. Desirably, the tires, prior to arrival at a gasification facility, have been treated with a first pass of granulation or shredding from the original form of the tire in order to separate coarse metal and textile belts/wires from the rubber prior to their arrival to the gasification facility and make it feasible to conduct fine granulation. The coarsely granulated tires are then further finely granulated, and optionally further pulverizing or milling, to the final desired particle size. The gasification facility can receive pre-granulated tires at their final particle size, or can receive coarsely ground tires and the operator/owner of the gasification facility can conduct the granulation step(s) necessary to obtain the desired particle size present in the feedstock stream.

[0118] The tires are pre-ground prior to addition to other fossil fuels, meaning they are ground, and optionally but desirably sieved, to the final particle size prior to combining them with coal or pet-coke. As explained below, the tires in their original size, or as coarsely ground (e.g. average of 1/4 inch or more in their largest dimension or even 0.5 inches or more), cannot be processed through an entrained flow coal gasifier. Further, the elasticity of the tires makes them unsuited for co-granulating with more hard and brittle carbonaceous fuel sources like coal or pet coke.

[0119] The tires are pre-ground to a suitable particle size, optionally sieved, and then combined with one or more fossil fuel components of the feedstock stream at any location prior to introducing the feedstock stream into gasification zone within the gasifier. As noted above, tires are not easily ground concurrently in the same equipment used to grind coal, particularly in a slurry, since the tires are soft, elastic and non-friable. However, the coal grinding equipment will provide an excellent source of energy for mixing pre-ground tires with the fossil fuel while reducing the size of the coal particles.

Therefore, one of the desirable locations for combining pre-ground tires having a target size for feeding into the gasifier is into the equipment used for grinding the other carbonaceous fossil fuel sources (e.g. coal, pet-coke). This location is particularly attractive in a slurry fed gasifier because it is desirable to use a feed having the highest stable solids concentration possible, and at higher solids concentration, the viscosity of the slurry is also high. The torque and shear forces employed in fossil fuel grinding equipment is high, and coupled with the shear thinning behavior of a coal slurry, good mixing of the pre-ground tires with the ground fossil fuel can be obtained in the fossil fuel grinding equipment.

[0120] Other locations for combining pre-ground tires with fossil fuel sources can be onto the fossil fuel loaded on the main fossil fuel belt feeding a grinder, or onto the main fossil fuel belt feeding a grinder before the fossil fuel is loaded onto the belt, or into a fossil fuel slurry storage tank containing a slurry of fossil fuel ground to the final size, particularly if the storage tank is agitated.

[0121] In additional embodiments of the invention, Figure 5 shows four locations where post-consumer tire content can be introduced.

[0122] Figure 5 illustrates the advantages of these addition points described above. All of these points are in the low-pressure section of the process thus reducing the cost of modifications which would be minor and could be relatively easy to add to an existing system. The addition points are similar in other gasification plants.

[0123] In an embodiment of the invention shown in Figure 5, the post-consumer tire content can be introduced and added to the solid fossil fuel at location **100**, the main coal feed belt. The post-consumer tires are metered onto the main coal feed belt as it moves past with the solid fossil fuel (e.g. coal) feed already loaded onto the belt. The post-consumer tires are added to the belt using a weigh belt feeder, or other similar device, to measure the mass of the material, and the speed of the belt to determine addition rate. Coal is similarly added to the same belt and would be underneath the post-

consumer tires. The combined solid mixture of the coal and post-consumer tires in the proper ratio are then conveyed to surge hoppers and other storage and conveying equipment until it is ultimately fed to the coal grinding mill. In the coal grinding mill, the coal, post-consumer tires, water and viscosity modifiers are mixed thoroughly, and the coal is reduced in size to the target grind size distribution and the mixture becomes a viscous slurry. The post-consumer tires undergoes very little size reduction since it is a softer material, but benefits from the extreme mixing in the mill due to its inclusion into the slurry production process. The post-consumer tires are pre-ground to the desired size, or a size as noted herein (e.g. a mean of less than 2 mm) and, other than processes which crush or size reduce the solid fossil fuel, does not undergo any further size reduction after combining with the solid fossil fuel. In one embodiment, the pre-ground tires are not further size reduces after combining with the solid fossil fuel and water.

[0124] In another embodiment of the invention, post-consumer tire content can be introduced as shown in Figure 5 location number **110**. This is the same process as described in location number **100** above, except that the post-consumer tires are added to the main coal belt first, before the coal is added. In this manner, coal is on top or covers the post consume tires. Since the post-consumer tires will be pre-ground and may inherently be less dense than coal, it may be easier for this material to be blown off of the belt in a strong wind. With the much coarser and more dense coal covering the recycled material, this dusting and loss of material will be greatly reduced.

[0125] In another embodiment the invention, the post-consumer tire content can be added at location number **120**, the grinding mill. The existing equipment, coal, water and viscosity modifiers are already added to the grinding mill to reduce the particle size of the coal and produce a viscous slurry high in solids. The post-consumer tires can be independently conveyed to the entry point of the mill and added directly to the mill in the proper ratio. The mill will then grind the coal, produce the slurry and thoroughly mix in the

post-consumer tires in the process. This avoids wind and weather effects on the coal, recycled material mixture.

[0126] In yet another embodiment of the invention the post-consumer tire content can be introduced at location number **130**, the slurry storage tank. Since the post-consumer tires are pre-ground to the proper particle size for introduction into the gasifier, it can be added to the slurry storage tank directly after the grinding/slurry operation. Alternatively, it can be added to the tank through a separate screen or the screen used by the slurry to ensure no large particles are passed to the tank. This is the last low-pressure addition point before the slurry is pumped at pressure to the gasifier. This will minimize the amount of material in process that is mixed together. The agitation in the slurry tanks will mix in the post-consumer tires to ensure it is evenly distributed.

[0127] The coal slurry is pumped at high pressure through an injector into the gasifier. Alternatively, to the options above, the recycled material, could be slurried and pumped to the gasifier in a similar way to a second feed injector or even share the coal slurry injector. This would give ultimate control of the two feed materials and would be desirable on a theoretical basis. However, this method would be extremely expensive to implement in an existing system and even in a new build. Also, the recycled material does not slurry as well as coal (lower slurry solids) and would therefore carry additional unwanted water to the gasifier system.

[0128] This invention is described for a coal/water slurry gasifier, but would apply directly to a gasifier utilizing petroleum coke, slurry fed gasifier as well as conceptually to a dry coal fed gasifier.

[0129] The fossil fuel (coal or petcoke) and the tires are ground or milled for multiple purposes. The tires must be ground to a small size as does the fossil fuel source to (i) allow for faster reaction once inside the gasifier due to mass transfer limitations, (ii) to create a slurry that is stable, fluid and flowable at high concentrations of coal to water, and (iii) to pass through processing equipment such as high-pressure pumps, valves, and feed injectors that have

tight clearances. Typically, this means that the solids in the feedstock, including the tires, are ground to a particle size in which at least 90% of the particles are 2 mm or smaller.

[0130] The tires are desirably ground to a particle size that, after optional sieving, is acceptable for gasifying within the design parameters of the gasifier. Desirably, the particle size of the tires used in the feedstock, or as fed to or combined with a solid fuel, is 2 mm and smaller or constitute those particles passing through a 10 mesh, or 1.7 mm or smaller (those particles passing through a 12 mesh), or 1.4 mm or smaller (those particles passing through a 14 mesh), or 1.2 mm or smaller (those particles passing through a 16 mesh), or 1 mm or smaller (those particles passing through a 18 mesh), or 0.85 mm or smaller (those particles passing through a 20 mesh), or 0.7 mm or smaller (those particles passing through a 25 mesh) or 0.6 mm or smaller (those particles passing through a 30 mesh), or 0.5 mm or smaller (those particles passing through a 35 mesh), or 0.4 mm or smaller (those particles passing through a 40 mesh), or 0.35 mm or smaller (those particles passing through a 45 mesh), or 0.3 mm or smaller (those particles passing through a 50 mesh), or 0.25 mm or smaller (those particles passing through a 60 mesh), or 0.15 mm or smaller (those particles passing through a 100 mesh), or 0.1 mm or smaller (those particles passing through a 140 mesh), or 0.07 mm or smaller (those particles passing through a 200 mesh), or 0.044 mm or smaller (those particles passing through a 325 mesh), or 0.037 mm or smaller (those particles passing through a 400 mesh). In another embodiment, the size of the ground tire particles is at least 0.037 mm (or 90% retained on a 400 mesh). The sample of pre-ground tires will be considered to be within a stated particle size limit if 90 vol.% of the sample is within the stated limits.

[0131] In one embodiment, the particle size of the pre-ground rubber tires as used in the feedstock composition is 0.1 mm or smaller (or those particles passing through a 140 mesh), or 0.7 mm or smaller (those particles passing through a 200 mesh), or 0.044 mm or smaller (those particles passing through

a 325 mesh), or 0.037 mm or smaller (those particles passing through a 400 mesh).

[0132] In another embodiment, the particle sizes of rubber and the fossil fuels can be sufficiently matched to retain the stability of the slurry and avoid a coal/rubber separation at high solids concentrations prior to entering the gasification zone in the gasifier. A feedstock stream that phase separates, whether between solids/liquid or rubber/fossil fuel, can plug lines, created localized zones of gasified rubber, create inconsistent ratios of fossil fuel/tire, and can impact the consistency of the syngas composition. Variables to consider for determining the optimal particle size of the ground tires include the bulk density of the ground coal, the concentration of all solids in the slurry if a slurry is used, the effectiveness of any additives employed such as surfactants/stabilizers/viscosity modifiers, and the velocity and turbulence of the feedstock stream to the gasifier and through the injector nozzles.

[0133] In one embodiment, the bulk density of the ground tires without compaction (loose) after final grinding is within 150%, or within 110%, or within 100%, or within 75%, or within 60%, or within 55%, or within 50%, or within 45%, or within 40%, or within 35% of the loose bulk density of the ground fossil fuel after its final grinding. For example, if the granulated coal has a loose bulk density of 40 lbs/ft^3 and the granulated tires have a loose bulk density of 33 lbs/ft^3, the bulk density of the tires would be within 21% of the ground coal. For measurement purposes, the bulk density of the pre-ground tires and the fossil fuel after final grinding is determined dry (without addition of water) even though they are ultimately used as a slurry.

[0134] In an alternative embodiment or in addition to any other embodiment described herein, the maximum particle size of the ground rubber tires is selected to be similar (below or above) to the maximum particle size of the ground coal. The maximum particle size of the ground rubber tires is desirably within (meaning below or above) 50%, or within 45%, or within 40%, or within 35%, or within 30%, or within 25%, or within 20%, or within 15%, or within 10%, or within 5% of the maximum particle size of the ground

coal. The maximum particle size is not determined as the maximum size of the particle distribution but rather by sieving through meshes. The maximum particle size is determined as the first mesh which allows at least 90 volume % of a sample of the ground particles to pass. For example, if less than 90 volume % of a sample passes through a 300 mesh, then a 100 mesh, a 50 mesh, a 30 mesh, a 16 mesh, but succeeds at a 14 mesh, then the maximum particle size of that sample is deemed to correspond to the first mesh size that allowed at least 90 volume % to pass through, and in this case, a 14 mesh corresponding to a maximum particle size of 1.4 mm.

[0135] The amount of ground tires present in the feedstock stream can range from 0.1 wt.% to 50 wt.%, desirably from 0.1 wt.% to 25 wt.%, based on the weight of all solids. The pre-ground tires at a concentration of less than 25 wt.%, or not more than 20 wt.%, or not more than 15 wt.%, or not more than 5 wt.%, based on the weight of the solids in the feedstock stream, can be incorporated into the feedstock stream without substantially impacting the reaction time, the flowability, the stability, or the physical processing of the feedstock stream feeding into the gasifier and inside the gasifier. The tire content can be at least 0.25 wt.%, or at least 0.5 wt.%, or at least 0.75 wt.%, or at least 1 wt.%, or at least 1.5 wt.%, or at least 1.75 wt.%, or at least 2 wt.%, or at least 2.5 wt.%, or at least 3 wt.%, or at least 3.5 wt.%, or at least 4 wt.%, or at least 4.5 wt.%, or at least 5 wt.%, or at least 6 wt.% or at least 10 wt.%, or at least 13 wt.%, or at least 15 wt.%, or at least 18 wt.%, based on the weight of all solids. Desirably, the content of ground tire present in the feedstock stream is from 0.25 wt.% to 15 wt.%, or from 0.25 wt.% to 13 wt.%, or from 0.25 wt.% to 10 wt.%, or from 0.25 wt.% to 8 wt.%, or from 0.25 wt.% to 6 wt.%, or from 0.25 wt.% to 5 wt.%, or from 0.25 wt.% to 4 wt.%, or from 0.25 wt.% to 3 wt.%, or from 0.25 wt.% to 2.5 wt.%, or from 0.5 wt.% to 15 wt.%, or from 0.5 wt.% to 13 wt.%, or from 0.5 wt.% to 10 wt.%, or from 0.5 wt.% to 8 wt.%, or from 0.5 wt.% to 6 wt.%, or from 0.5 wt.% to 5 wt.%, or from 0.5 wt.% to 4 wt.%, or from 0.5 wt.% to 3 wt.%, or from 0.5 wt.% to 2.5 wt.%, or from 1 wt.% to 15 wt.%, or from 1 wt.% to 13 wt.%, or from 1 wt.% to

10 wt.%, or from 1 wt.% to 8 wt.%, or from 1 wt.% to 6 wt.%, or from 1 wt.% to 5 wt.%, or from 1 wt.% to 4 wt.%, or from 1 wt.% to 3 wt.%, or from 1 wt.% to 2.5 wt.% each based on the weight of the solids in the feedstock stream.

[0136] The pre-ground tires are desirably isolated as a ground tire feed for ultimate destination to be mixed with one or more components of the feedstock stream. In one embodiment, at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 96 wt.%, or at least 97 wt.%, or at least 98 wt.%, or at least 99 wt.%, or at least 99.5 wt.%, or 100 wt.% of all post- consumer recycle content in the feedstock stream fed into the gasifier is ground tires, which includes both the rubber and the components that were contained in the tires (e.g. steel, metals, sulfur and elements other than rubber found in tires). In another embodiment, at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 96 wt.%, or at least 97 wt.%, or at least 98 wt.%, or at least 99 wt.%, or at least 99.5 wt.%, or 100 wt.% of all feedstock other than solid fossil fuels in the feedstock stream fed into the gasifier is pre-ground tires, which includes both the rubber and the components that were contained in the tires (e.g. steel, metals, sulfur and elements other than rubber found in tires).

[0137] The post-consumer pre-ground tires will, even after final grinding, contain some level of materials other than rubber, such as metals, traces of textile cord/belting or steel wires particles, or other materials. The quantity of such materials in the pre-ground tires that feed into the feedstock stream, other than rubber, is desirably less than 8 wt.%, or not more than 6 wt.%, or not more than 5 wt.%, or not more than 4 wt.%, or not more than 3.5 wt.%, or not more than 2 wt.%, or not more than 1.5 wt.%, or not more than 1 wt.%, or not more than 0.75 wt.%, or not more than 0.5 wt.%. based on the weight of the pre-ground tire particles.

[0138] Coal contains a quantity of ash that also contains elements other than carbon, oxygen, and hydrogen. The quantity of elements other than carbon, hydrogen, oxygen, and sulfur in the feedstock stream is desirably not more than 9 wt.%, or not more than 8.5 wt.%, or not more than 8 wt.%, or not

more than 7.5 wt.%, or not more than 7 wt.%, or not more than 7.5 wt.%, or not more than 7 wt.%, or not more than 6.5 wt.%, or not more than 6 wt.%, or not more than 5.5 wt.%, or not more than 5 wt.%, or not more than 4.5 wt.%, based on the weight of all dry solids in the feedstock stream, or alternatively based on the weight of the feedstock stream.

[0139] Coal contains a quantity of ash that also contains elements other than carbon, oxygen, and hydrogen. The quantity of elements other than carbon, hydrogen, and oxygen in the feedstock stream is desirably not more than 15 wt.%, or not more than 12 wt.%, or not more than 10 wt.%, or not more than 9 wt.%, or not more than 8.5 wt.%, or not more than 8 wt.%, or not more than 7.5 wt.%, or not more than 7 wt.%, or not more than 7.5 wt.%, or not more than 7 wt.%, or not more than 6.5 wt.%, or not more than 6 wt.%, or not more than 5.5 wt.%, or not more than 5 wt.%, or not more than 4.5 wt.%, based on the weight of all dry solids in the feedstock stream, or alternatively based on the weight of the feedstock stream.

[0140] In one embodiment, the average quantity of zinc in the pre-ground rubber tire feed is less than 4 wt.%, or not more than 3.5 wt.%, or not more than 3 wt.%, or not more than 2.5 wt.%, or not more than 2.2 wt.%, or not more than 2.0 wt.%, based on the weight of the pre-ground rubber tires to be used in the feedstock stream.

[0141] Unlike the highly variable content of material in a municipal solid waste stream resulting in variability to the syngas composition and output, the post recycle composition of tires in the feedstock stream in the present invention is substantially consistent over time as a rubber tire content and its amount can also be controlled to be consistent, thereby reducing fluctuations in the syngas composition and output and without impacting the operations of the gasifier. Tires, being mostly organic material with a similar carbon content, will gasify as well or better than coal. The caloric heat value of rubber tires is also similar to or better than that of coal, making it an attractive co-feed constituent with coal. For example, standard passenger tires have a heat value in the range of 13,000 to 15,000 BTU/lb (30 MJ/Kg – 35 MJ/Kg),

while bituminous coal can have a heat value in a range of 12,500 to 13,300 BTU/lb (29 – 31 MJ/Kg). Further, any ash or non-organic material will be melted and vitrified into the ash matrix that is produced from the inorganics in the coal. Therefore, the tires can be viewed as a direct replacement for coal in the feed process.

[0142] The concentration of solids (e.g. fossil fuel and tires) in the feedstock stream should not exceed the stability limits of the slurry, or the ability to pump or feed the feedstock at the target solids concentration to the gasifier. Desirably, the solids content of the slurry should be at least 50 wt.%, or at least 55 wt.%, or at least 60 wt.%, or at least 62 wt.%, or at least 65 wt.%, or at least 68 wt.%, or at least 69 wt.%, or at least 70 wt.%, or at least 75 wt.%, the remainder being a liquid phase that can include water and liquid additives. The upper limit is not particularly limited because it is dependent upon the gasifier design. However, given the practical pumpability limits of a solid fossil fuels feed and maintaining a homogeneous distribution of solids in the slurry, the solids content for a solid fossil slurry fed slagging gasifier desirably should not exceed 75 wt.%, or 73 wt.%, the remainder being a liquid phase that can include water and liquid additives (as noted above, gases are not included in the calculation of weight percentages).

[0143] The feedstock stream is desirably stable at 5 minutes, or even 10 minutes, or even 15 minutes, or even 20 minutes, or even ½ hour, or even 1 hour, or even two hours. A feedstock slurry is deemed stable if its initial viscosity is 100,000 cP or less. The initial viscosity can be obtained by the following method. A 500-600 g of a well-mixed sample is allowed to stand still in a 600 mL liter glass beaker at ambient conditions (e.g. 25°C and about 1 atm). A Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s is submerged into the slurry to the bottom of the beaker after the slurry is well mixed (e.g. a homogeneous distribution of solids was formed). After a designated period of time, a viscosity reading is obtained at the start of rotation, which is the initial viscosity reading. The slurry is considered to be stable if the initial reading on starting a viscosity

measurement is not more than 100,000 cP at the designated period of time. Alternatively, the same procedure can be used with a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm. Since different viscosity value will be obtained using the different equipment, the type of equipment used should be reported. However, regardless of the differences, the slurry is considered stable under either method only if its viscosity is not more than 100,000 cP at the reported time.

[0144] The quantity of solids in the feedstock stream and their particle size are adjusted to maximize the solids content while maintaining a stable and pumpable slurry. A pumpable slurry is one which has a viscosity under 30,000 cP, or not more than 25,000 cP, or not more than 23,000 cP, and desirably not more than 20,000 cP, or not more than 18,000 cP, or not more than 15,000 cP, or not more than 13,000 cP, in each case at ambient conditions (e.g. 25°C and 1 atm). At higher viscosities, the slurry becomes too thick to practically pump. The viscosity measurement to determine the pumpability of the slurry is taken by mixing a sample of the slurry until a homogeneous distribution of particles is obtained, thereafter immediately submerging a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm into the well mixed slurry and taking a reading without delay. Alternatively, a Brookfield R/S rheometer with V80-40 vane spindle operating at a shear rate of 1.83/s can be used. The method of measurement is reported since the measured values between the two rheometers at their difference shear rates will generate different values. However, the cP values stated above apply to either of the rheometer devices and procedures.

[0145] Conventional rubber tires granulators can be used to obtain the desires particle size. These can include systems for shredding the tires using high capacity shredders to chips, systems for loosening and separating the textile and steel wires through magnetic and screening technology, followed by granulation which also involves some loosening and separation of the steel and textile material in a tire and if necessary a fine/powder granulator can be used in a last step. The steel material can be magnetically separated before

or after sieving, and the textile balls can be physically separated after sieving. For the last step, the fine/powder granulators can be in communication with a conveying system to transport the granulated tires to a storage vessel from which the granulated tires can be fed to any location for making the feedstock stream, or the granulated particles can be fed continuously from the fine granulator to the desired location for making the feedstock stream. The feed of granulated tire particles from a storage vessel can be in a batch mode or in a continuous mode.

[0146] The carbonaceous materials, e.g. fossil fuel and rubber tires, are advantageously loose and not densified by mechanical or chemical means after granulation (other than natural compaction that may result from storage under its own weight). For example, coal chunks are granulated in the presence of water and not thereafter compacted, and rubber tires are fine ground/pulverized without densification operations prior to their addition into water.

[0147] The coal must be ground prior to feeding into a gasifier to achieve an acceptable particle size for the reasons noted above. These same considerations apply to the tire granulates, although as noted above, since the coal grinding equipment is not suitable to grind tires, the tires must be pre-ground prior to combining them to the feedstock composition or before adding to the coal grinding equipment.

[0148] The coal is typically ground to a size of 2 mm or less, and can be ground to any of the sizes noted above with respect to the granulated tire particle sizes. The small size of the coal and rubber tire particles is important to assure a uniform suspension in the liquid vehicle which will not settle out, to allow sufficient motion relative to the gaseous reactants, to assure substantially complete gasification, and to provide pumpable slurries of high solids content with a minimum of grinding.

[0149] The quality of the coal employed is not limited. Anthracite, bituminous, sub-bituminous, brown coal, and lignite coal can be sources of coal feedstock. To increase the thermal efficiency of the reactor, the coal

employed desirably has a carbon content that exceeds 35 wt.%, or at least 42 wt.%, based on the weight of the coal. Accordingly, bituminous or anthracite coal is desirable due to their higher energy content.

[0150] In another embodiment, the fixed carbon content in the solid fossil fuel employed in the feedstock stream is similar to fixed carbon content of the cumulative amount of all other solids in the feedstock stream. The fixed carbon content is understood by those of skill in the art and is the combustible solids remaining (other than ash) after the coal is heated and volatiles removed. It can be determined by subtracting the percentages of moisture, volatile matter, and ash from a sample. If a solid is employed with a large mismatch in fixed carbon content, variations in syngas composition can be experienced outside of desirable limits. For example, a solid that has a very low fixed carbon content could, in an entrainment flow high temperature gasifier, gasify more readily than coal proceed from making carbon monoxide to generating more carbon dioxide within the residence time experienced by coal, while a co-feed of solids having a much higher fixed carbon content that coal would take longer to gasify and generate more unconverted solids. The degree of syngas compositional variations that can be tolerated will depend on the use of the syngas, and in the case of making chemicals, it is desirably to minimize the factors that could cause wider syngas compositional variations. Accordingly, in one embodiment, the fixed carbon content of solids other than solid fossil fuels is within +/- 10 percentage digits, or within +/- 9 percentage digits, or within +/- 8 percentage digits, or within +/- 7 percentage digits, or within +/- 6 percentage digits, or within +/- 5 percentage digits, or within +/- 4 percentage digits, or within +/- 3 percentage digits, or within +/- 2 percentage digits, or within +/- 1 percentage digits of the fixed carbon content of the solid fossil fuels in the feedstock composition. For example, a fixed carbon content of tires at 35% and a fixed carbon content of coal at 37.2% would be within 3 percentage digits of each other.

[0151] Sulfur is also typically present in solid fossil fuels. Desirably, the content of sulfur is less than 5 wt.%, not more than 4 wt.%, or not more than 3

wt.%, or not more than 2.5 wt.%, and also can contain a measure of sulfur, such as at least 0.25 wt.%, or at least 0.5 wt.%, or at least 0.75 wt.%.

[0152] It is also desirable to employ coal with a low inherent moisture content to improve the thermal efficiency of the gasifier. Using coal having moisture contents less than 25 wt.% or less than 20 wt.% or less than 15 wt.% or not more than 10 wt.% or not more than 8 wt.% without the application of external artificially applied heat is desirable.

[0153] Desirably, the coal feedstock has a heat value of at least 11,000 BTU/lb, or at least 11,500 BTU/lb, or at least 12,500 BTU/lb, or at least 13,000 BTU/lb, or at least 13,500 BTU/lb, or at least 14,000 BTU/lb, or at least 14,250 BTU/lb, or at least 14,500 BTU/lb.

[0154] While it is possible that the feedstock stream may contain minor amounts of liquid hydrocarbon oils leached from tires or coal, the feedstock stream desirably contains less than 5 wt.%, or not more than 3 wt.%, or not more than 1 wt.%, or not more than 0.1 wt.% liquid (at ambient conditions) non-oxygenated hydrocarbon petroleum oils introduced as such into the feedstock stream. Desirably, the feedstock stream contains less than 2 wt.%, or not more than 1 wt.%, or no added liquid fraction from refining crude oil or reforming any such fraction. Desirably, the quantity of liquids in the feedstock stream is other than the solids content. The content of liquids, or the content of water, present in the feedstock stream is desirably not more than 50 wt.%, or not more than 35 wt.%, or not more than 32 wt.%, or not more than 31 wt.%, or not more than 30 wt.%, based on the weight of the feedstock stream. Desirably, in each case, the content of liquids or water in the feedstock stream is desirably at least 10 wt.%, or at least 15 wt.%, or at least 20 wt.%, or at least 25 wt.%, or at least 27 wt.%, or at least 30 wt.%, based on the weight of the feedstock stream. Desirably, the liquids present in the feedstock stream contain at least 95 wt.% water, or at least 96 wt.% water, or at least 97 wt.% water, or at least 98 wt.% water, or at least 99 wt.% water, based on the weight of all liquids fed to the gasifier. In another embodiment, other than chemical additives that are chemically synthesized and contain oxygen or

sulfur or nitrogen atoms, the liquid content of the feedstock stream is at least 96 wt.% water, or at least 97 wt.% water, or at least 98 wt.% water, or at least 99 wt.% water, based on the weight of all liquids fed to the gasifier.

[0155] The feedstock stream comprises at least ground coal and ground tires. Desirably, the feedstock stream also comprises water. The amount of water in the feedstock stream can range from 0 wt.% up to 50 wt.%, or from 10 wt.% to 40 wt.%, or from 20 wt.% to 35 wt.%. The feedstock stream is desirably a slurry containing water.

[0156] In addition to coal, water, and rubber tires, other additives can be added to and contained in the feedstock stream, such as viscosity modifiers and pH modifiers. The total quantity of additives can range from 0.01 wt.% to 5 wt.%, or from 0.05 wt.% to 5 wt.%, or from 0.05 to 3 wt.%, or from 0.5 to 2.5 wt.%, based on the weight of the feedstock stream. The quantity of any individual additive can also be within these stated ranges.

[0157] The viscosity modifiers (which includes surfactants) can improve the solids concentration in the slurry. Examples of viscosity modifiers include:

(i) alkyl-substituted amine-based surfactant such as alkyl-substituted aminobutyric acid, alkyl-substituted polyethoxylated amide, and alkyl-substituted polyethoxylated quaternary ammonium salt; and

(ii) sulfates such as salts of organic sulfonic acids including ammonium, calcium and sodium sulfonates, particularly those with lignin and sulfo-alkylated lignites;

(iii) phosphate salts;

(iv) polyoxyalkylene anionic or nonionic surfactants.

[0158] More specific examples of alkyl-substituted aminobutyric acid surfactants include N-coco-beta-aminobutyric acid, N-tallow-beta-aminobutyric acid, N-lauryl-beta-aminobutyric acid, and N-oleyl-beta-aminobutyric acid. N-coco-beta-aminobutyric acid.

[0159] More specific examples of alkyl-substituted polyethoxylated amide surfactant include polyoxyethylene oleamide, polyoxyethylene tallowamide,

polyoxyethylene laurylamide, and polyoxyethylene cocoamide, with 5-50 polyoxyethylene moieties being present.

[0160] More specific examples of the alkyl-substituted polyethoxylated quaternary ammonium salt surfactant include methylbis (2-hydroxyethyl) cocoammonium chloride, methylpolyoxyethylene cocoammonium chloride, methylbis (2-hydroxyethyl) oleylammonium chloride, methylpolyoxyethylene oleylammonium chloride, methylbis (2-hydroxyethyl) octadecylammonium chloride, and methylpolyoxyethylene octadecylammonium chloride.

[0161] More specific examples of sulfonates include sulfonated formaldehyde condensates, naphthalene sulfonate formaldehyde condensates, benzene sulfonate - phenol - formaldehyde condensates, and lingosulfonates.

[0162] More specific examples of phosphate salts include trisodium phosphate, potassium phosphate, ammonium phosphate, sodium tripolyphosphate or potassium tripolyphosphate.

[0163] Examples of polyoxyalkylene anionic or nonionic surfactants have 1 or more repeating units derived from ethylene oxide or propylene oxide, or 1-200 oxyalkylene units.

[0164] Desirably, the surfactant is an anionic surfactant, such as salts of an organic sulfonic acid. Examples are calcium, sodium and ammonium salts of organic sulfonic acids such as 2,6-dihydroxy naphthalene sulfonic acid, lignite sulfonic acid, and ammonium lignosulfonate.

[0165] Examples of pH modifiers include aqueous alkali metal and alkaline earth hydroxides such as sodium hydroxide, and ammonium compounds such as 20-50 wt.% aqueous ammonium hydroxide solutions. The aqueous ammonium hydroxide solution can be added directly to the feedstock composition prior to entry into the gasifier, such as in the coal grinding equipment or any downstream vessels containing the slurry.

[0166] The atomic ratio of total oxygen to carbon entering the gasification zone can be a value in the range of 0.70 to less than 2, or from 0.9 to 1.9, or from 0.9 to 1.8, or from 0.9 to 1.5, or from 0.9 to 1.4, or from 0.9 to 1.2, or

from 1 to 1.9, or from 1 to 1.8, or from 1 to 1.5, or from 1 to 1.2, or from 1.05 to 1.9, or from 1.05 to 1.8, or from 1.05 to 1.5, or from 1.05 to 1.2. The atomic ratio of free oxygen to carbon entering the gasification zone can also be within these same values. The weight ratio of both total oxygen and free oxygen to carbon in pounds entering the gasification zone can also each be within these stated values.

[0167] The total carbon content in the feedstock stream is at least 40 wt.%, or at least 45 wt.%, or at least 50 wt.%, or at least 55 wt.%, or at least 60 wt.%, or at least 65 wt.%, and desirably at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, each based on the total solids content. High carbon contents contribute to fuel sources with higher heat values and promote improved reactor efficiency.

[0168] The feedstock stream is desirably injected along with an oxidizer into the refractory-lined combustion chamber of the synthesis gas generating gasifier. The feedstock stream (desirably a slurry) and oxidizer are desirably sprayed through an injector into a gasification zone that is under significant pressure, typically about 500 psig or more, or 600 psig or more, or 800 psig or more, or 1000 psig or more. The velocity or flow rate of the feedstock and oxidizer streams ejected from the injector nozzle into the combustion chamber will exceed the rate of flame propagation to avoid backflash.

[0169] In one embodiment of the invention, advantageously only one feedstock stream is charged to the gasifier or gasification zone, or in other words, all sources of carbon fuel are fed to the gasifier in only one stream. In another embodiment, only one feedstock stream is necessary or employed to produce a syngas or product stream that is a raw material to synthesize a chemical compound.

[0170] In another embodiment, a chemical is made from a first syngas sourced from a first gasifier fed with a first feedstock stream containing coal and the first syngas stream is not combined with a second syngas sourced from any other gasifier fed with second feedstock stream where the coal content between the first and second feedstock streams differs by more than

20%, or more than 10%, or more than 5%. For example, a first syngas stream generated from a first feedstock stream containing 90 wt.% coal would not be combined with a syngas stream generated from a different gasifier fed with a feedstock stream containing 70 wt.% coal or no coal, but could be combined with one containing 72 wt.% coal or more.

[0171] Prior to entry into the gasifier, the feedstock stream may be subjected to a variety of other optional processes. For example, the coal-rubber slurry can flow through a thickener in which excess water is eliminated from the slurry to obtain the final desired solids concentration of the slurry entering into the gasifier vessel. Additionally, the feedstock stream may be pre-heated to prior to entry into the gasifier. In this embodiment, the feedstock stream is heated to a temperature below the boiling point of water at the operating pressure existing in reaction zone. The preheater, when employed, reduces the heat load on the gasifier and improves the efficiency of utilization of both fuel and oxygen. In this embodiment, all of the water required for the generation of synthesis gas in reaction zone is supplied in liquid phase. When petroleum coke is employed as fuel for the gas generator, part of the water, e.g., from 1 to about 90 percent by weight based on the weight of water, may be vaporized in the slurry feed preheater or combined with the oxidizing stream as vaporized water.

[0172] The oxidizer is desirably an oxidizing gas that can include air, and desirably is a gas enriched in oxygen at quantities greater than that found in air. The reaction of oxygen and solid fossil fuel is exothermic. Desirably, the oxidant gas contains at least 25 mole% oxygen, or at least 35 mole%, or at least 40 mole%, or at least 50 mol%, or at least 70 mole%, or at least 85 mole%, or at least 90 mole%, or at least 95 mole%, or at least 97 mole%, or at least 98 mole% oxygen, or at least 99 mole%, or at least 99.5 mole% based on all moles in the oxidant gas stream injected into the reaction (combustion) zone of the gasifier. In another embodiment, the combined concentration of oxygen in all gases supplied to the gasification zone is also in the above stated amount. The particular amount of oxygen as supplied to the

reaction zone is desirably sufficient to obtain near or maximum yields of carbon monoxide and hydrogen obtained from the gasification reaction relative to the components in the feedstock stream, considering the amount relative to the feedstock stream, and the amount of feedstock charged, the process conditions, and the reactor design.

[0173] In one embodiment, steam is not supplied to the gasification zone. The amount of water in a slurry fed system is typically more than sufficient a co-reactant and heat sink to regulate the gasification temperature. The addition of stream in a slurry fed gasifier will generally unduly withdraw heat from the reaction zone and reduce its efficiency.

[0174] Other reducible oxygen-containing gases may be supplied to the reaction zone, for example, carbon dioxide, nitrogen, or simply air. In one embodiment, no gas stream enriched in carbon dioxide or nitrogen (e.g. greater than the molar quantity found in air, or greater than 2 mole%, or greater than 5 mole%, or greater than 10 mole%, or greater than 40 mole%) is charged into the gasifier. Many of these gases serve as carrier gases to propel a dry feed to a gasification zone. Due to the pressure within the gasification zone, these carrier gases are compressed to provide the motive force for introduction into the gasification zone. The expenditure of energy and equipment for compressing carrier gases to the feedstock stream is avoided is a slurry feed. Accordingly, in another embodiment, the feedstock stream containing at least pre-ground tires and ground solid fossil fuel flowing to the gasifier, or this feedstock stream introduced to an injector or charge pipe, or this feedstock stream introduced into the gasification zone, or a combination of all the above, does not contain gases compressed in equipment for gas compression. Alternatively, or in addition, other than the oxygen rich stream described above, no gas compressed in equipment for gas compression is fed to the gasification zone or even to the gasifier. It is noteworthy that high pressure charge pumps that process the slurry feed for introduction into the gasification zone are not considered gas compressing equipment.

[0175] Desirably, no gas stream containing more than 0.03 mole%, or more than 0.02 mole%, or more than 0.01 mole% carbon dioxide is charged to the gasifier or gasification zone. In another embodiment, no gas stream containing more than 77 mole%, or more than 70 mole%, or more than 50 mole%, or more than 30 mole%, or more than 10 mole%, or more than 5 mole%, or more than 3 mole% nitrogen is charged to the gasifier or gasification zone. In another embodiment, steam is not charged into the gasification zone or to the gasifier. In yet another embodiment, a gaseous hydrogen stream (e.g. one containing more than 0.1 mole% hydrogen, or more than 0.5 mole%, or more than 1 mole%, or more than 5 mole%) is not charged to the gasifier or to the gasification zone. In another embodiment, a stream of methane gas (e.g. one containing more than 0.1 mole% methane, or more than 0.5 mole%, or more than 1 mole%, or more than 5 mole% methane) is not charged to the gasifier or to the gasification zone. In another embodiment, the only gaseous stream introduced to the gasification zone is an oxygen rich gas stream as described above.

[0176] The gasification process desirably employed is a partial oxidation gasification reaction. To enhance the production of hydrogen and carbon monoxide, the oxidation process involves partial, rather than complete, oxidization of the fossil fuel and tires and therefore is desirably operated in an oxygen-lean environment, relative to the amount needed to completely oxidize 100% of the carbon and hydrogen bonds. The total oxygen requirements for the gasifier is desirably at least 5%, or at least 10%, or at least 15%, or at least 20%, in excess of the amount theoretically required to convert the carbon content of the solid fuel and tires to carbon monoxide. In general, satisfactory operation may be obtained with a total oxygen supply of 10 to 80 percent in excess of the theoretical requirements. An example of a suitable amount of oxygen per pound of carbon is in the range of 0.4 to about 3.0 pound free oxygen per pound of carbon, or from 0.6 to 2.5, or from 0.9 to 2.5, or from 1 to 2.5, or from 1.1 to 2.5, or from 1.2 to 2.5 pounds of free oxygen per pound of carbon.

[0177] Mixing of the feedstock stream and the oxidant is desirably accomplished entirely within the reaction zone by introducing the separate streams of feedstock and oxidant so that they impinge upon each other within the reaction zone. Desirably, the oxidant stream is introduced into the reaction zone of the gasifier as high velocity to both exceed the rate of flame propagation and to improve mixing with the feedstock stream. The oxidant is desirably injected into the gasification zone in the range of 25 to 500 feet per second, or 50 to 400 ft/s, or 100 to 400 ft/s. These values would be the velocity of the gaseous oxidizing stream at the injector-gasification zone interface, or the injector tip velocity.

[0178] One method for increasing the velocity of the oxidant feed to the gasification zone is by reducing the diameter of the oxidant annulus near the tip of the injector or injector. Near the tip of the injector the annular passage converges inwardly in the shape of a hollow cone as shown in Figures 3 and 4. The oxidizing gas is thereby accelerated and discharged from the injector as a high velocity conical stream having an apex angle in the desirably range of about 30° to 45°. The streams from the injector converge at a point located about 0-6 inches beyond the injector face. The high velocity stream of oxidizing gas hits the relatively low velocity feedstock stream, atomizing it and forming a fine mist comprising minute particles of water and particulate solid carboniferous fuel highly dispersed in the oxidizing gas. The particles of solid carboniferous matter impinge against one another and are fragmented further.

[0179] The velocity of the feedstock slurry is determined by the desired throughput of syngas generation. Suitable examples of feedstock velocity introduced into gasification zone prior to contact with the oxidizing agent is in the range of 5 to 50 feet per second.

[0180] The feedstock stream and the oxidant can optionally be preheated to a temperature above about 200°C, or at least 300°C, or at least 400°C. Advantageously the gasification process employed does not require preheating the feedstock stream to efficiently gasifying the fuel, and a pre-heat treatment step would result in lowering the energy efficiency of the

process. Desirably, the feedstock stream, and optionally the oxidant, are not preheated prior to their introduction into the gasifier. A preheat treatment step would be contacting the feedstock stream or oxidant with equipment that raises the temperature of the feedstock stream sufficiently such that the temperature of the feedstock stream or oxidant stream is above 200 °C, or above 190 °C, or above 170 °C, or above 150 °C, or above 130 °C, or above 110 °C, or above 100 °C, or above 98 °C, or above 90 °C, or above 80 °C, or above 70 °C, or above 60 °C, immediately prior to introduction into a injector on the gasifier. For example, while coal can be dried with hot air above 200 °C, this step would not be considered a preheat of the feedstock stream if the feedstock stream is below 200 °C upon its introduction into the injector.

[0181] In another embodiment, no thermal energy (other than incidental heat from processing equipment such as mills, grinders or pumps) is applied to the feedstock stream containing both tires and the solid fossil fuel, or to the oxidant stream, at any point prior to its introduction into the injector, or gasifier, or gasification zone (other than the temperature increase experienced in a injector) that would increase the temperature of the stream by more than 180 °C, or more than 170 °C, or more than 160 °C, or more than 150 °C, or more than 140 °C, or more than 130 °C, or more than 120 °C, or more than 110 °C, or more than 100 °C, or more than 90 °C, or more than 80 °C, or more than 70 °C, or more than 60 °C, or more than 50 °C, or more than 40 °C, or more than 30 °C.

[0182] The process of the invention employs a gasification process, which is distinct from pyrolysis (which is a thermal process that degrades a fuel source in the absence of air or oxygen) or plasma processes in that gasification does not employ a plasma arc.

[0183] Desirably, the type of gasification technology employed is a partial oxidation entrained flow gasifier that generates syngas. This technology is distinct from fixed bed (alternatively called moving bed) gasifiers and from fluidized bed gasifiers. In fixed bed (or moving bed gasifiers), the feedstock stream moves in a countercurrent flow with the oxidant gas, and the oxidant

gas typically employed is air. The feedstock stream falls into the gasification chamber, accumulates, and forms a bed of feedstock. Air (or alternatively oxygen) flows from the bottom of the gasifier up through the bed of feedstock material continuously while fresh feedstock continuously falls down from the top by gravity to refresh the bed as it is being combusted. The combustion temperatures are typically below the fusion temperature of the ash and are non-slagging. Whether the fixed bed operated in countercurrent flow or in some instances in co-current flow, the fixed bed reaction process generates high amount of tars, oils, and methane produced by pyrolysis of the feedstock in the bed, thereby both contaminating the syngas produced and the gasifier. The contaminated syngas requires significant effort and cost to remove tarry residues that would condense once the syngas is cooled, and because of this, such syngas streams are generally not used to make chemicals and is instead used in direct heating applications. In a fluidized bed, the feedstock material in the gasification zone is fluidized by action of the oxidant flowing through the bed at a high enough velocity to fluidize the particles in the bed. In a fluidized bed, the homogeneous reaction temperatures and low reaction temperatures in the gasification zone also promotes the production of high amounts of unreacted feedstock material and low carbon conversion, and operating temperatures in the fluidized bed are typically between 800-1000℃. Further, in a fluidized bed it is important to operate below slagging conditions to maintain the fluidization of the feedstock particles which would otherwise stick to the slag and agglomerate. By employing an entrained flow gasification, these deficiencies present with fixed (or moving bed) and fluidized bed gasifiers that are typically used to process waste materials is overcome.

[0184] In one embodiment, the feedstock stream is introduced at the top 1/8 section of the gasifier, desirably at the top 1/12 of the gasifier height defined by the gasifier shell (not including the injector height protruding from the top of the shell or pipes protruding from the bottom of the shell). The feedstock stream is desirably not introduced into a side wall of the gasifier. In another embodiment, the feedstock stream is not a tangential feed injector.

[0185] In another embodiment, oxidant is introduced at the top 1/8 section of the gasifier, desirably at the top 1/12 of the gasifier height defined by the gasifier shell. The oxidant is desirably not introduced into the side wall of the reactor or bottom of the reactor. In another embodiment, both the feedstock stream and oxidant are introduced at the top 1/8 section of the gasifier, desirably at the top 1/12 of the gasifier height defined by the gasifier shell. Desirably, the oxidant and feedstock stream are fed co-currently to ensure good mixing. In this regard, a co-current feed means that the axis of the feedstock and oxidant streams are substantially parallel (e.g. not more than a 25° deviation, or not more than a 20°, or not more than a 15°, or not more than a 10°, or not more than a 8°, or not more than a 6°, or not more than a 4°, or not more than a 2°, or not more than a 1° deviation from each other) and in the same direction.

[0186] The feedstock and oxidant streams are desirably introduced into the gasification zone through one or more injector nozzles. Desirably, the gasifier is equipped with at least one of the injector nozzles in which through that injector nozzle both a feedstock stream and an oxidant stream are introduced into the gasification zone.

[0187] While the feedstock stream can be a dry feed or a slurry feed, the feedstock stream is desirably a slurry. The syngas produced in the gasification process is desirably used at least in part for making chemicals. Many synthesis processes for making chemicals are at high pressure, and to avoid energy input into pressurizing the syngas stream, desirably the gasifier is also run at high pressure, particularly when the syngas stream is directly or indirectly in gaseous communication with a vessel in which a chemical is synthesized. Dry feeds to a gasifier operating at high pressure are specially treated to ensure that the feed can be effectively blown and injected into the high-pressure gasification zone. Some techniques include entraining a flow of nitrogen at high pressure and velocity, which tends to dilute the syngas stream and reduce the concentration of desirably components such as carbon monoxide and hydrogen. Other carrier or motive gases include carbon

monoxide, but like nitrogen, these gases are compressed before feeding into or compressed with the solid fossil fuels, adding to the energy requirements and capital cost of feed lock hoppers and/or compressing equipment. To deal with these issues, many dry feed gasifiers will operate at lower pressures, which for the mere production of electricity is sufficient, but is undesirable for gasifiers producing a syngas stream for making chemicals. With a slurry feed, a motive gas is not necessary and can readily be fed to a high-pressure gasifier that produces syngas as high pressure, which is desirable for making chemicals. In one embodiment, the feedstock stream is not processed through a lock hopper prior to entering an injector or entering the gasification zone. In another embodiment, the feedstock composition containing ground tires and solid fossil fuel is not pressurized in a lock hopper.

[0188] Desirably, the gasifier is non-catalytic, meaning that gasifier does not contain a catalyst bed, and desirably the gasification process is non-catalytic, meaning that a catalyst is not introduced into the gasification zone as a discrete unbound catalyst (as opposed to captive metals in the tires or solid fossil fuel that can incidentally have catalytic activity). The gasification process in the reaction zone is desirably conducted in the absence of added catalysts and contains no catalyst bed. The gasification process is also desirably a slagging gasification process; that is, operated under slagging conditions (well above the fusion temperature of ash) such that a molten slag is formed in the gasification zone and runs along and down the refractory walls.

[0189] In another embodiment, the gasifier is not designed to contain a pyrolysis zone. Desirably, the gasifier is not designed to contain a combustion zone. Most preferably, the gasifier is designed to not contain, or does not contain, either a combustion zone or a pyrolysis zone. The pyrolysis zone incompletely consumes the fuel source leading to potentially high amounts of ash, char, and tarry products. A combustion zone, while absent in tars, produces high amounts of CO_2 and lower amounts of the more desirably carbon monoxide and hydrogen. Desirably, the gasifier is a single stage

reactor, meaning that there is only one zone for conversion of the carbon in the feedstock to gases within the gasifier shell.

[0190] The gasification zone is void or empty space defined by walls in which oxidation reactions occur and allow gases to form within the space. Desirably, gasification zone does not have a bath of molten material or molten material that accumulates at the bottom of the gasification zone to form a bath. The gasification zone is desirably not enclosed on the bottom but rather is in gaseous communication with other zones below the gasification zone. Slag, while molten, does not accumulate at the bottom of the gasification zone but rather runs down the sides of the refractory and into a zone below the gasification zone, such as a quench zone to solidify the slag.

[0191] The flow of hot raw syngas in the gasifier desirably is vertically downward, or a down-flow reactor. Desirably, the flow of syngas generated in the gasifier is downward from the highest point of injecting the feedstock stream, desirably from the point of all feedstock stream locations. In another embodiment, the location for withdrawing the syngas stream from the gasifier is lower that at least one location for introducing the feedstock stream, desirably lower than all locations for introducing a feedstock stream.

[0192] The gasifier desirably contains refractory lining in the gasification zone. While a steam generating membrane or jacket between the gasifier wall and the surfaces facing the gasification zone can be employed, desirably the gasifier does not contain a membrane wall, or a steam generating membrane, or a steam jacket in the gasification zone or between inner surfaces facing the gasification zone and the gasifier shell walls as this removes heat from the gasification zone. Desirably, the gasification zone is lined with refractory, and optionally there is no air or steam or water jacket between the refractory lining the gasification zone (or optionally in any reaction zone such as combustion or pyrolysis) and the outer shell of the gasifier.

[0193] The gasification process is desirably a continuous process meaning that the gasifier operates in a continuous mode. The inclusion of pre-

granulated tires into the feedstock stream can be intermittent or continuous provided that a continuous feed of fossil fuel is fed to the gasifier since the gasification process in the gasifier is in a continuous mode. By a continuous mode for gasifier operation is meant that the gasification process is continuous for at least 1 month, or at least 6 months, or at least 1 year. Desirably, the inclusion of granulated tires in the feedstock stream is continuous for at least 1 day, or at least 3 days, or at least 14 days, or at least 1 month, or at least 6 months, or at least 1 year. A process is deemed continuous despite shut-downs due to maintenance or repair.

[0194] The feedstock can be fed into the gasification zone through one or more injectors. In one embodiment, the gasifier contains only one injector. In another embodiment, the gasifier contains only one location for introducing feedstock. Typically, the injector nozzle serving the gasification chamber is configured to have the feedstock stream concentrically surround the oxidizer gas stream along the axial core of the nozzle. Optionally, the oxidizer gas stream can also surround the feedstock stream annulus as a larger, substantially concentric annulus. Radially surrounding an outer wall of the outer oxidizer gas channel can be an annular cooling water jacket terminated with a substantially flat end-face heat sink aligned in a plane substantially perpendicular to the nozzle discharge axis. Cool water is conducted from outside the combustion chamber into direct contact with the backside of the heat sink end-face for conductive heat extraction.

[0195] The reaction between the hydrocarbon and oxygen should take place entirely outside the injector proper to prevent localized concentration of combustible mixtures at or near the surfaces of the injector elements.

[0196] The gasification zone, and optionally all reaction zones in the gasifier are operated at a temperature in the range of at least 1000° C, or at least 1100°C, or at least 1200°C, or at least 1250°C, or at least 1300°C, and up to about 2500°C, or up to 2000° C., or up to 1800°C, or up to 1600°C, each of which are well above the fusion temperature of ash and are desirably operated to form a molten slag in the reaction zone. In one embodiment, the

reaction temperature is desirably autogenous. Advantageously, the gasifier operating in steady state mode is at an autogenous temperature and does not require application of external energy sources to heat the gasification zone.

[0197] In one embodiment, the gasifier does not contain a zone within the gasifier shell to dry feedstock such as the coal, pet-coke, or tires prior to gasification. The increase in temperature within the injector is not considered a zone for drying.

[0198] Desirably, the gasification zone is not under negative pressure during operations, but rather is under positive pressure during operation. The gasification zone is desirably not equipped with any aspirator or other device to create a negative pressure under steady state operation.

[0199] The gasifier is operated at a pressure within the gasification zone (or combustion chamber) of at least 200 psig (1.38 MPa), or at least 300 psig (2.06 MPa), or at least 350 psig (2.41 MPa), and desirably at least 400 psig (2.76 MPa), or at least 420 psig (2.89 MPa), or at least 450 psig (3.10 MPa), or at least 475 psig (3.27 MPa), or at least 500 psig (3.44 MPa), or at least 550 psig (3.79 MPa), or at least 600 psig (4.13 MPa), or at least 650 psig (4.48 MPa), or at least 700 psig (4.82 MPa), or at least 750 psig (5.17 MPa), or at least 800 psig (5.51 MPa), or at least 900 psig (6.2 MPa), or at least 1000 psig (6.89 MPa), or at least 1100 psig (7.58 MPa), or at least 1200 psig (8.2 MPa). The particular operating pressure on the high end is regulated with a variety of considerations, including operating efficiency, the operating pressures needed in chemical synthesis reactors particularly with integrated plants, and process chemistry. Suitable operating pressures in the gasification zone on the high end need not exceed 1300 psig (8.96 MPa), or need not exceed 1250 psig (8.61 MPa), or need not exceed 1200 psig (8.27 MPa), or need not exceed 1150 psig (7.92 MPa), or need not exceed 1100 psig (7.58 MPa), or need not exceed 1050 psig (7.23 MPa), or need not exceed 1000 psig (6.89 MPa), or need not exceed 900 psig (6.2 MPa), or need not exceed 800 psig (5.51 MPa), or need not exceed 750 psig (5.17 MPa). Examples of suitable desirably ranges include 400 to 1000, or 425 to

900, or 450 to 900, or 475 to 900, or 500 to 900, or 550 to 900, or 600 to 900, or 650 to 900, or 400 to 800, or 425 to 800, or 450 to 800, or 475 to 800, or 500 to 800, or 550 to 800, or 600 to 800, or 650 to 800, or 400 to 750, or 425 to 750, or 450 to 750, or 475 to 750, or 500 to 750, or 550 to 750, each in psig.

[0200] Desirably, the average residence time of gases in the gasifier reactor is desirably very short to increase throughput. Since the gasifier is desirably operated at high temperature and pressure, substantially complete conversion of the feedstock to gases can occur in a very short time frame. The average residence time of the gases in the gasifier can be as short as less than 30 seconds, or not more than 25 seconds, or not more than 20 seconds, or not more than 15 seconds, or not more than 10 seconds, or not more than 7 seconds. Desirably, the average residence time of gases in all zones designed for conversion of feedstock material to gases is also quite short, e.g. less than 25 seconds, or not more than 15 seconds, or not more than 10 seconds, or not more than 7 seconds, or not more than 4 seconds. In these time frames, at least 85 wt.%, or at least or more than 90 wt.%, or at least 92 wt.%, or at least 94 wt.% of the solids in the feedstock can be converted to gases (substances which remain as a gas if the gas stream were cooled to 25℃ and 1 atm) and liquid (substances which are in liquid state if the gas stream is cooled to 25℃ and 1 atm such as water), or more than 93 wt.%, or more than 95 wt.%, or more than 96 wt.%, or more than 97 wt.%, or more than 98 wt.%, or more than 99 wt.%, or more than 99.5 wt.%.

[0201] A portion of ash and/or char in the gasifier can be entrained in the hot raw syngas stream leaving the gasification reaction zone. Ash particles in the raw syngas stream within the gasifier are particles which have not reached the melting temperature of the mineral matter in the solid fuel. Slag is substantially molten ash or molten ash which has solidified into glassy particles and remains within the gasifier. Slag is molten until quenched and then form beads of fused mineral matter. Char are porous particles that are devolatilized and partially combusted (incompletely converted) fuel particles.

The particulate matter gathered in the bottom part of the reactor, or the quench zone, are predominately slag (e.g. above 80 wt.% slag) and the remainder is char and ash. Desirably, only trace amounts of tar or no tar is present in the gasifier, or in the quench zone, or in the gasification zone, or present in the hot raw syngas within the gasifier, or present in the raw syngas discharged from the gasifier (which can be determined by the amount of tar condensing from the syngas stream when cooled to a temperature below 50℃.). Trace amounts are less than 0.1 wt.% (or less than 0.05 wt.% or less than 0.01 wt.%) of solids present in the gasifier, or less than 0.05 volume%, or not more than 0.01 vol%, or not more than 0.005 vol%, or not more than 0.001 volume%, or not more than 0.0005 vol%, or not more than 0.0001 vol% in the raw syngas stream discharged from the gasifier.

[0202] In another embodiment, the process does not increase the amount of tar to a substantial extent relative to the same process except replacing the tires with the same amount and type of solid fossil fuel used in the mixed feedstock composition.

[0203] The quantity of tar generated in the process with the mixed feedstock is less than 10% higher, or less than 5% higher, or less than 3 % higher, or less than 2% higher, or not higher at all, than the amount of tar generated with the same feedstock replacing the tires with the same solid fossil fuel under the same conditions.

[0204] To avoid fouling downstream equipment from the gasifier (scrubbers, CO/H_2 shift reactors, acid gas removal, chemical synthesis), and the piping in-between, the syngas stream should have low or no tar content. The syngas stream as discharged from the gasifier desirably contains no or less than 4 wt.%, or less than 3 wt.%, or not more than 2 wt.%, or not more than 1 wt.%, or not more than 0.5 wt.%, or not more than 0.2 wt.%, or not more than 0.1 wt.%, or not more than 0.08 wt.%, or not more than 0.05 wt.%, or not more than 0.02 wt.%, or not more than 0.01 wt.%, or nor more than 0.005 wt.% tar, based on the weight of all condensable solids in the syngas

stream. For purposes of measurement, condensable solids are those compounds and elements that condense at a temperature of 15°C/1atm.

[0205] In another embodiment, the tar present, if at all, in the syngas stream discharged from the gasifier is less than 10 g/m^3 of the syngas discharged, or not more than 9 g/m^3, or not more than 8 g/m^3, or not more than 7 g/m^3,or not more than 6 g/m^3, or not more than 5 g/m^3, or not more than 4 g/m^3, or not more than 3 g/m^3, or not more than 2 g/m^3, and desirably not more than 1 g/m^3, or not more than 0.8 g/m^3, or not more than 0.75 g/m^3, or not more than 0.7 g/m^3, or not more than 0.6 g/m^3, or not more than 0.55g/m^3, or not more than 0.45 g/m^3, or not more than 0.4 g/m^3, or not more than 0.3 g/m^3, or not more than 0.2 g/m^3, or not more than 0.1 g/m^3, or not more than 0.05 g/m^3, or not more than 0.01 g/m^3, or not more than 0.005 g/m^3, or not more than 0.001 g/m^3, or not more than 0.0005 g/m^3, in each case Normal (15°C/1atm). For purposes of measurement, the tars are those tars that would condense at a temperature of 15°C/1atm, and includes primary, secondary and tertiary tars, and are aromatic organic compounds and other than ash, char, soot, or dust. Examples of tar products include naphthalenes, cresols, xylenols, anthracenes, phenanthrenes, phenols, benzene, toluene, pyridine, catechols, biphenyls, benzofurans, benzaldehydes, acenaphthylenes, fluorenes, naphthofurans, benzanthracenes, pyrenes, acephenanthrylenes, benzopyrenes, and other high molecular weight aromatic polynuclear compounds. The tar content can be determined by GC-MSD.

[0206] In another embodiment, the tar yield of the gasifier (combination of tar in syngas and tar in reactor bottoms and in or on the ash, char, and slag) is not more than 4 wt.%, or not more than 3 wt.%, or not more than 2.5 wt.%, or not more than 2.0 wt.%, or not more than 1.8 wt.%, or not more than 1.5 wt.%, or not more than 1.25 wt.%, or not more than 1 wt.%, or not more than 0.9 wt.%, or not more than 0.8 wt.%, or not more than 0.7 wt.%, or not more than 0.5 wt.%, or not more than 0.3 wt.%, or not more than 0.2 wt.%, or not more than 0.1 wt.%, or not more than 0.05 wt.%, or not more than 0.01 wt.%,

or not more than 0.005 wt.%, or not more than 0.001 wt.%, or not more than 0.0005 wt.%, or not more than 0.0001 wt.%, based on the weight of solids in the feedstock stream fed to the gasification zone.

[0207] Because of the gasification technique employed, the amount of char generated by gasifying the tire-solid fossil fuel feedstock stream can remain within acceptable limits. For example, the amount of char (or incompletely converted carbon in the feedstock) generated by conversion of the carbon sources in the feedstock stream is not more than 15 wt.%, or not more than 12 wt.%, or not more than 10 wt.%, or not more than 8 wt.%, or not more than 5 wt.%, or not more than 4.5 wt.%, or not more than 4 wt.%, or not more than 3.5 wt.%, or not more than 3 wt.%, or not more than 2.8 wt.%, or not more than 2.5 wt.%, or not more than 2.3 wt.%, or not more than 4.5 wt.%, or not more than 4.5 wt.%, or not more than 4.5 wt.%.

[0208] In the process, char can be recycled back to the feedstock stream. In another embodiment, the efficiencies and features of the invention can be obtained without recycling char back to the gasification zone.

[0209] The total amount of char (or incompletely converted carbon in the feedstock) and slag generated in the gasifier or by the process is desirably not more than 20 wt.%, or not more than 17 wt.%, or not more than 15 wt.%, or not more than 13 wt.%, or not more than 10 wt.%, or not more than 9 wt.%, or not more than 8.9 wt.%, or not more than 8.5 wt.%, or not more than 8.3 wt.%, or not more than 8 wt.%, or not more than 7.9 wt.%, or not more than 7.5 wt.%, or not more than 7.3 wt.%, or not more than 7 wt.%, or not more than 6.9 wt.%, or not more than 6.5 wt.%, or not more than 6.3 wt.%, or not more than 6 wt.%, or not more than 5.9 wt.%, or not more than 5.5 wt.%, in each case based on the weight of the solids in the feedstock stream. In another embodiment, the same values apply with respect to the total amount of ash, slag, and char generated in the gasifier or by the process, based on the weight of the solids in the feedstock stream. In another embodiment, the same values apply with respect to the total amount of ash, slag, char and tar

generated in the gasifier or by the process, based on the weight of the solids in the feedstock stream.

[0210] The raw syngas stream flows from the gasification zone to a quench zone at the bottom of the gasifier where the slag and raw syngas stream are cooled, generally to a temperature below 550℃, or below 500℃, or below 450℃. The quench zone contains water in a liquid state. The hot syngas from the gasification zone may be cooled by directly contacting the syngas stream with liquid water. The syngas stream can be bubbled through the pool of liquid water, or merely contact the surface of the water pool. In addition, the hot syngas stream may be cooled in a water jacketed chamber having a height that above the top surface of the water pool to allow the hot syngas to both contact the water pool and be cooled in the water jacketed chamber. Molten slag is solidified by the quench water and most of the ash, slag and char are transferred to the water in the quench tank. The partially cooled gas stream, having passed through the water in the quench zone, may be then discharged from the gasifier as a raw syngas stream and passed through a water scrubbing operation to remove any remaining entrained particulate matter.

[0211] The pressure in the quench zone is substantially the same as the pressure in the gasification zone located above the water level in the gasifier, and a portion of the quench water and solids at the bottom of the quench tank is removed by way of a lock hopper system. A stream of quench water carrying fine particles exits the gasifier quench zone in response to a liquid level controller and can be directed to a settler. The solids and water from the lock hopper may then flow into a water sump or settler where optionally the coarse particulate solids may be removed by screens or filter thereby producing a dispersion of fine particulate solids.

[0212] The raw gas stream discharged from the gasification vessel includes such gasses as hydrogen, carbon monoxide, carbon dioxide and can include other gases such as methane, hydrogen sulfide and nitrogen depending on the fuel source and reaction conditions. Carbon dioxide in the

raw syngas stream discharged from the gasification vessel is desirably present in an amount of less than 20 mole%, or less than 18 mole%, or less than 15 mole%, or less than 13 mole%, or not more than 11 mole %, based on all moles of gases in the stream. Some nitrogen and argon can be present in the raw syngas stream depending upon the purity of the fuel and oxygen supplied to the process.

[0213] In one embodiment, the raw syngas stream (the stream discharged from the gasifier and before any further treatment by way of scrubbing, shift, or acid gas removal) can have the following composition in mole % on a dry basis and based on the moles of all gases (elements or compounds in gaseous state at 25℃ and 1 atm) in the raw syngas stream:

a. H_2: 15 to 60, or 18 to 50, or 18 to 45, or 18 to 40, or 23 to 40, or 25 to 40, or 23 to 38, or 29 to 40, or 31 to 40
b. CO: 20 to 75, or 20 to 65, or 30 to 70, or 35 to 68, or 40 to 68, or 40 to 60, or 35 to 55, or 40 to 52
c. CO2:1.0 to 30, or 2 to 25, or 2 to 21, or 10 to 25, or 10 to 20
d. H2O: 2.0 to 40.0, or 5 to 35, or 5 to 30, or 10 to 30
e. CH4: 0.0 to 30, or 0.01 to 15, or 0.01 to 10, or 0.01 to 8, or 0.01 to 7, or 0.01 to 5, or 0.01 to 3, or 0.1 to 1.5, or 0.1 to 1
f. H2S: 0.01 to 2.0, or 0.05 to 1.5, or 0.1 to 1, or 0.1 to 0.5
g. COS: 0.05 to 1.0, or 0.05 to 0.7, or 0.05 to 0.3
h. Total sulfur: 0.015 to 3.0, or 0.02 to 2, or 0.05 to 1.5, or 0.1 to 1
i. N2: 0.0 to 5, or 0.005 to 3, or 0.01 to 2, or 0.005 to 1, or 0.005 to 0.5, or 0.005 to 0.3

[0214] The gas components can be determined by FID-GC and TCD-GC or any other method recognized for analyzing the components of a gas stream.

[0215] The molar hydrogen/carbon monoxide ratio is desirably at least 0.65, or at least 0.68, or at least 0.7, or at least 0.73, or at least 0.75, or at least 0.78, or at least 0.8, or at least 0.85, or at least 0.88, or at least 0.9, or at least 0.93, or at least 0.95, or at least 0.98, or at least 1.

[0216] The total amount of hydrogen and carbon monoxide on a relative to the total amount of syngas discharged from the gasifier on a dry basis is high, on the order of greater than 70 mole%, or at least 73 mole%, or at least 75 mole%, or at least 77 mole%, or at least 79 mole%, or at least 80 mole%, based on the syngas discharged.

[0217] In another embodiment, the dry syngas production expressed as gas volume discharged from the gasifier per kg of solid fuel (e.g. tires and coal) charged to all locations on the gasifier is at least 1.7, or at least 1.75, or at least 1.8, or at least 1.85, or at least 1.87, or at least 1.9, or at least 1.95, or at least 1.97, or at least 2.0, in each case as N m^3 gas/kg solids fed

[0218] The carbon conversion efficiency in one pass is good and can be calculated according to the following formula:

$$= \frac{total\ carbon\ in\ feed - total\ carbon\ in\ char\ and\ tar}{total\ carbon\ in\ feed}\ x\ 100$$

[0219] The carbon conversion efficiency in the process in one pass can be at least 70%, or at least 73%, or at least 75%, or at least 77%, or at least 80%, or at least 82%, or at least 85%, or at least 88%, or at least 90%, or at least 93%.

[0220] In another embodiment, the raw syngas stream contains particulate solids in an amount of greater than 0 wt.% up to 30 wt. %, or greater than 0 wt.% up to 10 wt.%, or greater than 0 wt.% up to 5 wt.%, or greater than 0 wt.% up to 1 wt.%, or greater than 0 wt.% up to 0.5 wt.%, or greater than 0 wt.% up to 0.3 wt.%, or greater than 0 wt.% up to 0.2 wt.%, or greater than 0 wt.% up to 0.1 wt.%, or greater than 0 wt.% up to 0.05 wt.%, each based on the weight of solids in the feedstock stream. The amount of particulate solids in this case is determined by cooling the syngas stream to a temperature of below 200℃, such as would occur in a scrubbing operation.

[0221] The cold gas efficiency of the process using the mixed tire/solid fossil fuel as a percent can be calculated as:

$$= \frac{Produced\ gas\ (mole) x\ HHV\ (MJ\ per\ mole)}{Feedstock\ (kg)\ x\ HHV\ (MJ\ per\ kg)} x\ 100$$

[0222] The cold gas efficiency is at least 60%, or at least 65%, or at least 66%, or at least 67%, or at least 68%, or at least 69%, or desirably at least 70%, or at least 71%, or at least 72%, or at least 73%, or at least 74%, or at least 75%, or at least 76%, or at least 77%, or at least 78%, or at least 79%.

[0223] In one embodiment, hydrogen and carbon monoxide from the raw syngas stream discharged from the gasifier or from a scrubbed or purified syngas stream are not recycled or recirculated back to a gasification zone in a gasifier. Desirably, carbon dioxide from the raw syngas stream discharged from the gasifier or from a scrubbed or purified syngas stream is not recycled or recirculated back to a gasification zone in a gasifier. Desirably, no portion of the syngas stream discharged from the gasifier or from a scrubbed or purified syngas stream is recycled or recirculated back to a gasification zone in a gasifier. In another embodiment, no portion of the syngas discharged from the gasifier is used to heat the gasifier. Desirably, no portion of the syngas made in the gasifier is burned to dry the solid fossil fuel.

[0224] The feedstock stream is gasified with the oxidizer such as oxygen desirably in an entrained flow reaction zone under conditions sufficient to generate a molten slag and ash. The molten slag and ash are separated from the syngas and quench cooled and solidified. In a partial oxidation reactor, the coal/rubber tire/water mixture is injected with oxygen and the coal/rubber will react with oxygen to generate a variety of gases, including carbon monoxide and hydrogen (syngas). The molten slag and unreacted carbon/rubber tires accumulate into a pool of water in the quench zone at the bottom part of the reactor to cool and solidify these residues.

[0225] In one embodiment, the slag discharged from the gasifier as a solid. Slag is cooled and solidified within the gasifier in a quench zone within the shell of the gasifier, and is discharged from the gasifier shell as a solid. The

same applies to ash and char. These solids discharged from the gasifier are accumulated into a lock hopper which can then be emptied. The lock hopper is generally isolated from the gasifier and the quench zone within the gasifier.

[0226] The process can be practiced on an industrial scale and on a scale sufficient to provide syngas as a raw material to make chemicals on an industrial scale. At least 300 tons/day, or at least 500 t/d, or at least 750 t/d, or at least 850 t/d, or at least 1000 t/d, or at least 1250 t/d, and desirably at least 1500 t/d, or at least 1750 t/d, or even at least 2000 t/d of solids can be fed to the gasifier. The gasifier is desirably not designed to be mobile and is fixed to the ground, and desirably stationary during operations.

[0227] The syngas compositional variability produced by gasifying the feedstock containing the solid fossil fuel and tires is quite low over time. In one embodiment, the compositional variability of the syngas stream is low during a time period when the feedstock stream contains the solid fossil fuel and the pre-ground tires. The compositional variability of the syngas stream can be determined by taking at least 6 measurements of the concentration of the relevant gaseous compound in moles in equal time sub-periods across the entire time that the feedstock solids content are consistent and contain tires, such entire time not to exceed 12 days. The mean concentration of the gaseous compound is determined over the 6 measurements. The absolute value of the difference between the number farthest away from the mean and the mean number is determined and divided into the mean number x 100 to obtain a percent compositional variability.

[0228] The compositional variability of any one of:

a. CO amount, or
b. H_2 amount, or
c. CO2 amount, or
d. CH4 amount, or
e. H2S amount, or
f. COS amount, or

g. H2 + CO amount, or its molar ratio in sequence (e.g. H2:CO ratio), or
h. H2 + CO + CO2 amount, or its molar ratio in sequence, or
i. H2 + CO + CH4 amount, or its molar ratio in sequence, or
j. H2 + CO + CO2 + CH_4 amount, or its molar ratio in sequence, or
k. H2S + COS amount, or its molar ratio in sequence, or
l. H2 + CO + CO_2 + CH_4 + H_2S + COS,

can be not more than 5%, or not more than 4%, or not more than 3%, or not more than 2%, or not more than 1%, or not more than 0.5%, or not more than 0.25% during the shorter of a 12-day period or the time that tires are present in the feedstock composition.

[0229] In another embodiment, variability of the syngas stream generated by the mixed feedstock containing tires ("mixed case") is compared to the benchmark variability of the syngas stream generated from the same feedstock without the tires and its amount replaced by a corresponding amount of the same fossil fuel ("solid fossil fuel only case") and processed under the same conditions to obtain a % switching variability, or in other words, the syngas variability generated by switching between the two feedstock compositions. The variation of the mixed case can be less than, or no different than, or if higher can be similar to the variation of the solid fossil fuel only case. The time periods to determine variations is set by the shorter of a 12-day period or the time that tires are present in the feedstock composition, and that time period is the same time period used for taking measurements in the solid fossil fuels only case. The measurements for the solid fossil fuels only case is taken within 1 month before feeding a feedstock containing tires to the gasifier or after the expiration of feeding a feedstock containing tires to the gasifier. The variations in syngas composition made by each of the streams is measured according to the procedures states above. The syngas mixed case variability is less than, or the same as, or not more than 15%, or not more than 10%, or not more than 5%, or not more than 4%, or not more than 3%, or not more than 2%, or not more than 1%, or not more

than 0.5%, or not more than 0.25% of the syngas solid fossil fuel only case. This can be calculated as:

$$\%SV = \frac{V_m - V_{ff}}{V_{ff}} \times 100$$

where %SW is percent syngas switching variability on one or more measured ingredients in the syngas composition; and

V_m is the syngas compositional variability using the mixed stream containing post-consumer tires and the fossil fuel; and

V_{ff} is the syngas compositional variability using the fossil fuel only stream, where the solids concentration is the same in both cases, the fossil fuel is the same in both cases, and the feedstocks are gasified under the same conditions, other than temperature fluctuations which may autogeneously differ as a result of having tires in the feedstock, and the variabilities are with respect to any one or more of the syngas compounds identified above. In the event that the %SV is negative, then the syngas mixed case variability is less than the syngas solid fossil fuel only case.

[0230] In another embodiment, there is provided a continuous process for feeding a gasifier with a continuous feedstock composition containing solid fossil fuel and intermittently feeding a feedstock composition containing post-consumer tires and solid fossil fuel, while maintaining a negative, zero, or minimal syngas compositional switching variability over time frames that includes feedstocks with and without the post-consumer waste material using syngas produced using feedstocks without the post-consumer waste material as the benchmark. For example, switching frequency between feedstocks without the post-consumer tires (FF only) and the identical feedstocks except replacing a portion of the solids with the post-consumer tires (Mixed) can be at least 52x/yr, or at least 48x/yr, or at least 36x/yr, or at least 24x/yr, or at least 12x/yr, or at least 6x/yr, or at least 4x/yr, or at least 2x/yr, or at least 1x/yr, or at least 1x/2yr, and up to 3x/2yr, without incurring a syngas switching

variability beyond the percentages express above. One switch is counted as the number of times in a period that the Mixed feedstock is used.

[0231] To illustrate an example of the overall process, reference made to Figure 1. Coal is fed through line 1 into a coal grinding zone 2 wherein it is mixed with a water from stream 3 and ground to the desired particle size. A suitable coal grinding process includes a shearing process. Examples of a suitable apparatus include ball mill, a rod mill, hammer mill, a raymond mill, or an ultrasonic mill; desirably a rod mill. The rod mill is desirably the wet grind type to prepare a slurry. A rod mill contains a number of rods within a cylinder where the rods rotate about a horizontal or near horizontal axis. The coal is ground when it is caught between the rods and cylinder wall by the rolling/rotating action of the rods. The rod mill can be the overflow type, end peripheral discharge, and center peripheral discharge, desirably the overflow type.

[0232] The grinder can also be equipped with a classifier to remove particles above the target maximum particle size. An example of a classifier is a vibrating sieve or a weir spiral classifier.

[0233] The coal grinder zone (which includes at least the grinding equipment, feed mechanisms to the grinder, and any classifiers) is a convenient location for combining pre-ground rubber tire particles through line 4 to the coal. The desired amount of coal and tires can be combined onto a weigh belt or separately fed though their dedicated weigh belts that feed the grinding apparatus. The water slurry of ground coal and rubber tires is discharged through line 5 and pumped into a storage/charge tank 6 that is desirably agitated to retain a uniform slurry suspension. Alternatively, or in addition to the grinder 2 location, pre-ground rubber tires can be added into the charge/storage tank 6 through line 7, particularly when this tank is agitated.

[0234] The feedstock stream is discharged from tank 6 directly or indirectly to the gasifier 9 through line 8 into the injector 10 in which the coal/rubber/water slurry is co-injected with an oxygen-rich gas from line 11

into the gasification reaction zone 12 where combustion takes place. The injector 10 may optionally be cooled with a water line 13 feeding a jacket on the injector and discharged through line 14. After start-up and in a steady state, the reaction in the reaction zone 12 takes place spontaneously at an autogenous temperature in the ranges noted above, e.g. 1200℃ to 1600℃ and at a pressure in the ranges note above, e.g. 10 – 100 atmospheres. The gaseous reaction products of the partial oxidation reaction include carbon monoxide, hydrogen, with lesser amounts of carbon dioxide and hydrogen sulfide. Molten ash, unconverted coal or rubber, and slag may also be present in the reaction zone 12.

[0235] The gasifier 9 is illustrated in more detail in Figure 2, also as shown in US Patent 3,544,291, the entire disclosure of which is incorporated herein by reference. The gasifier comprises a cylindrical pressure vessel 50 with a refractory lining 75 defining a cylindrical, compact, unpacked reaction zone 54. The mixture of coal, tires, water and oxygen is injected through an injector axially into the upper end of reaction zone 54 through inlet passageway 76. Products of reaction are discharged axially from the lower end of reaction zone 54 through an outlet passageway 77 into a slag quench chamber 71. The quench chamber 71 and the reaction zone 54 are within the outer shell 50 of the gasifier and are in continuous gaseous and fluid communication with each other during the combustion and reaction in reaction zone 54. A pool of water 78 is maintained in the lower portion of quench chamber 71 and a water jacket 79 is provided in the upper portion of the quench chamber 71 to protect the pressure vessel shell from becoming overheated by hot gases from the gasification zone 54. Unconverted solid fuel and molten slag and ash from the solid fuel is discharged with the product gas stream through outlet 77 into the quench chamber 71 where the larger particles of solid and any molten ash or slag drops into the pool of water. The partially cooled gas is discharged from the quench chamber 71 through line 58, which optionally is also provided with a refractory lining 75.

[0236] Turning back to Figure 1, the hot reaction product gas from reaction zone 12 along with the slag formed on the surfaces of refractory facing the reaction zone 12 are discharged into the quench chamber 15 where they are quickly cooled and solidified below the reaction temperature in zone 12 to form solid slag, ash, and unconverted coal which separates from the hot raw syngas to form a raw syngas stream which is discharged from the gasifier vessel. The process effectuates a separation of ash, slag, and unconverted products from the reaction product gases, and has the advantage over a fixed or moving bed waste gasifier in that within the gasifier vessel, a first step of purification of the gaseous reaction products from the reaction zone 12 has occurred prior to discharging the raw syngas stream from the gasification vessel. At the same time that the slag and vaporized unconverted fossil fuel elements are solidified in the quench water in quench zone 15, and part of the quench water is vaporized producing steam which is useful in subsequent operations, for example, for the water-gas shift reaction of the scrubbed raw syngas stream in which hydrogen is produced by reaction of carbon monoxide with water vapor in the presence of a suitable catalyst such as an iron oxide-chromic oxide catalyst.

[0237] The temperature of the raw syngas stream exiting the gasification vessel through line 16 can be within a range of 150 °C to 700 °C, or from 175 °C to 500 °C. Desirably, the temperature of the raw syngas discharged from the gasifier is not more than 500 °C, or less than 400 °C, or not more than 390 °C, or not more than 375 °C, or not more than 350 °C, or not more than 325 °C, or not more than 310 °C, or not more than 300 °C, or not more than 295 °C, or not more than 280 °C, or not more than 270 °C. The temperature of the raw syngas exiting the gasification vessel is substantially reduced from the temperature of the reaction product gases within the reaction zone. The temperature reduction between the gasification zone gas temperature (or alternatively all reaction zones if more than one stage is used) and the raw syngas temperature discharged from the gasifier vessel can be at least 300 °C, or at least 400 °C, or at least 450 °C, or at least 500 °C, or at least

550 °C, or at least 600 °C, or at least 650 °C, or at least 700 °C, or at least 800 °C, or at least 900 °C, or at least 1000 °C, or at least 1050 °C, or at least 1100 °C.

[0238] As shown in Figure 1, the raw syngas is discharged from the gasifier through line 16 to a suitable scrubber 17 where it is contacted with water from line 18 for the removal of remaining solid particles from the raw syngas stream. Gas scrubber 17 may comprise a venturi scrubber, a plate type scrubber or a packed column, or a combination thereof, in which raw syngas stream is intimately contacted with water to effect the removal of solid particles from the raw syngas stream. The scrubbed raw syngas stream is discharged through line 19 for further use in other processes, such as acid gas (e.g. sulfur compounds) removal processes to make the resulting purified syngas stream suitable for manufacture of chemicals. Suitable process for acid gas removal include the Rectisol™ and Selexol™ acid gas removal processes. Once the sulfur species are removed from the syngas stream, elemental sulfur can be recovered and converted to sulfuric acid and other sulfur products that can be commercialized through processes such as the Claus™ process.

[0239] As shown in Figure 1, the solids-water mixture from gas scrubber 17 is discharged from the scrubber passed through line 20 optionally to line 21 where it is mixed with quench water containing solids drawn from quench zone 15 via line 22 and the mixture passed through pressure reducing valve 23 into settling tank 24. A heat exchanger 25 serves to heat by heat exchange with hot quench water from line 22 the relatively cool make-up and recycle water supplied through line 26 from a suitable source and pumped to lines for quenching and/or scrubbing the product gas from the gas generator.

[0240] Solids, including unconverted particulate coal, settle by gravity from the water in settling tank 24 and are drawn off through line 27 as a concentrated slurry of ash, unconverted coal and soot in water. This slurry may be optionally be recycled to grinding zone 2 via line 28. If desired, a portion of the slurry from line 27 may be diverted through line 29 into mix tank

6 to adjust the concentration of solids in the water-coal-rubber slurry feedstream charged to the gasifier. Also, as shown in Figure 2, water and solids from settler tank 66 may be drawn off in line 83 for processing, while water and ash, unconverted coal and soot may be drawn off the settle tank 66 through line 84 and combined with the feedstock of coal, tires and water.

[0241] As shown in Figure 1, gases released in settler 24 may be discharged through line 30 and recovered as potential fuel gases. Clarified water from settler 24 is withdrawn through line 31 and recirculated to the quench water system through line 32. A portion of the water from line 32, after passing through heat exchanger 25, is supplied to the quench zone 15 through line 33 and a further portion of the water is passed through line 18 to gas scrubber 17. Further, water from the quench zone can be withdrawn through line 22 to settler 24 through a control valve 23. The water level can be controlled through a liquid level controller on the gasifier to maintain a substantially constant water level in quench zone.

[0242] Alternatively, or in addition, the quench water through line 33 feeding the quench water zone can supplied from a syngas scrubber downstream from the gasifier as shown in Figure 2. The quench water stream optionally also fed to the quench zone may be clarified or may contain from about 0.1 weight % soot to about 1.5 weight % soot based on the weight of the quench water stream feeding the gasifier.

[0243] If desired, high temperature surfactants can be added to the quench water directly into the quench zone/chamber. Examples of such surfactants include any one of the surfactants mentioned above to stabilize the feedstock stream, such as ammonium lignosulfonate or an equivalent surfactant which is thermally stable at temperatures of about 300° F. to about 600° F. Other surfactants include organic phosphates, sulfonates and amine surfactants. The surfactants are used to establish a stable suspension of soot in the water at the bottom of the quench chamber, where the soot concentration can be at least 1 wt.%, or in the range of about 3.0 weight % to about 15.0 weight %, each based on the weight of the water in the quench chamber. The

concentration of active surfactants in the bottom of the quench zone can vary from about 0.01 weight % to about 0.30 weight %.

[0244] Also, as illustrated in Figure 2, an internal water jacket 79 is provided within the pressure vessel shell 50 at the upper portion of the quench zone 71. Water jacket 79 prevents overheating of the pressure vessel shell below the level of refractory 75 surrounding reaction zone 54. Water is introduced into water jacket 79 from line 80 and discharged therefrom through line 81 through valve 82 and can be fed directly or indirectly (through a settler tank 66) to a scrubber 59.

[0245] As shown in Figure 1, periodically slag and other heavy incombustible solids settling to the bottom of quench zone 15 are withdrawn as a water-solids slurry through line 34 and valve 35 into lock hopper 36. Accumulated solid material from lock hopper 36 is discharged through line 37 as controlled by valve 38. In the operation of the lock hopper, valve 35 is opened and valve 38 closed during the filling period in which solid material from quench chamber 15 is transferred to lock hopper 36. Valve 35 is then closed and the lock hopper 36 emptied through line 37 by opening valve 38. From lock hopper 36, solid residue and water are discharged through line 37. The equivalent equipment and lines are shown in Figure 2 as outlet 85, valves 86 and 88, line 89, and lock hopper 87.

[0246] In an alternative embodiment as shown in Figure 1, fresh water can be charged to the lock hopper 36 to displace the sour water in the lock hopper 36. Cold clean water from line 39 is introduced through valve 40 into the lower part of lock hopper 36. Valve 41 in line 42 is opened to establish communication between line 33 and lock hopper 36. As the cold clean water enters the lower part of lock hopper 36, hot sour water is displaced from the lock hopper and flows through line 42 and line 33 into the quench zone 15 as part of the make-up water for the quench system. After the sour water has been displaced from lock hopper 36 valves 40 and 41 are closed and valve 38 opened to permit discharge of slag and clean water from the lock hopper through line 37.

[0247] In an alternate embodiment, as shown in Figure 1, stripping gas such as carbon dioxide, or gases produced by the gasifier from which acid gases have been removed by chemical treatment, can be introduced into the lower portion of lock hopper 36 through line 43 after the lock hopper has been charged with slag and sour water from the quench zone 15 and valve 35 closed. Stripping gas under pressure is introduced into the lower portion of lock hopper 36 by opening valve 44 in line 43. At the same time, valve 41 in line 42 is opened allowing gas to pass through lines 42 and 33 into the quench zone 15. The stripping gas from line 43 desorbs sour gases, i.e. sulfides, cyanides, and other noxious gases, from the water in lock hopper 36. When the desorbed gases are introduced back into the gasifier, they mix with hot product gases and, after passing through the quench zone are discharged through line 16 to gas scrubber 17 as a part of the product gas stream for further purification and utilization.

[0248] To illustrate one embodiment of an injector, reference is made to Figure 3, showing a partial cut-away view of a synthesis gas gasifier at the injector location. The gasifier vessel includes a structural shell 90 and an internal refractory liner 91 (or multiple liners) around an enclosed gasification zone 93. Projecting outwardly from the shell wall is an injector mounting neck 94 for supporting an elongated fuel injection injector assembly 95 within the reactor vessel. The injector assembly 95 is aligned and positioned so that the face 96 of the injector nozzle 97 is substantially flush with the inner surface of the refractory liner 91. An injector mounting flange 96 secures the injector assembly 95 to a mounting neck flange 97 of the gasifier vessel to prevent the injector assembly 95 from becoming ejected during operation. A feed of oxygen flows into a central inner nozzle through conduit 98. The feedstock stream is fed to the injector assembly through line 99 into an annular space around the central oxidant nozzle. A cooling jacket surrounding the injector assembly 95 above the injector mounting flange 96 is fed with cooling water 100 to prevent the injector assembly from overheating. An optional second

feed of oxidant flows through line 101 into an annular space around at least a portion of the outer surface of the shell defining the feedstock annulus.

[0249] A more detailed view of the injector is shown in Figure 4. A sectional view of a portion of the injector assembly 80 toward the injector nozzle tip is illustrated. The injector assembly 80 includes an injector nozzle assembly 125 comprising three concentric nozzle shells and an outer cooling water jacket 110. The inner nozzle shell 111 discharges from an axial bore opening 112 the oxidizer gas that is delivered along upper assembly axis conduit 98 in Figure 3. Intermediate nozzle shell 113 guides the feedstock stream into the gasification zone 93. As a fluidized solid, this coal slurry is extruded from the annular space 114 defined by the inner shell wall 111 and the intermediate shell wall 113. The outer, oxidizer gas nozzle shell 115 surrounds the outer nozzle discharge annulus 116. The upper assembly port 101, as shown in Figure 3, supplies the outer nozzle discharge annulus with an additional stream of oxidizing gas. Centralizing fins 117 and 118 extend laterally from the outer surface of the inner and intermediate nozzle shell walls 111 and 113, respectively to keep their respective shells coaxially centered relative to the longitudinal axis of the injector assembly. It will be understood that the structure of the fins 117 and 118 form discontinuous bands about the inner and intermediate shells and offer small resistance to fluid flow within the respective annular spaces.

[0250] The internal nozzle shell 111 and intermediate nozzle shell 113 can both be axially adjustable relative to the outer nozzle shell 115 for the purpose flow capacity variation. As intermediate nozzle 113 is axially displaced from the conically tapered internal surface of outer nozzle 115, the outer discharge annulus 116 is enlarged to permit a greater oxygen gas flow. Similarly, as the outer tapered surface of the internal nozzle 111 is axially drawn toward the internally conical surface of the intermediate nozzle 113, the feedstock slurry discharge area 114 is reduced.

[0251] Surrounding the outer nozzle shell 115 is a coolant fluid jacket 110 having an annular end closure 119. A coolant fluid conduit 120 delivers a

coolant, such as water, from the upper assembly supply port 100 in Figure 3 directly to the inside surface of the end closure plate 119. Flow channeling baffles 121 control the path of coolant flow around the outer nozzle shell to assure a substantially uniform heat extraction and to prevent the coolant from channeling and producing localized hot spots. The end closure 119 includes a nozzle lip 122 that defines an exit orifice or discharge opening for the feeding of reaction materials into the injection injector assembly.

[0252] The planar end of the cooling jacket 119 includes an annular surface 123 which is disposed facing the combustion chamber. Typically, the annular surface 123 of cooling jacket is composed of cobalt base metal alloy materials. Although cobalt is the preferred material of construction for the nozzle assembly 125, other high temperature melting point alloys, such as molybdenum or tantalum may also be used. The heat shield 124 is formed from a high temperature melting point material such as silicon nitride, silicon carbide, zirconia, molybdenum, tungsten or tantalum.

[0253] While this discussion was based on a injector and feed stream arrangement as previously described, it is understood that the injector may consist of only two passages for introducing and injecting the oxidant and feedstock stream, and they may be in any order with the feedstock stream passing through the central axial bore opening while the feedstock is fed through an annulus surrounding at least a portion of the central oxidant conduit, or the order may be reversed as described above.

[0254] An example of the operation of the gasifier and scrubber is illustrated in Figure 2. The coal/tires feedstock slurry is fed to the gas generator 50 through injector 51 mounted at the top 52 of the gasifier and is fed with oxygen through line 53 and injected into the gasification zone 54 to generate a raw syngas. The raw syngas gases discharged from the gasifier is fed to a contactor 55. Water is injected into contactor 55 from line 56 through injectors 56 and 57. Intimate contact between the raw syngas from line 58 and water from line 56 is effected desirably by way of a venturi, nozzle, or plate orifice. In contactor 55, the syngas stream is accelerated, and water is

injected into the accelerated gas stream at the throat of the nozzle, venturi or orifice, from a plurality of injectors 56 and 57.

[0255] The resulting mixture of gas and water formed in contactor 55 is directed into scrubber 59 through a dip leg 60 which extends downwardly into the lower portion of scrubber 59. The gas stream from contactor 55 also carries entrained solid particles of unconsumed fuel or ash. A body of water is maintained in the scrubber 59, the level of which may be controlled in any suitable manner, for example by means of a liquid level controller 61, shown diagrammatically. The dip leg 60 discharges the mixture of water and gas below the level of water contained in the scrubber 59. By discharging the mixture of gas and water through the open end of dip leg 60 into intimate contact with water, solid particles from the gas stream are trapped in the water.

[0256] Scrubber 59 is suitably in the form of a tower having an optionally packed section 62 above the point of entry of the gas stream from contactor 55. Water from line 63 is introduced into scrubber 59 above the level of the packing material 62. In packed section 62, the gas stream is intimately contacted with water in the presence of suitable packing material, such as ceramic shapes, effecting substantially complete removal of solid particles from the gas stream. Product gas, comprising carbon monoxide and hydrogen and containing water vapor, atmospheric gases, and carbon dioxide, is discharged from the upper end of scrubber 59 through line 64 at a temperature corresponding to the equilibrium vaporization temperature of water at the pressure existing in scrubber 59. Clean syngas from line 64 may be further processed, for example, for the production of higher concentrations of hydrogen by water-gas shift reaction and suitable downstream purification to remove sulfur.

[0257] Water from the lower portion of scrubber 59 is passed by pump 65 through line 56 to injectors 56 and 57. Clarified water from settler 66 also may be supplied to line 56 by pump 67 through line 68. Water is withdrawn from scrubber 59 by pump 69 and passed through valve 70 responsive to

liquid level control 61 on the scrubber and passed into quench zone 71 via line 72 to control the liquid level in scrubber 59.

[0258] Any heavy solid particles removed from the gas stream in the dip leg 60 settling into water slurry are collected the water bath at the bottom of the scrubber 59 and discharged at the bottom leg 73 at periodic intervals through line 74 as controlled by valve 75.

[0259] Any suitable scrubber design can be used in the process. Other scrubber designs include a tray type contacting tower wherein the gases are counter currently contacted with water. Water is introduced into the scrubber at a point near the top of the tower.

EXAMPLES

Example 1

[0260] Ground post-consumer rubber tires are milled to a nominal particle size between 1 mm and 0.5 mm. Coal is dried and crushed in a Retsch jaw crusher to a nominal size of <2mm. A predetermined amount of water is added to a 4.5 L metal bucket. Ammonium lignosulfonate is added to the water in the metal bucket and mixed with a spatula until it is distributed evenly. Ground tires and coal are added to the water and ALS mixture in the metal bucket and then the blend is mixed by an overhead mixer. Aqueous ammonia is added to the slurry to adjust the pH to 8 ± 0.2. After being well mixed, the sample is placed in the laboratory rod mill equipped with 5 stainless steel rods at ½" X 9", 8 rods at 5/8" X 9", 8 rods at ¾" X 9", 2 rods at 1" X 9", and 1 rod at 1 ¼" X 9". The slurry is milled for 1 hour at approximately 28 rpm (mill outside diameter = 11.75 inches). The aqueous ammonia is again used to adjust the pH to 8 ± 0.2 while the slurry is mixed by the overhead mixer. Each batch of slurry is made to be a total of approximately 3000 grams with approximately 69% solids with varying amounts of recycled materials as reported in Table 1 below. Viscosity and stability tests are conducted with the results listed in Table 1.

[0261] 500-550g samples of coal slurry are transferred to a 600 mL glass beaker to measure the viscosity and stability. The stability of each sample can be judged by visual observation. The slurry is well mixed to generate a homogeneous distribution of particles throughout the sample and letting the slurry sit undisturbed for a period of time. The slurry is then remixed. If a layer of particles separated out at the bottom of the beaker, the slurry will be difficult to remix, and it is then considered to have settled. Over a period of time, the slurries will have settling. However, the longer the amount of time required to settle determines whether the stability of the slurry is considered good, moderate, or poor. If the slurry settles before 5 minutes, it is considered poor.

[0262] In an alternative method, the stability of the slurry can be determined quantitively. The viscosities of the slurry samples are measured at room temperature using either a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm (method A) or a Brookfield R/S rheometer with V80-40 vane spindle operating at a shear rate of 1.83/s (method B). An average of 3 viscosity measurements is reported.

[0263] The stability is measured, by either Method A or Method B, by submerging the spindle of the rheometer into the slurry at the bottom of the beaker after the slurry is well mixed to form a homogeneous distribution of solids. After a designated period of time, the viscosity is measured with the spindle at the bottom of the beaker. The viscosity increases with settling and the slurry is considered to have settled if the initial reading on starting a viscosity measurement is 100,000 cP. Thus, slurries are considered stable if the initial viscosity is 100,000 cP or less after standing still for 5 minutes.

[0264] The pumpability of a slurry is measured by Method A or Method B. The slurry is considered pumpable if the viscosity reading is 30,000 cP or less (desirably 25,000 or less or better is 20,000 or less) when taking a reading immediately after well mixing the slurry to form a homogeneous distribution of solids.

[0265] The results of stability are determined by visual observation, and the results of pumpability are reported in Table 1 in the viscosity column using Method A. Stability is determined at the 5-minute mark.

TABLE 1 – Effect of increasing ground tire loadings (mesh of 20 or higher) on coal-water slurry properties.

Substrate ID	Substrate % of solids	Substrate % of total	ALS %	Target Solids %	Measured Solids %	Viscosity[a]	Stability	Overall
Control	0%	0%	0.40%	69%	69.5%	4040 cP	Moderate	Good
Tires	2.9%	2.0%	0.20%	69%	70.0%	2990 cP	Moderate	Good
Tires	7.3%	5.0%	0.40%	69%	69.4%	3200 cP	Moderate	Good
Tires	14.5%	10.0%	0.40%	69%	69.9%	11470 cP	Good	Good
Tires	18.6%	12.8%	0.38%	69%	70.0%	26240 cP	Good	Borderline
Tires	36.2%	25.0%	0.40%	69%	68.5%	High	High	Too Thick

[a]Measured by method A.

[0266] All mixtures show moderate to good stability, but the viscosity of the slurry at 18.6% rubber is nearly at the maximum value that can be reliably pumped into the gasifier. The viscosity of the slurry at 36.2% rubber is too high and would not be pumpable at 69% solids loading. The 18.6% slurry would be usable, more preferably at a slightly lower total solids loading. Loadings of 15% and below are acceptable for normal production uses. 100% is not stable (settled) and is very low total solids.

Example 2

[0267] Batches of the coal/tire slurry are prepared as stated in Example 1 and in the amounts reported in Table 2. The results of stability and pumpability are reported below in Table 2 using Method B in each case. A report of "stable" in the stability column indicates a viscosity reading of less than 100,000 cP at the time period stated.

TABLE 2 – Effect of increasing ground tire loadings (20-99 mesh) on coal-water slurry properties.

Substrate ID	Substrate % of solids	Substrate % of total	ALS %	Target Solids %	Measured Solids %	Viscosity	Stability 5 min	Stability 10 min	Stability 20 min	Overall
Control	0%	0%	0.20%	69%	69.4%	4554 cP	Stable	Stable	Stable	Good
Tires	2.0%	1.4%	0.20%	69%	69.7%	4387 cP	Stable	Stable	Stable	Good
Tires	5.0%	3.4%	0.20%	69%	69.8%	4716 cP	Stable	Stable	Stable	Good
Tires	10.0%	6.9%	0.20%	69%	69.7%	7007 cP	Stable	Stable	Not Stable	Good
Tires	15.0%	10.3%	0.20%	69%	69.5%	13624 cP	Stable	Stable	Stable	Good
Tires	20.0%	13.8%	0.40%	69%	68.1%	34497 cP	Stable	Stable	Stable	Too Viscous

[0268] All samples remained stable at 5 and 10 minutes. However, at a 20% of solids loading, the tires sample would be considered too viscous to be effectively pumpable.

Example 3

[0269] Elemental analysis of the pre-ground tires is conducted, and the results are reported in Tables 3 and 4 below:

TABLE 3 – Major elements present

Element	wt%
C	82.68[a]
H	8.18[a]
S	1.67[b]
N	<1.0[a]
O+N	4.56[c]
Zn	2.20[b]
Si	0.71[b]

[a]By CHN elemental analyzer

[b]By Uniquant x-ray analysis

[c]By difference

TABLE 4 – Ground tire ash composition

Element	m/m%[a]
ZnO	49.45%
SiO_2	27.32%
Fe_2O_3	6.51%
Al_2O_3	5.56%
CaO	3.41%
MgO	3.47%
CuO	1.12%
Na_2O	1.17%
K_2O	0.99%
CoO	0.69%
TiO_2	0.18%
MnO	0.05%
V_2O_3	0.04%
Ga_2O_3	0.02%
ZrO_2	0.02%
Sum	100.00%

[a]By Calculated from uniquant x-ray analysis of tires.

CLAIMS

WHAT WE CLAIM IS:

1. A process for preparing a cellulose ester comprising: (1) preparing a post-consumer tire content syngas in a synthesis gas operation by gasifying a feedstock containing a solid fossil fuel source and at least some content of post-consumer tires; (2) using the post-consumer tire content syngas as a feedstock in a reaction scheme to produce at least one cellulose reactant for preparing a cellulose ester; and (3) reacting said at least one cellulose reactant to prepare at least one cellulose ester.

2. The process according to claim 1, wherein the at least one cellulose reactant is chosen from acetic acid, acetic anhydride, propionic acid, butyric acid, and combinations thereof.

3. The process according to claim 1, wherein the at least one cellulose ester is chosen from cellulose acetate (CA), cellulose diacetate (CDA), cellulose triacetate (CTA), cellulose butyrate (CB), cellulose propionate (CP), cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP), or combinations thereof.

4. The process according to claim 1, wherein the reaction scheme to produce at least one cellulose reactant comprises one or more of the following reactions: (1) converting said post-consumer tire content syngas to methanol; (2) reacting said methanol to produce acetic acid; (3) reacting said methanol and/or said acetic acid to produce methyl acetate; and (4) reacting said methyl acetate and/or said methanol to produce acetic anhydride.

5. The process according to claim 4, wherein the reaction scheme to produce at least one cellulose reactant comprises all of reactions (1) through (4).

6. Use of post-consumer tire content syngas to produce at least one cellulose reactant.

7. Use of post-consumer tire content syngas to produce at least one cellulose ester.

8. A cellulose ester composition comprising at least one cellulose ester prepared according to claim 1, wherein said cellulose ester has at least one substituent on an anhydroglucose unit (AGU) derived from post-consumer tire content syngas.

9. The cellulose ester composition according to claim 8, wherein the substituent is a combination of acetyl and propionyl functional groups.

10. The cellulose ester composition according to claim 8, wherein the substituent is a combination of acetyl and butyryl functional groups.

11. The cellulose ester composition according to claim 8, wherein the substituent is any combination of organic acid functional groups.

12. The cellulose ester composition according to claim 8, wherein said at least one substituent is an acetyl functional group.

13. The cellulose ester composition according to claim 8 or 12, wherein the cellulose ester is cellulose di-acetate (CDA).

14. The cellulose ester composition according to claim 8 or 12, wherein the cellulose ester is cellulose tri-acetate (CTA).

15. The cellulose ester composition according to any one of claims 8, 13, or 14, wherein the cellulose ester is prepared from a cellulose reactant that comprises acetic anhydride that is derived from post-consumer tire content syngas.

16. The cellulose ester composition according to any one of claims 8 to 15, wherein the post-consumer tire content syngas comprises gasification products from a gasification feedstock that comprises post-consumer tires and coal.

17. The cellulose ester composition according to claim 16, wherein the gasification feedstock comprises a liquid slurry that comprises coal and post-consumer tires.

18. The cellulose ester composition according to any one of claims 16 or 17, wherein the gasification process comprises gasifying said gasification feedstock in the presence of oxygen.

19. An article comprising the cellulose ester composition according to any one of claims 8 to 18.

20. The article according to claim 19, wherein the article is a textile fabric.

21. The article according to claim 19, wherein the article is biodegradable and/or compositable.

22. A staple fiber comprising the cellulose ester composition according to any one of claims 8 to 18, wherein the cellulose ester composition comprises cellulose acetate.

23. An integrated process for preparing a cellulose ester which comprises the processing steps of: (1) preparing a post-consumer tire content syngas in a synthesis gas operation utilizing a feedstock that contains a solid fossil fuel source and at least some content of post-consumer tires; (2) preparing at least one chemical intermediate from said syngas; (3) reacting said chemical intermediate in a reaction scheme to prepare at least one cellulose reactant for preparing a cellulose ester, and/or selecting said chemical intermediate to be at least one cellulose reactant for preparing a cellulose ester; and (4) reacting said at least one cellulose reactant to prepare said cellulose ester; wherein said cellulose ester comprises at least one substituent on an anhydroglucose unit (AGU) derived from post-consumer tire content syngas.

24. The integrated process according to claim 23, wherein the processing steps (1) to (4) are carried out in a system that is in fluid and/or gaseous communication

25. The process or composition according to any one of claims 1 to 24, wherein the post-consumer tire content syngas is prepared by a process comprising:

a. charging an oxidant and a feedstock composition comprising post-consumer tires and a solid fossil fuel, to a gasification zone within a gasifier;

b. gasifying the feedstock composition together with the oxidant in a gasification zone to produce a syngas composition; and

c. discharging at least a portion of the syngas composition from the gasifier;

wherein the gasifier is an entrained flow gasifier.

26. The process or composition according to any one of claims 1 to 24, wherein the post-consumer tire content syngas is prepared by a process comprising:

a. charging an oxidant and a feedstock composition comprising post-consumer tires and a solid fossil fuel, to a gasification zone within a gasifier;

b. gasifying the feedstock composition together with the oxidant in a gasification zone to produce a syngas composition; and

c. discharging at least a portion of the syngas composition from the gasifier,

wherein at least one of the following conditions is present:

(i) gasification within the gasification zone is conducted at a temperature of at least 1000 °C, or

(ii) the pressure within the gasification zone greater than 2.7 MPa, or

(iii) the feedstock composition is a slurry, or

(iv) no steam is introduced to the gasifier that flows into the gasification zone, or

(v) the tires are pre-ground such that at least 90% of the particles have a particle size of less than 2 mm, or

(vi) the tar yield is less than 4 wt.%, or

(vii) the gasifier contains no membrane wall in the gasification zone, or

(viii) a combination of two or more of the above conditions.

27. The process or composition according to any one of claims 1 to 26, wherein the the feedstock is in the form of a feedstock slurry composition comprising a post-consumer tires, a solid fossil fuel, water, and a chemical additive, wherein the post-consumer tires are pre-ground to a particle size of less than 2 mm, the solid fossil fuel in the feedstock composition has a particle size of less than 2 mm, the solids content in the slurry is at least 62 wt.% (or at least 65 wt.%, or at least 68 wt.%, or at least 69 wt.%, or at least 70 wt.%), the amount of pre-ground tires present in the feedstock stream slurry composition is 0.1 wt.% to 25 wt.% based on the weight of all solids (or 0.5 wt.% to 10 wt.%), and the amount of water is at least 20 wt.% based on the weight of the feedstock slurry composition, and wherein either:

a. the slurry is stable as determined by having an initial viscosity of 100,000 cP or less at 5 minutes, or 10 minutes, or 15 minutes, or 20 minutes, or 25 minutes, or even for 30 minutes using a Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm, measured at ambient conditions; or

b. the slurry is pumpable as determined by having a viscosity of less than 30,000 cP, or 25,000 cP or less, or not more than 23,000 cP, or not more than 20,000 cP, or not more than 18,000 cP, or not more than 15,000 cP, or not more than 13,000 cP, after mixing to obtain a homogeneous distribution of solids throughout the slurry and using a Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm Brookfield R/S Rheometer equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm Brookfield R/S Rheometer

equipped with V80-40 vane operating at a shear rate of 1.83/s or a Brookfield viscometer with an LV-2 spindle rotating at a rate of 0.5 rpm, measured at ambient conditions , or

c. both.

28. The process or composition of any one of claims 1 to 27, wherein the post-consumer tires in the feedstock composition or as fed to or combined with a solid fuel are ground to a size that is 2 mm or smaller, or 1.7 mm or smaller, or 1.2 mm or smaller, or 0.4 mm or smaller 0.25 mm or smaller, or 0.15 mm or smaller, or 0.07 mm or smaller.

29. The process or composition of any one of claims 1 to 28, wherein the maximum particle size of the ground rubber tires is within 50%, or within 45%, or within 40%, or within 35%, or within 30%, or within 25%, or within 20%, or within 15%, or within 10%, or within 5% of the maximum particle size of the ground solid fossil fuel.

30. The process or composition of any one of claims 1 to 29, wherein at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 96 wt.%, or at least 97 wt.%, or at least 98 wt.%, or at least 99 wt.%, or at least 99.5 wt.%, or 100 wt.% of all feedstock other than solid fossil fuels in the feedstock stream fed into the gasifier is pre-ground tires.

31. The process or composition of any one of claims 1 to 30, wherein the particle size of the solid fuel in the feedstock composition is 2 mm or less.

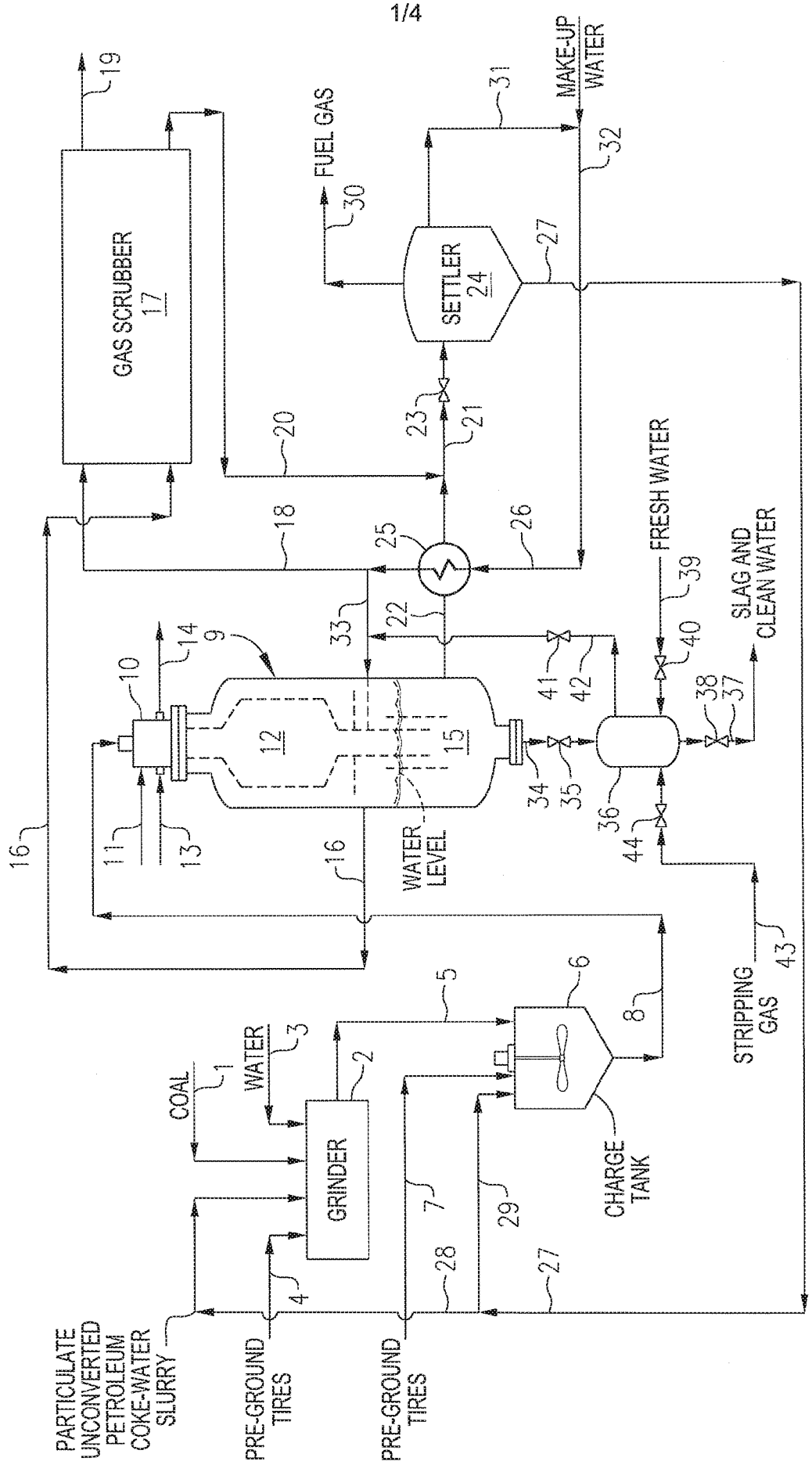

PARTICULATE UNCONVERTED PETROLEUM COKE-WATER SLURRY
PRE-GROUND TIRES
PRE-GROUND TIRES
COAL
WATER
GRINDER
CHARGE TANK
STRIPPING GAS
SLAG AND CLEAN WATER
FRESH WATER
MAKE-UP WATER
FUEL GAS
SETTLER 24
GAS SCRUBBER 17
WATER LEVEL
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FIG. 1

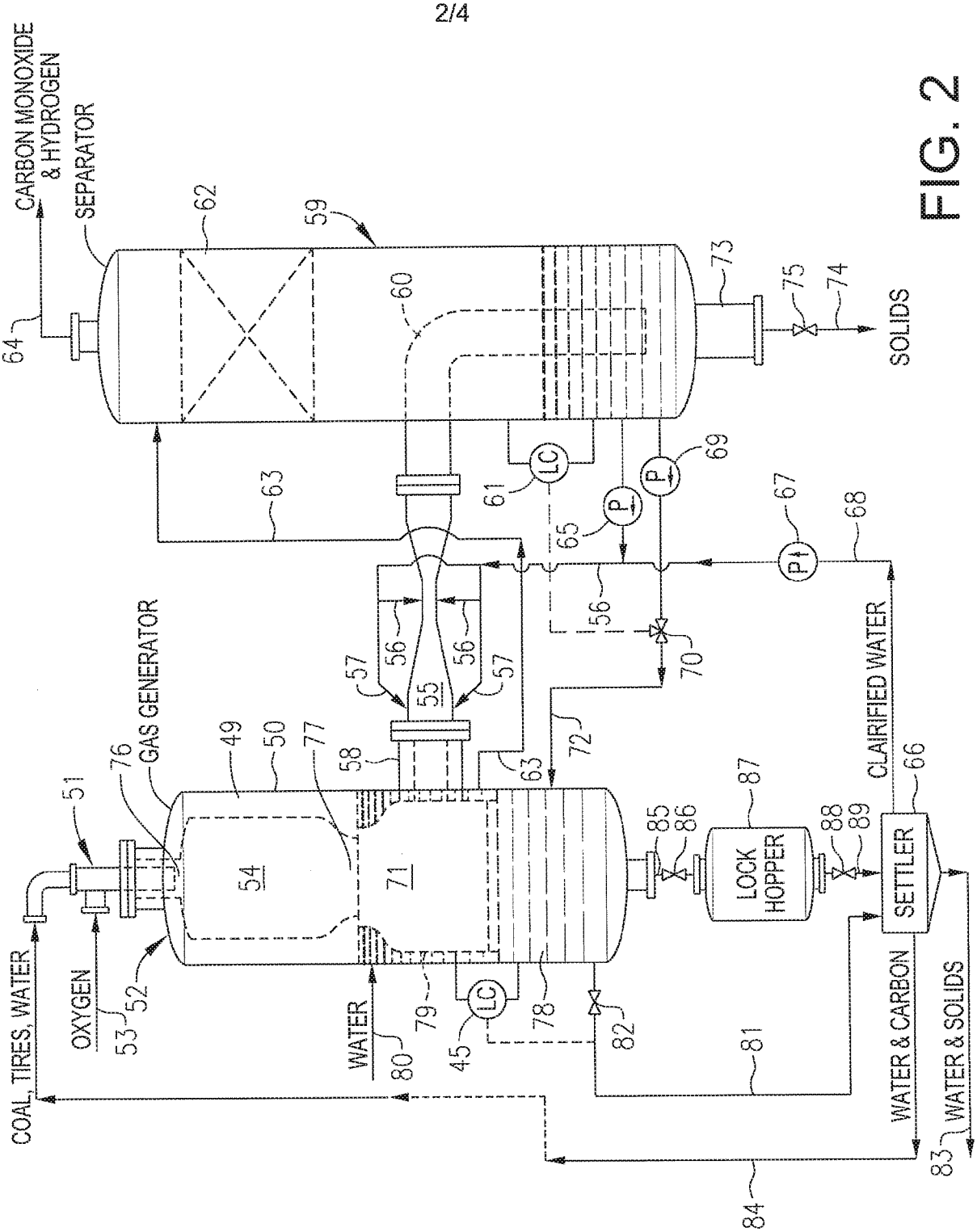

CARBON MONOXIDE & HYDROGEN
SEPARATOR
SOLIDS
GAS GENERATOR
CLAIRIFIED WATER
LOCK HOPPER
SETTLER
COAL, TIRES, WATER
OXYGEN
WATER
WATER & CARBON
WATER & SOLIDS
LC
P
PI

FIG. 2

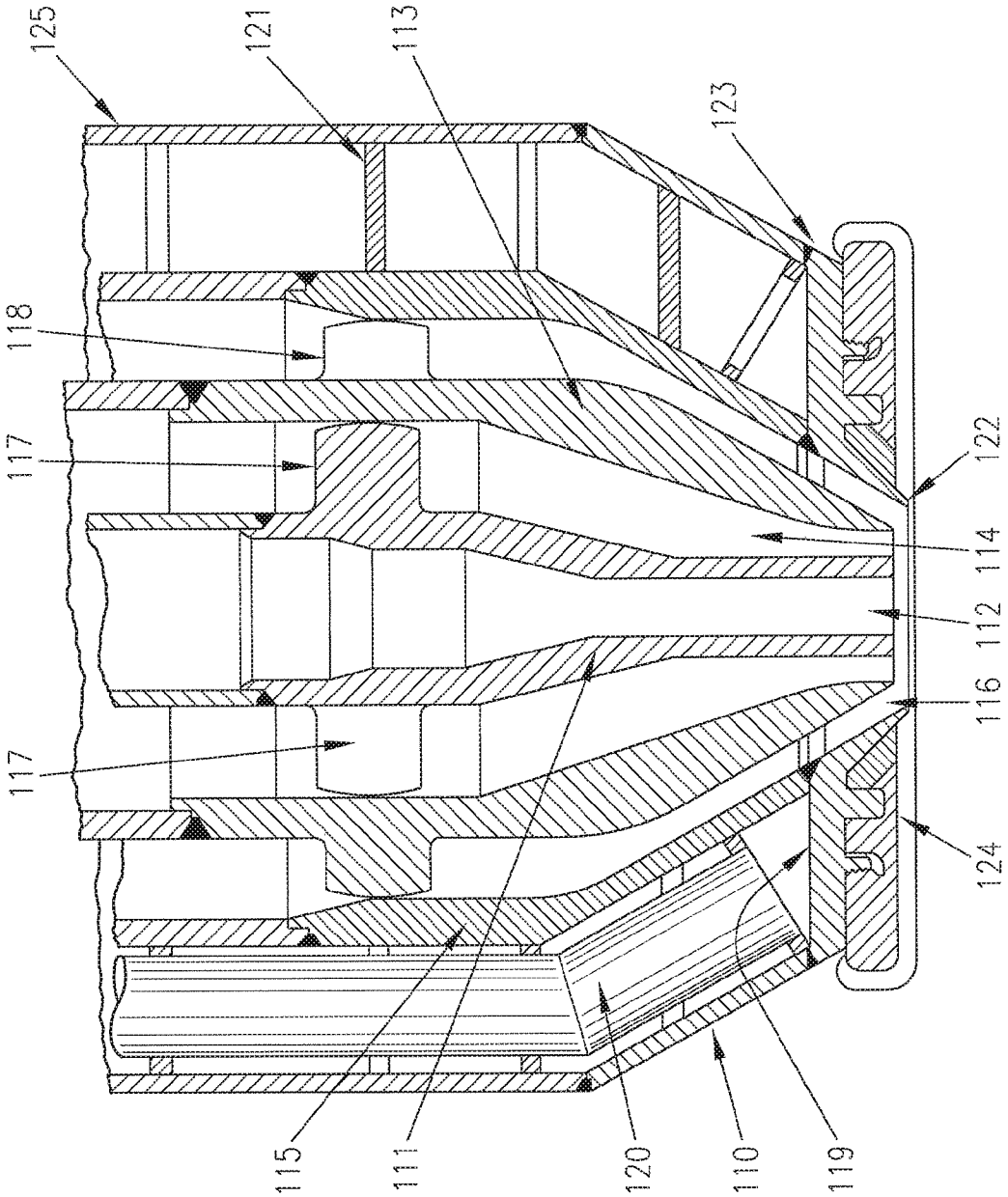

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FIG. 4

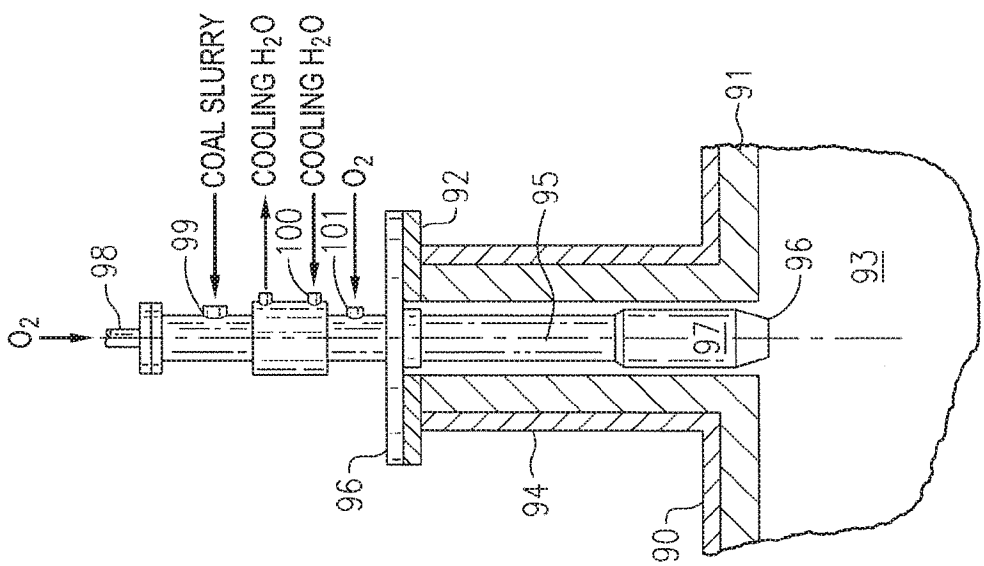

O_2
98
99
COAL SLURRY
100
COOLING H_2O
101
COOLING H_2O
O_2
92
95
91
96
93
97
96
94
90

FIG. 3

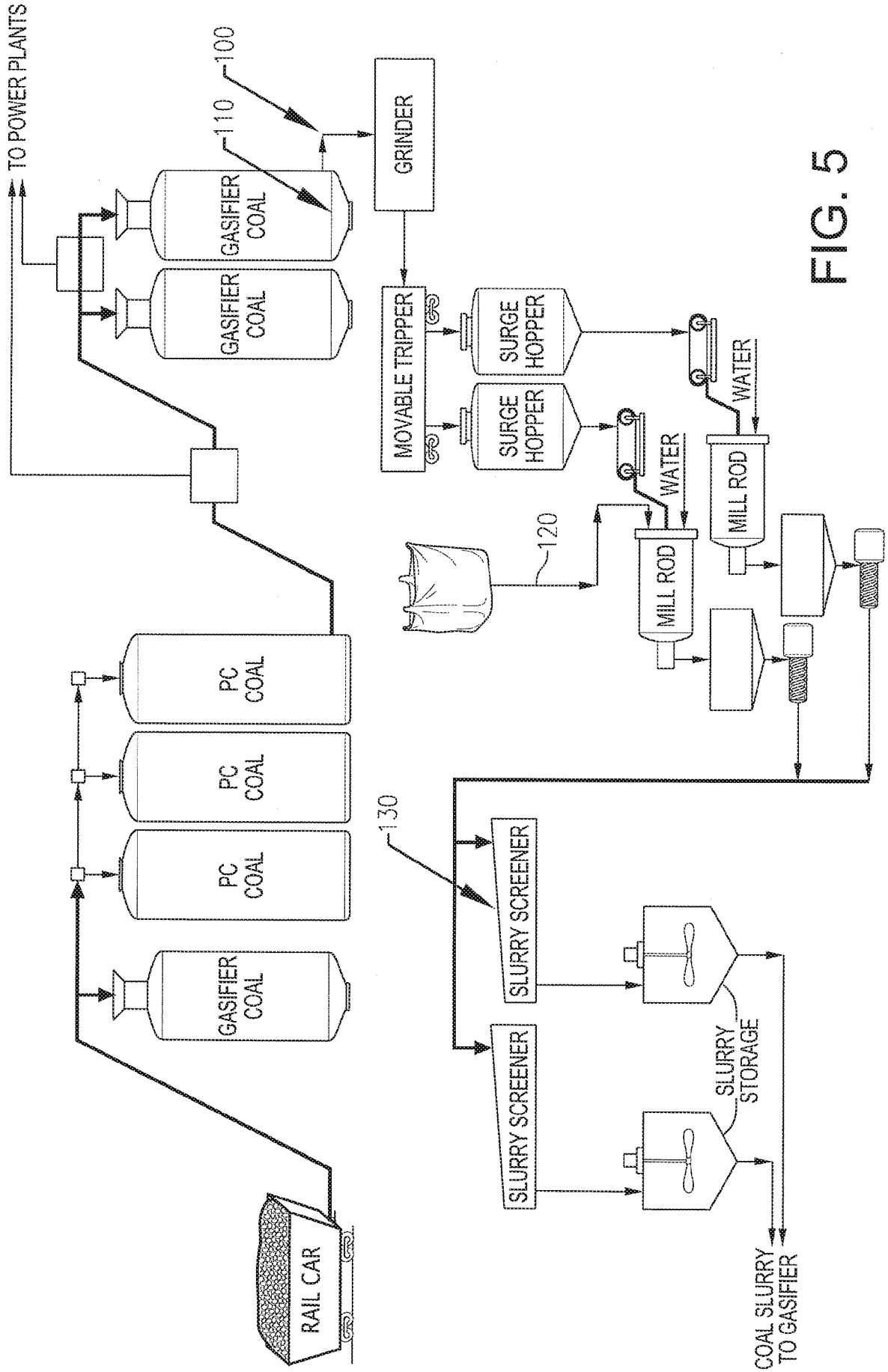

TO POWER PLANTS
100
110
GRINDER
GASIFIER COAL
GASIFIER COAL
MOVABLE TRIPPER
SURGE HOPPER
SURGE HOPPER
WATER
WATER
MILL ROD
MILL ROD
120
PC COAL
PC COAL
PC COAL
GASIFIER COAL
130
SLURRY SCREENER
SLURRY SCREENER
SLURRY STORAGE
RAIL CAR
COAL SLURRY TO GASIFIER

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/016481

A. CLASSIFICATION OF SUBJECT MATTER

C08B 1/00(2006.01)i, C08B 3/00(2006.01)i, C08B 3/06(2006.01)i, C08B 16/00(2006.01)i, C08J 11/22(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)
C08B 1/00; C07C 29/44; C08B 3/16; C08B 3/18; F01K 15/00; F01K 7/16; C08B 3/00; C08B 3/06; C08B 16/00; C08J 11/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: cellulose ester, solid fossil fuel, post-consumer tires, syngas, anhydroglucose unit, substituent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013-0143973 A1 (CELANESE INTERNATIONAL CORPORATION) 06 June 2013 See paragraphs [0075]-[0110].	1-14,23,24
Y	OBOIRIEN, B. O. et al., "A review of waste tyre gasification", Journal of Environmental Chemical Engineering, 2017, Vol. 5, pages 5169-5178 (2017.09.28. online publication date) See abstract; page 5175, right column, lines 1, 2 and 17-19; and page 5176, left column, lines 2-14.	1-14,23,24
Y	US 2011-0282049 A1 (SHELTON, MICHAEL CHARLES et al.) 17 November 2011 See paragraphs [0014], [0032]-[0039]; and claim 1.	8-14,23,24
Y	US 2012-0073292 A1 (KOSEOGLU, OMER REFA) 29 March 2012 See the whole document.	1-14,23,24
Y	US 2012-0238741 A1 (BUCHANAN, CHARLES MICHAEL et al.) 20 September 2012 See the whole document.	1-14,23,24

☐ 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
"D" document cited by the applicant in the international application
"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
29 May 2020 (29.05.2020)	**29 May 2020 (29.05.2020)**

Name and mailing address of the ISA/KR
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/016481

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 17,20,21
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 17, 20, 21 refer to one of claims which are not drafted in accordance with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 15,16,18,19,22,25-31
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/016481

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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