

US Patent & Trademark Office

Patent Public Search | Text View

United States Patent Application Publication

20250257187

Kind Code

A1

Publication Date

August 14, 2025

Inventor(s)

HOGAN; Terrence E. et al.

BUTADIENE PRODUCTION FROM USED TIRES

Abstract

A process comprising (a) providing a feedstock that includes carbonaceous materials; (b) gasifying the feedstock to produce a gaseous stream including carbon monoxide, hydrogen, and carbon dioxide; (c) converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol; and (d) converting at least a portion of the ethanol to butadiene monomer.

Inventors: HOGAN; Terrence E. (Akron, OH), NIAURA; William S. (Akron, OH), SMALE; Mark W. (Akron, OH)

Applicant: Bridgestone Americas Tire Operations, LLC (Nashville, TN)

Family ID: 1000008615722

Appl. No.: 18/856295

Filed (or PCT Filed): April 12, 2023

PCT No.: PCT/US2023/065645

Related U.S. Application Data

us-provisional-application US 63330246 20220412

Publication Classification

Int. Cl.: C08J11/12 (20060101); B60C1/00 (20060101); C07C1/207 (20060101); C07C29/151 (20060101); C07C45/38 (20060101); C08C19/08 (20060101); C08F110/08 (20060101)

U.S. Cl.:

CPC C08J11/12 (20130101); B60C1/00 (20130101); C07C1/2076 (20130101); C07C29/1518 (20130101); C07C45/38 (20130101); C08C19/08 (20130101); C08F110/08 (20130101);

Background/Summary

FIELD OF THE INVENTION

[0001] Embodiments of the present invention are directed toward a process for converting used tires to butadiene monomer.

BACKGROUND OF THE INVENTION

[0002] Butadiene monomer is polymerized to polybutadiene and polybutadiene copolymers such as poly(styrene-co-butadiene), poly(isoprene-co-butadiene), and poly(styrene-co-isoprene-co-butadiene). While these polymers have many uses, they are significantly used in the manufacture of tires. Used tires, on the other hand, are not easily recycled and have been landfilled or incinerated for fuel value. Methods have been proposed to thermally decompose waste, including tires into syngas, and then convert the syngas to useful materials. These methods lack industrial applicability, and therefore improvements to this general pathway are desired.

SUMMARY OF THE INVENTION

[0003] One or more embodiments of the present invention provide a process comprising (a) providing a feedstock that includes carbonaceous materials; (b) gasifying the feedstock to produce a gaseous stream including carbon monoxide, hydrogen, and carbon dioxide; (c) converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol; and (d) converting at least a portion of the ethanol to butadiene monomer.

[0004] Other embodiments of the present invention provide a method for producing an elastomeric polymer, the method comprising (a) providing 1,3-butadiene monomer synthesized from constituents of a gaseous stream that is obtained from the gasification of a feedstock including carbonaceous materials; and (b) polymerizing the 1,3-butadiene monomer to form a polymer.

[0005] Still other embodiments of the present invention provide a tire component comprising a cured rubber matrix with filler dispersed therein, where the cured rubber matrix includes greater than 40 wt %, or 50 wt %, or 60 wt %, or 70 wt %, or 80 wt %, or 90 wt %, or 99 wt % of a crosslinked circular synthetic rubber that is obtained by polymerizing monomer synthesized from constituents of a gaseous stream that is obtained from the gasification of a feedstock including carbonaceous materials.

Description

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0006] Embodiments of the invention are based, at least in part, on the discovery of a process for consuming used tires in the production of butadiene monomer (e.g. 1,3-butadiene). The butadiene monomer can advantageously be polymerized to polybutadiene or butadiene copolymers, and tire components can be produced from the polybutadiene or polybutadiene copolymers. Embodiments of the invention therefore provide a methodology for converting used tires back to useful tires or tire components. According to one or more embodiments, used tires are thermally decomposed to form a gaseous stream. One or more components of this gaseous stream are then converted to butadiene monomer. In one or more embodiments, one or more components of the gaseous stream are biosynthetically converted to ethanol, and the ethanol is then converted to butadiene. In one or more embodiments, the conversion of ethanol to butadiene proceeds by a one-step conversion, and in other embodiments, the conversion of ethanol to butadiene proceeds by a two-step conversion.

Process Overview

[0007] As suggested above, the process of the present invention provides a feedstock, which

according to one or more embodiments, may include tire feedstock, and the feedstock is converted, via thermal decomposition, to a gaseous stream that includes hydrogen, carbon monoxide, and optionally carbon dioxide. This gaseous stream, which may be referred to as synthesis gas or syngas, is then converted to ethanol by using biological fermentation processes. The ethanol is then converted to butadiene (e.g. 1,3-butadiene) by a one-step route or via a two-step route where ethanol is converted, at least partially to acetaldehyde, in the presence of a first catalyst, and then the acetaldehyde, together with ethanol, is converted to butadiene in the presence of a second catalyst.

Characteristics of Feedstock

[0008] In one or more embodiments, the feedstock that is thermally decomposed to form the gaseous stream may include tire feedstock from used tires, which may also be referred to as used tire feedstock. As the skilled person appreciates, tire feedstock may include vulcanized polymer, carbon black filler, silica, resins, oils, fibrous yarn, and metal. The vulcanized polymer may include the sulfur-crosslinked residue of natural rubber and/or one or more synthetic elastomers including diene polymers and copolymers. In one or more embodiments, the used tire feedstock may include shredded or otherwise ground tires with one or more constituents of the used tire removed. For example, the tire feedstock may be treated to remove metal by methods known in the art (e.g. magnetic separation). Alternatively, or in combination therewith, the used tire feedstock may be optionally treated to remove fibrous reinforcement such as fiber yarn or cord, which the skilled person understands is often found in conjunction with the vulcanized rubber within many tire components. Alternatively, or in combination with the foregoing, the used tire feedstock may be optionally treated to remove inorganic materials such as silica filler, which the skilled person appreciates is often found used tire components. In any event, the tire feedstock can be processed into tire shreds, tire chips, or ground or crumb rubber and fed to the thermal decomposition unit.

[0009] In one or more embodiments, the tire feedstock is characterized by relatively low amounts of metal, which may result from pre-treatment of the tire feedstock to remove metal. In one or more embodiments, the tire feedstock includes less than 25 wt %, in other embodiments less than 15 wt %, and in other embodiments less than 1 wt % metal based on the entire weight of the feedstock fed to thermal decomposition in accordance with the present invention.

[0010] In one or more embodiments, the tire feedstock is characterized by relatively low amounts of fibrous yarn or cord, which may result from pre-treatment of the tire feedstock to remove fibrous yarn or cord. In one or more embodiments, the tire feedstock includes less than 5 wt %, in other embodiments less than 4 wt %, in other embodiments less than 3 wt %, in other embodiments less than 2 wt %, and in other embodiments less than 1 wt % fibrous yarn or cord based on the entire weight of the feedstock fed to thermal decomposition in accordance with the present invention.

[0011] In one or more embodiments, the tire feedstock is characterized by relatively low amounts of inorganic filler (e.g. silica), which may result from pre-treatment of the tire feedstock to remove inorganic filler. In one or more embodiments, the tire feedstock includes less than 30 wt %, in other embodiments less than 20 wt %, in other embodiments less than 10 wt %, and in other embodiments less than 5 wt % inorganic filler based on the entire weight of the feedstock fed to thermal decomposition in accordance with the present invention.

[0012] In one or more embodiments, the used tire feedstock includes tire remains from passenger tires. In other embodiments, the used tire feedstock includes tire remains from non-passenger tires such as, but not limited to, truck and bus tires, off-road vehicle tires, agricultural tires, and race tires.

[0013] In one or more embodiments, the used tires may be characterized by a compacted density of greater than 640 kg/m.^{sup.3}, in other embodiments greater than 720 kg/m.^{sup.3}, and in other embodiments greater than 770 kg/m.^{sup.3}, where density is determined by ASTM D 698-07.

[0014] In one or more embodiments, the feedstock provided to the thermal decomposition unit includes tire feedstock and optionally complementary feedstock. In one or more embodiments, the

complementary feedstock, which may also be referred to as co-feed, includes carbonaceous materials other than the tire feed stock. Carbonaceous material refers to any carbon material whether in solid, liquid, gas, or plasma state. Non-limiting examples of carbonaceous materials include carbonaceous liquid product, industrial liquid recycle, municipal solid waste (MSW or msw), urban waste, agricultural material, forestry material, wood waste, construction material, vegetative material, industrial waste, fermentation waste, petrochemical coproducts, alcohol production coproducts, coal, plastics, waste plastic, coke oven tar, lignin, black liquor, polymers, waste polymers, polyethylene terephthalate (PETA), polystyrene (PS), sewage sludge, animal waste, crop residues, energy crops, forest processing residues, wood processing residues, livestock wastes, poultry wastes, food processing residues, ethanol coproducts, spent grain, spent microorganisms, municipal waste, construction waste, demolition waste, biomedical waste, hazardous waste, or their combinations. In one or more embodiments, the carbonaceous material includes biomass. In one or more embodiments, the biomass is bagasse including, but not limited to, the bagasse of sugar cane, sorghum, and guayule plant.

[0015] In a further embodiment, the guayule bagasse is produced as the result of a process to extract rubber and resin from the guayule plant, such as described in U.S. Publication No. 2022/0356273, which is incorporated herein by reference. Methods for the desolventization of guayule bagasse are described in U.S. Pat. No. 10,132,563, which is also incorporated herein by reference. In one or more embodiments, the guayule bagasse contains no more than 1 wt % organic solvent (based upon the total weight of the dried bagasse). In certain embodiments, the dried bagasse contains no more than 0.5 wt % organic solvent (based upon the total weight of the dried bagasse). In one or more embodiments, the dried bagasse may contain a quantity of water and higher boiling point terpenes. In certain embodiments, the total quantity of water and higher boiling point terpenes in the dried bagasse may be higher than the content of organic solvents. In certain embodiments, resin content (including the higher boiling point terpenes) in the dried bagasse is generally acceptable and, in some instances, actually preferred.

[0016] In one or more embodiments, the co-feed (e.g. biomass or municipal waste) may be characterized by a compacted density of less than 600 kg/m³, in other embodiments less than 580 kg/m³, and in other embodiments less than 560 kg/m³, where density is determined by ASTM D 698-07.

[0017] The feedstock may be characterized by the amount of co-feed (e.g. biomass or municipal waste). In one or more embodiments, the feedstock includes from about 0 to about 95, in other embodiments from about 1 to about 75, and in other embodiments from about 2 to about 55 wt % co-feed with the balance including used tire. In one or more embodiments, the feedstock includes less than 95, in other embodiments less than 80, and in other embodiments less than 70 wt % co-feed. In these or other embodiments, the feedstock includes greater than 10, in other embodiments greater than 20, in other embodiments greater than 30, in other embodiments greater than 40, in other embodiments greater than 50, and in other embodiments greater than 70 wt % used tires, with the balance including complementary feedstock.

[0018] In alternative embodiments, the feedstock is substantially, and in certain embodiments exclusively, comprised of those carbonaceous materials identified above other than tire feedstock; i.e. the feedstock is substantially or exclusively comprised of the co-feed materials identified above. For example, in one or more embodiments, the feedstock includes greater than 80 wt %, in other embodiments greater than 90 wt %, and in other embodiments greater than 99 wt % municipal solid waste. Or, in other exemplary embodiments, the feedstock includes greater than 80 wt %, in other embodiments greater than 90 wt %, and in other embodiments greater than 99 wt % biomass.

Thermal Decomposition of Feedstock

[0019] As indicated above, the feedstock (which may include tire feedstock and optionally co-feed) is thermally decomposed into gaseous streams including hydrogen, carbon monoxide, and

optionally carbon dioxide by employing techniques that are generally known in the art. As the skilled person understands, these processes may include gasification processes, and it is also known that these processes can be tailored to control the chemical nature of the resulting gaseous stream. For example, the degree of combustion can be controlled by controlling the amount of oxygen present during thermal decomposition. In one or more embodiments, the step of thermal decomposition takes place in a substantially inert environment.

[0020] Processes that may be used for the thermal decomposition step may include pyrolysis or gasification reactions as disclosed in U.S. Publication Nos. 2021/0207037; 2019/0295734; 2019/0249089; 2018/0273415; 2017/0009162; 2017/0002271; 2016/0107913; 2016/0068773; 2016/0024404; 2014/0182205; 2014/0157667; and 2014/0100294, which are incorporated herein by reference.

[0021] In one or more embodiments, where the feedstock includes both tire feedstock and co-feed, the tire feedstock and the co-feed can be introduced to the same thermal decomposition unit simultaneously. For example, the tire feedstock and the co-feed can be pre-mixed at a desired ratio to form the feedstock that is fed to the thermal decomposition unit. Alternatively, separate streams of tire feedstock and co-feed can be separately and individually fed to the thermal decomposition unit at a desired rate. In yet other embodiment, the two feedstocks (i.e. the tire feedstock and the co-feed) can be sequentially treated within the same thermal decomposition unit. In still other embodiments, the two feedstocks (i.e. the tire feedstock and the co-feed) can be treated within separate thermal decomposition units operating in parallel, and then the gaseous streams produced by the respective units can be combined to attain the desired ratio of gaseous constituents.

Characteristics of Gaseous Product Stream

[0022] As indicated above, the gaseous product stream produced by thermal decomposition of the feedstock includes carbon monoxide, hydrogen and optionally carbon dioxide. In one or more embodiments, the gaseous product stream includes from about 5 to about 50, or in other embodiments from about 7 to about 25, or in other embodiments from about 8 to about 15 volume percent carbon dioxide. In these or other embodiments, the gaseous product stream includes from about 10 to about 85, or in other embodiments from about 20 to about 65, or in other embodiments from about 25 to about 45 volume percent hydrogen. In these or other embodiments, the gaseous product stream includes from about 20 to about 85, or in other embodiments from about 30 to about 75, or in other embodiments from about 40 to about 60 volume percent carbon monoxide. In one or more embodiments, the gaseous product stream produced by thermal decomposition includes from about 40 to about 80 wt %, in other embodiments from about 45 to about 75 wt %, and in other embodiments from about 50 to about 70 wt % carbon (i.e. carbon within carbon-based compounds) based on the total weight of the gaseous product stream.

Conditioning of Gaseous Stream

[0023] In one or more embodiments, the gaseous stream is conditioned (i.e. treated) prior to biosynthetically converting the gaseous stream to ethanol. In one or more embodiments, the gaseous product stream from thermal decomposition may be pressurized. In one or more embodiments, pressurization of the gaseous stream achieves sufficient pressure to overcome counter forces within the bioreactor. As the skilled person understands, this will permit flow of the gas through the bioreactor and allow inert gases (e.g. nitrogen) within the gaseous stream to enter the head space of the reactor. In one or more embodiments, the gaseous stream is pressurized to a pressure of from about 5 to about 20 barr.

[0024] Also, the gaseous stream can be cooled. As the skilled person will appreciate, the gaseous stream can be cooled, for example, within a heat exchanger such as a water-cooled unit. In one or more embodiments, the gaseous stream is cooled to a temperature below that which would otherwise have a deleterious impact on the microorganism culture within the bioreactor. In one or more embodiments, the gaseous stream is cooled to a temperature of from about 25 to about 45° C. prior to delivery to the bioreactor.

[0025] Still further, the gaseous stream can be treated to remove undesirable constituents that may be entrained within the stream. For example, the gaseous stream can be treated within a scrubber prior to being introduced to the bioreactor. In one or more embodiments, this may include the use of a catalyst to remove hydrogen sulfide (e.g. iron oxide). The stream may also be treated to remove halides (e.g. treatment with calcium or sodium carbonate).

Syngas to Ethanol

[0026] As indicated above, constituents of the gaseous stream are converted to ethanol that is contained within an ethanol-containing stream; i.e. a product stream that includes ethanol. In one or more embodiments, the gaseous stream is supplemented with hydrogen prior to converting the gaseous stream to an ethanol-containing stream. Also, the gaseous stream can be treated to remove undesirable constituents prior to converting the gaseous stream to an ethanol-containing stream. For example, the skilled person understands that certain additives can be introduced to the gaseous stream to thereby remove (e.g. scavenge) sulfur and other impurities.

[0027] In one or more embodiments, the gaseous stream is converted to ethanol via biosynthetic techniques. For example, it is known that syngas can be converted to ethanol by fermentation utilizing microorganisms, such as bacteria. The microorganisms may be acetogenic autotrophic microbes. Acetogenic microbes (i.e. bacteria) generally transform the CO, H₂, and CO₂ in syngas into acetyl-CoA. The acetyl-CoA is then converted to organic products, such as acetic acid and ethanol. In one or more embodiments of the present invention, it may be desirable to preferentially produce ethanol relative to acetic acid.

[0028] As another potential pathway, some microorganisms (e.g. acetogens) can reduce the acetic acid (i.e. an organic acid) into an alcohol (e.g. ethanol). The acetogenic mechanism and the particular microorganisms chosen may be considered relative to preferentially producing ethanol. Microorganisms other than acetogens may be suitable with different pathways to reaching ethanol. The microorganisms may simultaneously uptake both CO and H₂ in the syngas.

[0029] The skilled person also appreciates that various conditions of microorganism-driven biosynthesis may be adjusted relative to preferential production of ethanol. For example, the pH, temperature, and concentrations of nutrients within the bioreactor where in the biosynthesis takes place can be adjusted. The desirable pH, temperature, and concentrations of nutrients may depend on the particular microorganisms employed.

[0030] As indicated above, the resultant ethanol is contained within an ethanol-containing stream. According to embodiments of the invention, a crude ethanol-containing stream, which is obtained directly from the bioreactor in which the ethanol is synthesized, is delivered to downstream steps. In other embodiments, the ethanol-containing stream is purified to produce an ethanol-containing stream that is higher in ethanol content. In one or more embodiments, the ethanol-containing stream exiting the step wherein syngas is converted to ethanol (i.e. the bioreactor) and delivered to the downstream steps where butanediol is converted (optionally after purification) includes greater than 80 wt %, in other embodiments greater than 90 wt %, and in other embodiments greater than 95 wt % ethanol based upon the entire weight of the ethanol-containing stream.

Ethanol to Butadiene—One-Step Synthesis

[0031] As indicated above, ethanol within the ethanol-containing stream can be converted to butadiene (e.g. 1,3-butadiene) by a one-step synthesis, which may also be referred to as a direct synthesis. In one or more embodiments, the direct synthesis of ethanol to butadiene takes place as a condensation reaction in the presence of a polyfunctional catalyst, including those disclosed in U.S. Pat. No. 8,921,635, which is incorporated herein by reference. Another known synthesis for converting ethanol directly to butadiene is the Lebedev process. Still other processes for directly converting ethanol to butadiene include those marketed by ETB Catalytic Technologies and those techniques marketed by Synthos.

[0032] As the skilled person understands, the direct conversion of ethanol to butadiene may include the use of a two-stage extractive distillation that utilizes n-methyl pyrrolidone (NMP) as solvent.

Direct conversion techniques may also include conventional distillation for recovering the butadiene.

Ethanol to Butadiene—Two-Step Synthesis

[0033] In alternative embodiments, ethanol within the ethanol-containing stream can be converted to butadiene (e.g. 1,3-butadiene) by a two-step synthesis, wherein acetaldehyde is synthesized as an intermediate. In one or more embodiments, the acetaldehyde, which is contained within an acetaldehyde-containing stream, is isolated before being delivered to downstream synthesis steps. In other embodiments, the acetaldehyde-containing stream, as a crude stream, is delivered to downstream synthesis steps. According to embodiments of the invention, the acetaldehyde is reacted with ethanol in a second step to yield the desired 1,3-butadiene.

[0034] As the skilled person appreciates, ethanol can be converted to acetaldehyde by oxidative dehydrogenation of the ethanol. In one or more embodiments, the conversion of ethanol to acetaldehyde generally proceeds by partial oxidation of the ethanol in an exothermic reaction. In this partial oxidation process, the reaction may be conducted over a silver catalyst at about 500° C. to about 650° C. In one or more embodiments, the conversion of ethanol to acetaldehyde may include avoiding or inhibiting the production of acetic acid relative to the acetaldehyde. This can be accomplished by selecting catalysts and/or reaction conditions that are known to avoid the production of acetic acid relative to the acetaldehyde. In one or more embodiments, the conversion of ethanol to acetaldehyde takes place in the absence of evaporating the acetaldehyde. In one or more embodiments, the conversion of ethanol to acetaldehyde takes place at relatively low pressure and in the gas-phase as to increase selectivity for acetaldehyde. In one or more embodiments, the first step of partial dehydrogenation of ethanol to acetaldehyde to achieve an ethanol-acetaldehyde mixture, and a second step for converting the ethanol-acetaldehyde mixture to butadiene 200. This may include supplementing the ethanol-acetaldehyde mixture with additional ethanol and/or acetaldehyde as to achieve a desirable ratio. This process may be referred to as an Ostromislensky process.

INDUSTRIAL APPLICABILITY

[0035] In one or more embodiments, the butadiene monomer (e.g. 1,3-butadiene) produced by the methods of this invention can be used in the production of polybutadiene or butadiene copolymers (which may also be referred to as polybutadiene copolymers). For purposes of this specification, these polymers may be referred to as circular synthetic rubber, or circular synthetic polybutadiene to butadiene copolymers. In one or more embodiments, this circular synthetic rubber can be used in the manufacture of tire components. As a result, practice of the present invention provides a method by which waste material, in particular that waste material from used tires, is converted back to useful tires. In other words, a tire recycling or tire circularity method is provided.

[0036] The synthesis of polybutadiene or polybutadiene copolymers from butadiene monomer is well known and can be accomplished by using several synthetic routes (i.e. polymerization mechanisms and techniques). For example, the monomer can be polymerized by free-radical emulsion polymerization, anionic polymerization, or coordination catalysis using, for example, nickel or neodymium-based catalyst systems.

[0037] As the skilled person appreciates, comonomers that can be copolymerized with butadiene to form polybutadiene copolymers include, but are not limited to, vinyl aromatic monomer such as styrene, as well as other diene monomer such as isoprene. In one or more embodiments, the comonomer is a sustainable comonomer. For example, styrene can be obtained from bio-synthesized feedstock, such as bioethanol, that is subsequently converted to styrene; see, e.g. U.S. Pat. No. 9,663,445. Alternatively, styrene can be synthesized from bio-based materials such as cinnamic acid or hydrocinnamic acid; see, U.S. Pat. No. 9,868,853. Yet other examples include styrene obtained from the depolymerization of polystyrene from post-consumer waste; see U.S. Publication No. 2022/0411351. The skilled person also understands that styrene can be obtained from those processes that are mass balanced to qualify as bio-based, bio-circular, or circular as

designated by the International Sustainability and Carbon Certification ISCC.

[0038] It should be appreciated that the polybutadiene polymers prepared by polymerizing the butadiene of the present invention have a relatively high percentage of mer units deriving from the butadiene produced by the invention, and therefore the polybutadiene polymers of this invention have a relatively high sustainable content. In one or more embodiments, the polybutadiene polymers synthesized by polymerizing the butadiene of the present invention include greater than 50 mol %, in other embodiments greater than 60 mol %, in other embodiments greater than 70 mol %, in other embodiments greater than 80 mol %, in other embodiments greater than 90 mol %, in other embodiments greater than 95 mol %, and in other embodiments greater than 99 mol % sustainable mer units, which obtained from polymerization of butadiene obtained by the present invention (i.e. mer units obtained from monomer that is synthesized from a gaseous stream obtained by gasification of carbonaceous materials). Likewise, where the polymer synthesized is a polybutadiene copolymer by copolymerizing the butadiene monomer obtained by practice of this invention together with sustainable comonomer, the resulting polybutadiene copolymer has a relatively high sustainable content. In one or more embodiments, the polybutadiene copolymers synthesized by polymerizing the butadiene of the present invention together with sustainable comonomer include greater than 50 mol %, in other embodiments greater than 60 mol %, in other embodiments greater than 70 mol %, in other embodiments greater than 80 mol %, in other embodiments greater than 90 mol %, in other embodiments greater than 95 mol %, and in other embodiments greater than 99 mol % sustainable mer units (i.e. mer units that are obtained from monomer synthesized from a gaseous stream obtained by gasification of carbonaceous materials and other sustainable comonomer).

[0039] The polymers synthesized from butadiene monomer produced by embodiments of the invention may be referred to as vulcanizable polymers, or as elastomeric polymers, and generally include polydienes and polydiene copolymers. Specific of polymers that can be produced and used in the manufacture of tires include, but are not limited to, polybutadiene, poly(styrene-co-butadiene), poly(styrene-co-isoprene-co-butadiene), poly(isoprene-co-butadiene), and functionalized derivatives thereof.

[0040] The polybutadiene and polybutadiene copolymers produced by the present invention exhibit excellent viscoelastic properties and are particularly useful in the manufacture of various tire components including, but not limited to, tire treads, sidewalls, subreads, and bead fillers. These polymers can be used as all or part of the elastomeric component of a tire stock. When the polymers produced by the present invention are used in conjunction with other vulcanizable polymers to form the elastomeric component of a tire stock, these other vulcanizable polymers may include natural rubber, synthetic rubbers, and mixtures thereof. Examples of synthetic rubber include polyisoprene, poly(styrene-co-butadiene), and other polybutadienes with low and/or cis-1,4-linkage content, poly(styrene-co-butadiene-co-isoprene), and mixtures thereof. The polymers of this invention can also be used in the manufacture of hoses, belts, shoe soles, window seals, other seals, vibration damping rubber, and other industrial products.

[0041] Practice of the present invention not only offers a method for recycling tires by employing used tires as a feedstock to produce polymer that can be formulated back into tires, but the practice of the present invention also advantageously provides a method whereby a tire is produced that has a relatively high content of sustainable constituents, which include recycled materials, naturally-derived materials and/or materials synthesized from bio-synthesized feedstock or bio-based materials. Moreover, these tires or tire components include threshold amounts of circular synthetic rubber while being characterized by high sustainable content. For example, the tires or tire components of the present invention can include greater than 40 wt %, in other embodiments greater than 50 wt %, and in other embodiments greater than 60 wt % sustainable materials. In these or other embodiments, the tire or tire components include from about 40 to about 90 wt %, in other embodiments from about 45 to about 85 wt %, and in other embodiments from about 50 to

about 80 wt % sustainable material. In combination therewith, the rubber component of the tires or tire components of the present invention include greater than 10 wt %, in other embodiments greater than 20 wt %, in other embodiments greater than 30 wt %, in other embodiments greater than 40 wt %, in other embodiments greater than 45 wt %, and in other embodiments greater than 50 wt % circular synthetic rubber, which includes synthetic rubber produced according to embodiments of the present invention.

[0042] As indicated above, the vulcanizable compositions of this invention include a rubber component. This rubber component includes the circular synthetic rubber produced according to aspects of this invention. The rubber component may also include other synthetic rubber, such as synthetic rubber that derives from petroleum-based raw materials and has not been recycled, synthetic rubber that derives from other sustainable processes, as well as natural rubber. As the skilled person understands, natural rubber is synthesized by and obtained from plant life. For example, natural rubber can be obtained from Hevea rubber trees, guayule shrub, gopher plant, mariola, rabbitbrush, milkweeds, goldenrods, pale Indian plantain, rubber vine, Russian dandelions, mountain mint, American germander, and tall bellflower.

[0043] Other synthetic polymers, if used, can include, without limitation, synthetic polyisoprene, polybutadiene, polyisobutylene-co-isoprene, neoprene, poly(ethylene-co-propylene), poly(styrene-co-butadiene), poly(styrene-co-isoprene), poly(styrene-co-isoprene-co-butadiene), poly(isoprene-co-butadiene), poly(ethylene-co-propylene-co-diene), polysulfide rubber, acrylic rubber, urethane rubber, silicone rubber, epichlorohydrin rubber, and mixtures thereof. These elastomers can have a myriad of macromolecular structures including linear, branched, and star-shaped structures.

[0044] Generally, the rubber compositions of this invention include from about 30 to about 65 wt %, in other embodiments from about 35 to about 60 wt %, and in other embodiments from about 40 to about 55 wt % elastomer, based on the total weight of the tire component.

[0045] As suggested above, the rubber compositions include fillers such as organic and inorganic fillers. Examples of organic fillers include carbon black and starch. Examples of inorganic fillers include silica, aluminum hydroxide, magnesium hydroxide, mica, talc (hydrated magnesium silicate), and clays (hydrated aluminum silicates). In certain embodiments, a mixture of different fillers may be advantageously employed.

[0046] The amount of total filler employed in the rubber compositions can be up to about 150 parts by weight per 100 parts by weight of rubber (phr), with about 30 to about 125 phr, or about 40 to about 110 phr being typical. In certain embodiments the total filler content is greater than about 100 phr. In other embodiments, the total filler content is from about 50 to about 100 phr, and in in further embodiments from about 55 to about 95 phr.

[0047] Conventional carbon black can be used, which is generally known in the art. In one or more embodiments, carbon blacks include furnace blacks, channel blacks, and lamp blacks. More specific examples of carbon blacks include super abrasion furnace blacks, intermediate super abrasion furnace blacks, high abrasion furnace blacks, fast extrusion furnace blacks, fine furnace blacks, semi-reinforcing furnace blacks, medium processing channel blacks, hard processing channel blacks, conducting channel blacks, and acetylene blacks.

[0048] In particular embodiments, the carbon blacks may have a surface area (EMSA) of at least 20 m²/g and in other embodiments at least 35 m²/g; surface area values can be determined by ASTM D-1765 using the cetyltrimethylammonium bromide (CTAB) technique. The carbon blacks may be in a pelletized form or an unpelletized flocculent form. The preferred form of carbon black may depend upon the type of mixing equipment used to mix the rubber compound.

[0049] In one or more embodiments, carbon black can be sourced from a recycled material. Such recycled material can include reclaimed or recycled vulcanized rubber, whereby the vulcanized rubber is typically reclaimed from manufactured articles such as a pneumatic tire, an industrial conveyor belt, a power transmission belt, and a rubber hose. The recycled carbon black may be obtained by a pyrolysis process or other methods known for obtaining recycled carbon black. In an

aspect, a recycled carbon black can be formed from incomplete combustion of recycled rubber feedstock or rubber articles. In another aspect, the recycled carbon black can be formed from the incomplete combustion of feedstock including oil resulting from the tire pyrolysis process. The carbon blacks utilized in the preparation of the vulcanizable elastomeric compositions can be in pelletized form or an unpelletized flocculent mass.

[0050] The amount of carbon black employed in the rubber compositions can be up to about 75 parts by weight per 100 parts by weight of rubber (phr), with about 5 to about 60 phr, or about 10 to about 55 phr being typical.

[0051] The rubber composition can further include filler in the form of one or more recycled rubbers in a particulate form. Recycled particulate rubber is typically broken down and reclaimed (or recycled) by any of a plurality of processes, which can include physical breakdown, grinding, chemical breakdown, devulcanization, cryogenic grinding, a combination thereof, etc. The term recycled particulate rubber can relate to both vulcanized and devulcanized rubber, where devulcanized recycle or recycled rubber (reclaim rubber) relates to rubber which has been vulcanized, ground into particulates and may have further undergone substantial or partial devulcanization. In an example, the recycled particulate rubber used in the rubber composition is essentially free of recycled rubber resulting from devulcanization. In a situation where the vulcanized rubber contains wire or textile fiber reinforcement, such wire or fiber reinforcement can be removed by any suitable process such as magnetic separation, air aspiration and/or air flotation step. In certain embodiments, the “recycled particulate rubber” comprises cured, i.e., vulcanized (crosslinked) rubber that has been ground or pulverized into particulate matter having a mean average particle size as discussed below.

[0052] Certain silicas may be considered sustainable materials. Some commercially available silicas which may be used as sustainable materials for the current invention include Hi-Sil™ 215, Hi-Sil™ 233, and Hi-Sil™ 190 (PPG Industries, Inc.; Pittsburgh, Pa.). Other suppliers of commercially available silica include Grace Davison (Baltimore, Md.), Degussa Corp. (Parsippany, N.J.), Rhodia Silica Systems (Cranbury, N.J.), and J.M. Huber Corp. (Edison, N.J.). Other sustainable silicas include those derived from rice husk ash.

[0053] In one or more embodiments, silicas may be characterized by their surface areas, which give a measure of their reinforcing character. The Brunauer, Emmet and Teller (“BET”) method (described in J. Am. Chem. Soc., 1939, vol. 60, 2 p. 309-319) is a recognized method for determining the surface area. The BET surface area of silica is generally less than 450 m²/g. Useful ranges of surface area include from about 32 to about 400 m²/g, about 100 to about 250 m²/g, and about 130 to about 240 m²/g, and about 170 to about 220 m²/g. In certain embodiments, the silica may have a BET surface area of 190 to about 280 m²/g. The pH's of the silicas are generally from about 5 to about 7 or slightly over 7, or in other embodiments from about 5.5 to about 6.8.

[0054] In one or more embodiments, where silica is employed as a filler (alone or in combination with other fillers), a coupling agent and/or a shielding agent may be added to the rubber compositions during mixing in order to enhance the interaction of silica with the elastomers. Useful coupling agents and shielding agents are disclosed in U.S. Pat. Nos. 3,842,111; 3,873,489; 3,978,103; 3,997,581; 4,002,594; 5,580,919; 5,583,245; 5,663,396; 5,674,932; 5,684,171; 5,684,172; 5,696,197; 6,608,145; 6,667,362; 6,579,949; 6,590,017; 6,525,118; 6,342,552; and 6,683,135; which are incorporated herein by reference.

[0055] The amount of silica employed in the rubber compositions can be from about 1 to about 150 phr or in other embodiments from about 5 to about 130 phr. The useful upper range is limited by the high viscosity imparted by silicas. In certain embodiments, the silica employed in the rubber composition is derived from rice husk ash only, and in other embodiments the rubber compositions do not include silica from non-rice husk ash derived processes. When silica is used together with carbon black, the amount of the silica or carbon black individually can be as low as about 1 phr.

Generally, the amounts of coupling agents and shielding agents range from about 4 wt % to about 20 wt % based on the weight of silica used. In one or more embodiments, where carbon black and silica are employed in combination as a filler, the weight ratio of silica to total filler may be from about 5 wt % to about 99 wt % of the total filler, in other embodiments from about 10 wt % to about 90 wt % of the total filler, or in yet other embodiments from about 50 wt % to about 85 wt % of the total filler. In certain embodiments the silica and carbon black fillers employed in the rubber composition are selected from the group consisting of sustainable pyrolysis carbon black and/or rice husk ash derived silica.

[0056] A multitude of rubber curing agents (also called vulcanizing agents) may be employed, including sulfur or peroxide-based curing systems. Curing agents are described in Kirk-Othmer, *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, Vol. 20, pgs. 365-468, (3rd Ed. 1982), particularly Vulcanization Agents and Auxiliary Materials, pgs. 390-402, and A. Y. Coran, *Vulcanization*, *ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING*, (2nd Ed. 1989), which are incorporated herein by reference. Vulcanizing agents may be used alone or in combination.

[0057] Other ingredients that are typically employed in rubber compounding may also be added to the rubber compositions. These include accelerators, accelerator activators, oils, plasticizer, waxes, scorch inhibiting agents, processing aids, zinc oxide, tackifying resins, reinforcing resins, fatty acids such as stearic acid, peptizers, and antidegradants such as antioxidants and antiozonants.

[0058] With regard to oils, sustainable oils, which include plant-based oils and bio-based oils, may be used. Plant-based oils may include plant-based triglycerides. Exemplary oils include, without limitation, palm oil, soybean oil (also referred to herein as soy oil), rapeseed oil, sunflower seed, peanut oil, cottonseed oil, oil produced from palm kernel, coconut oil, olive oil, corn oil, grape seed oil, hemp oil, linseed oil, rice oil, safflower oil, sesame oil, mustard oil, flax oil. Other examples include nut-derived oils such as oils obtained from beech nuts, cashews, mongongo nuts, macadamia nuts, pine nuts, hazelnuts, chestnuts, acorns, almonds, pecans, pistachios, walnuts, or brazil nuts. As the skilled person will appreciate, these oils can be produced by any suitable process such as mechanical extraction (e.g., using an oil mill), chemical extraction (e.g., using a solvent, such as hexane or carbon dioxide), pressure extraction, distillation, leaching, maceration, purification, refining, hydrogenation, sparging, etc.

[0059] Bio-based oils, also referred to as bio-oils, can include oils produced by a recombinant cell. For example, bio-oils produced by recombinant cells can be produced using a select strain of algal cells that are fed with a supply of sugars (e.g., sucrose) and then allowed to ferment and produce a bio-oil with a selected profile; after sufficient growth or fermentation has taken place, the bio-oil is isolated from the cells and collected.

[0060] Generally, the rubber compositions of this invention can include from about 1 to about 70 parts by weight, or in other embodiments from about 5 to about 50 parts weight total oil per 100 parts by weight rubber. The amount of sustainable oil, relative to the total weight of oil included, may be from about 1 wt % to about 99 wt %, or in other embodiment from about 20 wt % to about 80 wt %.

[0061] With regard to waxes, the rubber compositions can include one or more sustainable waxes, which include natural waxes. A natural wax, or one with no petroleum as its raw material, can include carnauba wax, candelilla wax (e.g., extracted from candelilla flowers), rice wax (e.g., separated from rice bran oil) and Japan wax (e.g., extracted from Japanese wax tree).

[0062] Generally, the rubber compositions of this invention include from about 1 to about 20 parts by weight, or in other embodiments from about 2 to about 15 parts by weight total wax per 100 parts by weight rubber. The amount of sustainable wax, relative to the total weight of wax included, may be from about 1 wt % to about 99 wt %, or in other embodiment from about 20 wt % to about 80 wt % of the total wax. In certain embodiments, the rubber composition includes sustainable waxes only.

[0063] All ingredients of the rubber compositions can be mixed with standard mixing equipment such as Banbury or Brabender mixers, extruders, kneaders, and two-rolled mills. In one or more embodiments, the ingredients are mixed in two or more stages. In the first stage (often referred to as the masterbatch mixing stage), a so-called masterbatch, which typically includes the rubber component and filler, is prepared. To prevent premature vulcanization (also known as scorch), the masterbatch may exclude vulcanizing agents. The masterbatch may be mixed at a starting temperature of from about 25° C. to about 125° C. with a discharge temperature of about 135° C. to about 180° C. Once the masterbatch is prepared, the vulcanizing agents may be introduced and mixed into the masterbatch in a final mixing stage, which is typically conducted at relatively low temperatures so as to reduce the chances of premature vulcanization. Optionally, additional mixing stages, sometimes called remills, can be employed between the masterbatch mixing stage and the final mixing stage. One or more remill stages are often employed where the rubber composition includes silica as the filler. Various ingredients including the polymers of this invention can be added during these remills.

[0064] The mixing procedures and conditions particularly applicable to silica-filled tire formulations are described in U.S. Pat. Nos. 5,227,425; 5,719,207; and 5,717,022, as well as European Patent No. 890,606, all of which are incorporated herein by reference. In one embodiment, the initial masterbatch is prepared by including the polymer and silica in the substantial absence of coupling agents and shielding agents.

[0065] In order to fabricate tire components with the polymers produced by the invention, the skilled person appreciates that the polymers are mixed with various other ingredients (e.g. filler and curative) to produce a rubber composition (also referred to as vulcanizable composition), and the vulcanizable composition is then processed into tire components according to ordinary tire manufacturing techniques, which generally include standard rubber shaping and molding techniques. The tire components may include, but are not limited to, tire treads, sidewalls, subreads, body ply skims, and bead filler. The various tire components are then assembled into a green tire (i.e. an uncured tire), placed within a mold, and then vulcanized. Typically, vulcanization is effected by heating the vulcanizable composition in a mold; e.g., it may be heated to about 140° C. to about 180° C. Cured or crosslinked rubber compositions may be referred to as vulcanizates, which generally contain three-dimensional polymeric networks that are thermoset. The other ingredients, such as fillers and processing aids, may be evenly dispersed throughout the crosslinked network. Pneumatic tires can be made as discussed in U.S. Pat. Nos. 5,866,171; 5,876,527; 5,931,211; and 5,971,046, which are incorporated herein by reference.

[0066] In one or more embodiments, the tires can include fabric reinforcement made by using non-petroleum materials in place of synthetic fibers. For example, mechanical recycled fibers, chemical recycled fibers, or bio-based fibers can be used. Likewise, the tires can include metal reinforcement made from recycled steel and/or other circular or sustainable metals. These non-petroleum fabrics and recycled metals can be used exclusively within the tires or in combination with traditional fabric and/or metal reinforcement.

[0067] Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

Claims

1. A process comprising: (a) providing a feedstock that includes carbonaceous materials; (b) gasifying the feedstock to produce a gaseous stream including carbon monoxide, hydrogen, and carbon dioxide; (c) converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol; and (d) converting at least a portion of the ethanol to butadiene monomer.
2. The process of claim 1, where the step of converting includes preferentially producing the

ethanol relative to other potential products.

3. The process of claim 1, where said the step of converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol includes biosynthetically converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol.

4. The process of claim 1, where said step of converting at least a portion of the ethanol to butadiene monomer includes a one-step synthesis whereby ethanol is converted to butadiene in the presence of a polyfunctional catalyst.

5. The process of claim 1, where said step of converting at least a portion of the ethanol to butadiene monomer includes a two-step synthesis whereby ethanol is converted to acetaldehyde in the presence of a first catalyst, and then the acetaldehyde is reacted with ethanol in the presence of a second catalyst to thereby form butadiene.

6. The process of claim 1, where the feedstock includes used tire feedstock.

7. The process of claim 1, where the feedstock includes biomass.

8. The process of claim 1, where the feedstock includes municipal solid waste.

9. The process of claim 1, where the feedstock includes a mixture of tire feedstock and a complementary feedstock.

10. The process of claim 1, further comprising the step of polymerizing the butadiene monomer to thereby produce a polymer that is a polybutadiene polymer.

11. The process of claim 10, further comprising the step of providing comonomer, and where said step of polymerizing the butadiene monomer includes copolymerizing the butadiene monomer with the comonomer to thereby produce a polymer that is a polybutadiene copolymer.

12. The process of claim 11, where the comonomer is a sustainable comonomer.

13. The process of claim 10, further comprising the step of fabricating a tire component with the polymer.

14. A method for producing an elastomeric polymer, the method comprising: (a) providing 1,3-butadiene monomer synthesized from constituents of a gaseous stream that is obtained from the gasification of a feedstock including carbonaceous materials; and (b) polymerizing the 1,3-butadiene monomer to form a polymer.

15. The method of claim 14, where the gaseous stream includes carbon monoxide, hydrogen, and carbon dioxide, and wherein the 1,3-butadiene monomer is formed by converting at least a portion of the carbon monoxide, hydrogen, and carbon dioxide to ethanol, and converting at least a portion of the ethanol to butadiene monomer.

16. (canceled)

17. (canceled)

18. (canceled)

19. The method of any of the preceding claims claim 14, where the carbonaceous material includes used tire feedstock.

20. The method of claim 14, where the carbonaceous material includes biomass.

21. The method of claim 14, where the carbonaceous material includes solid municipal waste.

22. The method of claim 14, where the carbonaceous material includes a mixture of used tire feedstock together with a complementary feedstock.

23. A tire component comprising: a cured rubber matrix with filler dispersed therein, where the cured rubber matrix includes greater than 40 wt % of a crosslinked circular synthetic rubber that is obtained by polymerizing monomer synthesized from constituents of a gaseous stream that is obtained from the gasification of a feedstock including carbonaceous materials.

24. (canceled)

25. (canceled)

26. (canceled)

27. (canceled)

28. (canceled)

- 29. (canceled)
 - 30. (canceled)
 - 31. (canceled)
 - 32. (canceled)
 - 33. (canceled)
 - 34. (canceled)
 - 35. (canceled)
 - 36. (canceled)
-