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(54) **Title:** METHODS FOR MODIFYING ASPHALT USING LOW GREENHOUSE GAS LIQUIDS OBTAINED FROM DEPOLYMERIZATION OF WASTE PLASTICS

(57) **Abstract:** The present invention relates to environmentally friendly, low greenhouse gas (GHG) liquid asphalt modifiers produced via a thermal depolymerization of solid plastic materials, particularly waste plastic materials, alone or in conjunction with other organic feedstocks, and their use to prepare carbon-efficient asphalt formulations and end-products. The carbon-neutral to carbon-negative liquid additives yield asphalt materials with enhanced performance and tolerance against detrimental effects from aging and temperature, along with a reduced carbon-footprint. The liquid modifiers described herein can be used to modify asphalt binders (bitumen) to provide lower temperature processability and/or improved performance and/or to rejuvenate recycled asphalt pavement (RAP) such that less virgin binder and aggregate needs to be produced and transported when repaving. The invention therefore allows waste plastics to be utilized as a desirable feedstock material and lessens the carbon footprint of the resulting asphalt end-products.

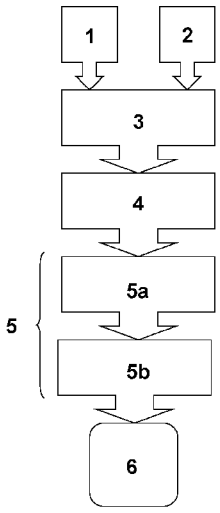

FIG. 1

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METHODS FOR MODIFYING ASPHALT USING LOW GREENHOUSE GAS LIQUIDS OBTAINED FROM DEPOLYMERIZATION OF WASTE PLASTICS

TECHNICAL FIELD

[0001] This invention relates to environmentally friendly, low greenhouse gas (GHG) asphalt modifiers. Specifically, the invention discloses carbon efficient liquid products derived from thermal depolymerization of waste plastics and/or other organic feedstocks and methods for modifying asphalt/bitumen products using said liquid products, singularly or together with other modifiers, to yield better performing, environmentally friendly asphalt pavement.

BACKGROUND

[0002] Under ambient conditions, the asphalt binder used for paving and industrial uses is a solid or semi-solid bituminous material. Such asphalt binder is either naturally occurring or derived from petroleum refining processes and includes a variety of paraffinic and aromatic hydrocarbons and heterocyclic compounds. Asphalt binder is a commonly used material for construction purposes such as roofing materials, water and damp-proofing products, bridge decks, racetracks, airport runways, parking lots, bicycle paths, and port facilities. A majority of asphalt binder is used in roadway and pavement applications. When asphalt binder is mixed with aggregate and used for paving it is called asphalt concrete mixture or simply asphalt pavement.

[0003] Asphalt alone, however, often does not possess all the physical characteristics desirable for many construction purposes and modifying asphalt is a common practice today. For instance, asphalt formulations incorporating unmodified asphalt binder may exhibit a poor performance grade rating (PG Rating) for pavements designed for high vehicular traffic or loading or severe climate zones. Temperatures and traffic conditions outside the pavement design range lead to deterioration of the asphalt pavement and short service life. Furthermore, as petroleum refining processes have become optimized to produce lighter liquid-range products (e.g., gasoline, diesel fuel, etc.), the resulting bottoms from which asphalt binders are derived have decreased in volume and become heavier, which further exacerbates the PG Rating problem. Hence, it has been an objective to broaden the PG Rating range of asphalt formulations used in road-pavement applications by the addition of various additives to the asphalt binder. Such additives commonly

include: petroleum extracts, waste motor oils and waste vegetable and soy oils. The terms "additive(s)" and "modifier(s)" convey similar meanings and are used interchangeably herein.

[0004] In addition to modifying above-mentioned virgin asphalt binders in the traditional paving process, recent effort to reduce paving carbon footprint has gained much industry wide interest to utilize modifier/additive further to achieve reduced blending temperatures as well as modifying aged binders from recycled asphalt mixtures. Due to the high molecular weight of the molecules present in asphalt binders, relatively high temperatures (135°C-160°C) are required when mixing unmodified asphalt binder with aggregate to produce asphalt pavement. Thus, traditional asphalt pavement formulations are commonly referred to as hot-mix asphalt (HMA). More than 90% of the carbon footprint of asphalt roads is attributable to the production and transport of the constituent materials (asphalt binder, petroleum-derived additives, and aggregate) and formulation (e.g., high-temperature mixing) and transport of the hot asphalt mixture to the paving site. This means that a significant amount of the annual carbon emissions from road construction could be avoided by enabling a process that addresses the method paving materials are produced, formulated, and transported. Currently two approaches have gained major attention: (1) modifying the asphalt binder to lower blending temperature to 105°C-150°C (so called warm-mix asphalt or WMA) to significantly reduce the emissions from burning diesel (or other heating fuels) and (2) incorporating recycled asphalt pavement (RAP) or recycled asphalt shingles (RAS) to reduce the amount of virgin binder and aggregate needed. These two approaches can work individually or can be combined to further reduce carbon footprint. As an example, according to a recent peer reviewed life cycle study (Sustainability 2021, 13(3), 1382; https://doi.org/10.3390/su13031382), a WMA with 93% RAP content reduces carbon emissions by 55-64% compared with a comparable HMA with virgin aggregate, which translate to 25 Million Metric tons of CO_2 emissions per year in the US alone, and 134 Million Metric tons of global CO_2 reduced globally.

[0005] Therefore, when repaving asphalt roadways, it is desirable to break up and reuse the old asphalt pavement (the RAP) in the new asphalt concrete mixture. However, due to oxidation and loss of small aromatic molecules, the asphalt binder in the old pavement becomes hard and brittle over time so the RAP must be rejuvenated to improve performance prior to laying the new asphalt concrete containing RAP. One key for incorporating RAP in both the HMA and the

WMA process is to add back lighter, mid-range hydrocarbons with significant aromatic content to revive the physical properties of the asphalt binder. In terms of rheological parameters, the goal is to decrease modulus and increase phase angle to have the rejuvenated asphalt binder meet a specified PG Rating again. However, the additives that are utilized to lower blending temperatures in WMA and to rejuvenate RAP are usually derived from petrochemical processes and carry their own significant carbon footprint.

[0006] Waste plastics are non-degradable constituents that can stay in the environment for centuries. Their large land space consumption is unsafe to humans and animals. Concomitantly, the continuous production of plastics poses another problem as they are petroleum-based material and thus contribute to depletion of the finite petroleum resources. In theory, the thermoplastic component of the polymeric solid waste stream can be recovered, segregated, and recycled into new useful products. In practice, however, only a small fraction of polymeric solid wastes are ultimately recycled, and there has not been a technology that can consume a large amount of such plastic waste and contribute to carbon footprint reduction in a significant way.

[0007] Pyrolysis is an alternate solution that breaks down many common solid waste plastics as well as a wide variety of solid waste biomass materials into more easily handled oils. Although such types of recovered oils could be potentially interesting as modifiers for asphalt modification, prior work has shown poor results in this regard. In terms of oils derived from plastics, efforts have primarily been focused on producing fuel oils comprising light weight aliphatic hydrocarbons for energy recovery. Such oil, however, will not work in asphalt modification due to its low boiling point (poor storage-ability) and excessively strong solvency, which prevents asphalt binder from bonding to aggregate surface. Bio-oils derived from biomass have high polar content and, when added to asphalt, have been found to accelerate binder aging and/or re-aging.

[0008] A low-cost method of producing additives that can be employed to achieve improved processing and more desirable physical characteristics of asphalt compositions, while ensuring good blending of the new asphalt and added RAP material, would be commercially and environmentally advantageous. Such a method would ideally employ a readily available,

inexpensive feedstock, preferably recyclable material, and employ an economical process. In addition to reducing cost, it is also preferred to produce additives that yield an overall lower carbon footprint, including, for example: (1) an environmentally friendly additive with a zero or negative footprint in its own production and (2) an additive that, when utilized in an asphalt mixture, enables a reduced carbon footprint in the overall paving process.

DISCLOSURE OF THE INVENTION

[0009] The present invention relates to asphalt materials with enhanced performance and tolerance against detrimental effects from aging and temperature, through use of a liquid or liquid mixture formed by a plastic depolymerization process, singularly or together with other modifiers, as an additive/modifier. The asphalt herein to be modified can be asphalt binder (bitumen) or recycled asphalt pavement (RAP). Shortcomings of conventional methods of producing additive-modified asphalt are overcome by a method for forming a liquid and employing the liquid to modify asphalt. The present invention also allows waste plastics to be utilized as a desirable feedstock material and lessens the carbon footprint of the resulting asphalt end-products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] These and other objects, features and attendant advantages of the present invention will be more fully appreciated or become better understood when considered in conjunction with the accompanying drawings, wherein:

FIG. 1 is a flowchart illustrating a process for creating depolymerized liquid materials from solid polymeric materials and/or other organic feedstocks;

FIG. 2 is a flowchart illustrating a process for employing depolymerized liquid materials as modifiers in asphalt modification.

FIG. 3 is a graph showing the product distribution of oil, gas, and solid products from the pyrolysis of representative waste plastic materials YM-1 and YM-2 at different temperatures.

FIG. 4 is a graph showing the product distribution of oil, gas, and solid products from the

co-pyrolysis of representative waste plastic materials YM-1 and YM-3 at 400°C.

FIG. 5 is a graph showing the product distribution of oil, gas, and solid products from the co-pyrolysis of representative waste plastic materials YM-2 and YM-3 at 400°C.

FIG. 6 is a graph showing the product distribution of oil, gas, and solid products from the co-pyrolysis of representative waste materials AS and YM-3 at 400°C.

FIG. 7 is a graph showing the performance of aged asphalt material rejuvenated with a representative depolymerized liquid material of the invention.

MODES FOR CARRYING OUT THE INVENTION

[0011] The description set forth below in connection with the appended drawings is intended as a description of presently-preferred embodiments of the invention and is not intended to represent the only forms in which the present invention may be constructed or utilized. The description sets forth the functions and the sequence of steps for constructing and operating the invention in connection with the illustrated embodiments. It is to be understood, however, that the same or equivalent functions and sequences may be accomplished by different embodiments that are also intended to be encompassed within the spirit and scope of the invention.

[0012] In the present invention, a solid polymeric material or a mixture of solid polymeric materials is heated in a reactor such that said polymeric material anaerobically turns into a vapor form. In some embodiments of the present invention, other organic feedstocks may be combined with the polymeric material(s). An inert gas stream or an applied vacuum is then utilized to transfer the vaporized material into a reactor where said vaporized material undergoes a thermal depolymerization process to produce a vapor stream consisting of a mixture of depolymerization products. A depolymerized liquid material product is collected from the vapor stream by condensation. The method can be operated in a batch, continuous, or semi-continuous fashion.

[0013] A flowchart illustrating an example of an overall process for creating a depolymerized liquid material is shown in FIG. 1. The solid polymeric material (1) and other organic feedstock

(2), if optionally utilized, are added to reactor (3) where they are vaporized at high temperature under anaerobic conditions. The vaporized material is transferred to reactor (4) optionally containing a catalyst to effect the depolymerization reaction. The depolymerized vapor stream is then transferred through one or more condensers (5) where the depolymerized liquid materials are collected as liquids. If multiple condensers (5) are utilized, each subsequent condenser after the first will generally be cooled at sequentially decreasing temperatures such that the highest molecular weight fractions will condense first (e.g., condenser 5a) and then sequentially lower molecular weight fractions will condense until only gaseous products remain. In some cases, the highest molecular weight fraction or fractions might be waxes at room temperature. Gaseous products (6) exit the condensers (5) and can be subsequently captured for future use, flared as waste, or utilized as fuel to provide heat for the process.

[0014] In some embodiments of the present invention, the polymeric material can be one or more polyolefin plastics such as high-density polyethylene (HDPE), low density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and/or polyethylene terephthalate (PET), and/or polypropylene (PP), and/or polyurethanes (PUR) such as polyester and polyether polyurethanes, and/or polystyrenes (PS). In some embodiments of the present invention, the polymeric material may comprise polyvinyl chloride (PVC). In some embodiments of the present invention, the polymeric material may comprise natural or synthetic rubber materials such as polyisoprenes and polybutadienes. The polymeric material may comprise recycled plastics. In some embodiments of the present invention, the polymeric materials may comprise various organic additives such as plasticizers and/or stabilizers. In some embodiments, the polymeric material may be a mixture of one or more or all of the plastics listed above.

[0015] In some embodiments of the present invention, other organic feedstocks may be combined with the polymeric material(s) prior to or during depolymerization (in-situ production). Without limitation, such organic feedstocks may include lignocellulosic feedstocks obtained from biomass resources such as, for example, wood and/or hemp pulp, flaxseed, etc. and/or proteinic feedstocks obtained from plant, animal, and/or algal resources. In some embodiments of the present invention, such organic feedstocks are derived from harvested biomass resources. In other embodiments, such organic feedstocks are derived from wastes or by-products derived from biomass processing operations, such as, for example, sawdust,

pomegranate peel and seed, almond shells, etc. In some embodiments, the amount and composition of such other organic feedstocks are chosen to optimize the amounts of polar functional groups present in the depolymerized liquid material. In some embodiments, the amount of other organic feedstocks added ranges from about 1-250% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 10-150% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 25-100% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 15-50% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 5-50% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 5-25% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 1-10% by weight relative to the amount of the solid polymeric material. In some embodiments, the amount of other organic feedstocks added ranges from about 2-6% by weight relative to the amount of the solid polymeric material.

[0016] In some embodiments of the present invention, the solid polymeric materials and the other organic feedstocks may be thermally depolymerized separately (ex-situ production) such that distinct depolymerized liquids are produced. The distinct depolymerization liquids may be utilized independently or blended together in various combinations to achieve the desired properties. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 1-200% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 5-150% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 25-100% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 15-50% by weight relative to the amount of depolymerized liquids derived from the solid

polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 1-20% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 1-10% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material. In some embodiments, the amount of depolymerized liquids derived from other organic feedstocks added ranges from about 2-6% by weight relative to the amount of depolymerized liquids derived from the solid polymeric material.

[0017] The depolymerization can be a purely thermal reaction or it can employ catalysts. Depending on the starting material and the desired end-product, depolymerization could be employed for a slight or extreme reduction of the molecular weight of the starting material. In some embodiments the depolymerization process preferably employs a catalyst. The preferred catalyst employs a biochar derived from biomass, an activated carbon material, a metal or metal oxide material, or a zeolite or alumina material. Biochar catalysts are particularly inexpensive and, at the end of their usefulness as catalysts, may be utilized as a component of the modified asphalt blend. Zeolite, metal oxide, or alumina catalysts offer high catalytic efficiencies and can be readily regenerated via calcination at high temperatures but are more expensive than biochar materials. In some embodiments of the present invention, certain components within the waste plastics or mixtures of waste plastics may act as catalysts or may generate catalytic species during pyrolysis. For example, chlorinated plastics, such as PVC, or chlorinated additives may generate chlorine radicals during pyrolysis which may promote a catalytic effect on the pyrolysis of other plastic materials or organic feedstocks that may be present. Mixtures of these various catalysts may also be utilized, along with reaction parameters such as temperature, reaction time, and condensation temperature to fine-tune the properties of the resulting depolymerization liquids.

[0018] In some embodiments of the present invention, the combination of other organic feedstocks with the polymeric materials will generate a positive synergistic depolymerization environment requiring lower depolymerization temperatures and, therefore, less energy consumption. In some embodiments, the synergistic effects of the other organic feedstocks may

reduce or even eliminate the need for a depolymerization catalyst to achieve a liquid product with a particular set of properties such as molecular weight, polar content, viscosity, etc.

[0019] In some embodiments, the vaporization process and depolymerization process employs two separate reactors. One or more of the reactors can include a static mixer. An inert gas such as nitrogen can be used to purge oxygen from the reactor and to carry the feedstock vapor from the vaporization reactor to the depolymerization reactor. In some embodiments of the present invention, an applied vacuum is utilized to purge oxygen from the reactor and to pull the feedstock vapor from the vaporization reactor to the depolymerization reactor. In some embodiments, the vaporization process and the depolymerization process may occur within a single reactor. In some embodiments, the vaporization and depolymerization temperatures are the same. In some embodiments, the vaporization and depolymerization temperatures may be different.

[0020] Temperatures greater than about 250°C are generally required to effect vaporization, depending on the composition of the feedstock. In some embodiments, vaporization temperatures such as 250-300°C , 300-350°C, 350-400°C, 450-500°C, 500-550°C, 550-600°C, 600-650°C, 650-700°C, 300-400°C, 400-500°C, 500-600°C, or 600-700°C might be utilized. In some embodiments, vaporization temperatures are between 250-400°C. In some embodiments, vaporization temperatures are between 400-500°C. In some embodiments, vaporization temperatures are between 450-550°C. In some embodiments, vaporization temperatures are between 500-600°C. Temperatures greater than about 250°C are generally desired to effect the thermal depolymerization process, depending on the composition of the feedstock and/or catalyst. In some embodiments, depolymerization temperatures such as 250-300°C , 300-350°C, 350-400°C, 450-500°C, 500-550°C, 550-600°C, 600-650°C, 650-700°C, 300-400°C, 400-500°C, 500-600°C, or 600-700°C might be utilized. In some embodiments, depolymerization temperatures are between 400-500°C. In some embodiments, depolymerization temperatures are between 450-550°C. In some embodiments, depolymerization temperatures are between 500-600°C. In some embodiments, depolymerization temperatures are between 550-650°C. In some embodiments, depolymerization temperatures are between 600-700°C.

[0021] The depolymerization process converts the solid polymeric material, alone or in combination with one or more other organic feedstocks, into a mixture of gaseous, liquid, and solid or wax fractions. The proportion of these different components vary with reaction conditions such as reaction temperature, reaction time, and choice of catalyst (including no catalyst). In some embodiments, it is desirable to minimize the amount of the solid or wax fraction by utilizing higher reaction temperatures. Proper choice of catalyst and a reduced reaction time may also decrease wax yield. In some embodiments, it is desirable to maximize the content of aromatic species in the liquid fraction. Proper choice of catalyst and temperature (higher temperatures, especially temperatures over about 550°C generally favor aromatic production) may also increase the yield of aromatics in the liquid fraction. In some embodiments, it is desirable to maximize the content of aliphatic species in the liquid fraction. In some embodiments, it is desirable to have a certain ratio of aromatic species and aliphatic species in the liquid fraction.

[0022] The depolymerization process generally produces a significant amount of gaseous products, especially under conditions intended to minimize wax formation. Wax products are less desirable products because they require further processing steps (e.g., grinding, pelletizing, prilling, etc.) to be easily handled and require higher blending temperatures when mixed with asphalt binder. Depolymerization conditions favoring low wax also produce higher amounts of aromatics and other unsaturated carbon containing products with concomitant hydrogen gas production. Liquid depolymerization products can be better utilized, and help to lower mixing temperatures, in WMA formulations and can help to soften HMA formulations, making them more ductile. In some embodiments, it may be desirable to collect and utilize the gaseous fraction, possibly including some of the liquid fraction, as fuel to generate the heat required for the vaporization and/or depolymerization reactor(s). In particular, the hydrogen produced during depolymerization is a clean burning fuel that does not contribute to carbon emissions.

[0023] In some embodiments, a typical molecule in the depolymerized liquid material comprises aromatic rings interconnected with one another directly and/or aromatic rings connected by aliphatic species. In some embodiments, the preferred ring count is about 2-6. In some embodiments, the preferred ring count is about 2-5. In some embodiments, the preferred ring count is about 2-4. In some embodiments, the depolymerized liquid material should contain a

small percentage of polar oxygen-containing and/or nitrogen-containing compounds, such as esters, phenolic compounds, and derivatives thereof. In some embodiments, the total heterogeneous element (O, N) in the oil shall be in the range of 1-5% by weight. In some embodiments, the total heterogeneous element (O, N) in the oil shall be in the range of 1-10% by weight. In some embodiments, the total heterogeneous element (O, N) in the oil shall be in the range of 2-6% by weight.

[0024] The depolymerized liquid fraction is generally collected by condensation from the depolymerized vapor stream exiting the reactor(s). A single liquid fraction may be obtained by passing the vapor stream through a single condenser set to a sufficiently low temperature to condense a liquid over a desired molecular weight or carbon (C_n) number. In embodiments of the present invention utilizing an applied vacuum instead of an inert gas purge, lower condenser temperatures will generally be required to condense a liquid of a particular molecular weight or C_n range. Alternatively, multiple fractions of varying molecular weight may be obtained by passing through a series of condensers at sequentially lower temperatures as described above. Any particular depolymerized liquid material fraction may also be further fractionated in a separate step by fractional distillation.

[0025] The present method involves two main concepts: (1) the creation of depolymerized liquid materials via depolymerization of solid plastic materials and/or other organic compounds, and (2) adding these liquids, or a mixture of these liquids, to modify various asphalt compositions. In some embodiments, the depolymerized liquid modifier(s) can be added during a "wet process" to the asphalt binder, i.e., prior to adding aggregates to the asphalt mixture to produce, for example but not limited to, an improved asphalt binder composition. In some embodiments, the depolymerized liquid modifier(s) can be added during a "dry process," i.e., in concurrence with aggregate, RAP, and/or other solid filler addition. A non-limiting example of a dry process is shown in FIG. 2. Depolymerization liquid(s) derived from depolymerization of plastics (7) and/or from depolymerization of other organic compounds (8) are mixed with asphalt binder (9), other common asphalt modifiers (10), and solid fillers such as aggregate (11) and/or RAP (12) at approximately 110-160°C to produce the final asphalt concrete formulation (14). In some embodiments, the depolymerized liquid modifier(s) can be sprayed on the RAP content prior to mixing the RAP with a virgin asphalt binder.

[0026] In some embodiments, ground or shredded waste plastic material, which may be the same as or different from the plastic material employed to produce the depolymerization liquid, may be added as a filler to produce a polymer modified asphalt. In some embodiments, SBS and/or crumb rubber can be ground up or partially depolymerized in a similar depolymerization process and blended in along with the liquid. In some embodiments, ground, crushed or shredded RAP and/or recycled asphalt shingle (RAS) may be added to produce a modified asphalt concrete mixture. In some embodiments, moderate blending temperatures of 100-130°C can be achieved by treating the asphalt binder with the depolymerization liquid prior to adding in aggregates (the liquid can be used as a softening agent for the asphalt binder allowing a WMA process). In some embodiments, the asphalt product can be further modified by materials such as an elastomer, plastomer, wax, poly phosphoric acid, sulfuric acids, amines, amide-diamine, phosphate esters, hydrolene aromatic oils, extender oils, vegetable oils, asphalt sand, naturally occurring bitumens and/or a combination thereof. In some embodiments, the modified asphalt product can be subjected to an emulsifying process by mixing in an emulsifier and water.

[0027] In some embodiments, the addition of the depolymerized liquid improves the processing and physical characteristics of the modified asphalt, including reduction in blend time and/or blend temperature to achieve optimal or near-optimal dispersion of the polymer fillers and/or dispersion of additional modifier(s), resulting in higher throughputs; enablement of higher RAP and RAS loading through reduced mix stiffness and increased ductility; and compaction and material handling. Furthermore, without wishing to be bound by theory, it is believed that modifiers with high aromatic content and/or polar functional groups such as, for example, phenolics and/or amide groups, are particularly effective in deagglomeration of asphaltene sheets present in asphalt materials, while aliphatics and saturated species are effective in softening asphalt binder during blending, and contribute to rutting resistance once applied, hence liquid with aliphatic species can be blended in as an additive to lower the viscosity of asphalt binder during the WMA process. In some embodiments, the liquid modifiers may incorporate 2-40% by weight of depolymerization liquids derived from organic compounds as such liquids contain enhanced amounts of polar functional groups that can facilitate deagglomeration of asphaltene sheets in asphalt formulations. In some embodiments, the depolymerization liquids derived from plastic materials, alone or in conjunction with liquids with polar functional groups, will contain small aromatic compounds along with some amount of saturated and unsaturated aliphatic

compounds which may aid in dispersing and stabilizing the detangled asphaltene sheets present in a solution.

[0028] In other or the same embodiments, the addition of depolymerized liquids improves the physical characteristics of the final asphalt product. The resulting final products can have various properties that differ from their unmodified forms. In some embodiments, the properties include, among other things, improved rutting susceptibility; improved fatigue cracking resistance; improved thermal cracking resistance; improved thermal stability; improved polymer dispersion and viscosity. Improvements to elastomeric properties and energy of deformation are also observed in some embodiments.

[0029] The said depolymerization process yields an additive with significant carbon footprint reduction in the following ways:

(a) It utilizes waste plastics as feedstock which stops said materials from being incinerated.

(b) The depolymerization process can be self-fueling and does not require external energy. The gaseous product in the depolymerization process in general provides adequate heating energy to self-fuel the ongoing said process. In addition, it is possible to optimize hydrogen in the gaseous product by keeping reaction temperatures in an desired range in a catalytic reaction, hence emitting mostly H_2O as steam (90%+ hydrogen by volume in gaseous product is achievable from experimental data).

(c) A negative carbon footprint is achievable with biochar-based catalyst (derived from organic products such as agricultural waste) and/or co-depolymerization with an organic product (such as agricultural waste). CO_2 was sequestered during the growth of the organic product, when used to produce biochar and/or co-depolymerization the originally sequestered carbon is locked in solid phase and/or liquid phase. For example, in the case of biochar once its catalytic uses are finished, such biochar solid is added into asphalt mixture as a filler, eventually locking up the sequestered CO_2. With a typical catalyst to feedstock ratio, the carbon footprint of the depolymerized product is further offset and

achieves carbon neutrality, yielding 1.6 metric tons of CO_2 captured from the environment for each ton of waste plastics depolymerized.

(d) When considering that such waste plastic material is likely to be incinerated otherwise (at an average of 2.9 ton CO_2 emission / ton of plastic), the carbon emission reduction is much more significant, which means for each ton of plastic waste utilized in said depolymerization process 4.5 tons of CO_2 emissions is offset.

(e) When such depolymerized product is applied to replace current popular commercial additives, the carbon footprint to produce such additives is further offset. For example, to produce 1 ton of RAP and WMA asphalt pavement mixture (at 50% RAP content), an average of 3.43 kg CO_2 is emitted from production of conventional additives. With a 5% asphalt binder dosage, the use of the depolymerized liquid additives of the present invention eliminates the above said emissions and contributes an effective negative 4.43 kg CO_2 - hence a total of 7.86 kg carbon footprint reduction for each ton of pavement constructed. This means there is potential to reduce the paving greenhouse gas (GHG) emissions by 48%. With a higher RAP content of 93%, the GHG emissions are further reduced by 84%, resulting in a CO_2 reduction of 35 metric tons in the US alone and an estimated 180 metric tons globally.

EXAMPLES

[0030] In the following examples, efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperature, etc.) but some experimental error and deviation should be accounted for. The examples are to be considered as not being limiting of the invention described herein.

General Procedures:

[0031] Ground almond shell (AS) was obtained from Northern California almond farms. Representative waste plastic materials were obtained from three different types of yoga mat products:

(i) YM-1 was a yoga mat comprising polyester and natural rubber;

(ii) YM-2 was a multilayered yoga mat comprising various plastics along with natural and synthetic rubbers; and

(iii) YM-3 was a yoga mat comprising polyvinyl chloride (PVC) and associated ester-based plasticizers.

All pyrolysis reactions were performed in a glass tube placed into a tube furnace with an inert gas purge or held under a vacuum (similar results were obtained). A section near one end of the glass tube was plugged with glass wool and an amount of one or more waste plastic material along with any catalyst, if used, was loaded into the tube. Another glass wool plug was inserted above the material to hold it in place. The end of the tube was connected to a condenser cooled to a temperature of about 10°C. The tube with the plastic material was loaded into a tube furnace and rapidly heated to the desired pyrolysis temperature. The resulting cracked products were then carried by the purge gas stream or applied vacuum through the condenser where hydrocarbons of approximately C_7-C_8 and greater were condensed out as liquids. Hydrocarbon products lighter than about C_7-C_8 passed through the condenser, and some amount of solid residue remained in the tube.

Example 1

Pyrolysis of Mixed Waste Plastics at Different Temperatures

[0032] Representative mixed waste plastic materials YM-1 and YM-2 were pyrolyzed according to the general procedure described above at different pyrolysis temperatures (400°C, 450°C, and 500°C) to yield the mix of depolymerized liquid, solid residue, and gas products as shown in Table 1 and represented graphically in FIG. 3. All of the values shown are an average of three runs. Generally, higher pyrolysis temperatures yielded higher depolymerized liquid and gas yields and reduced residual solid yields.

Table 1. Product Mix from Pyrolysis of Mixed Waste Plastic Materials

Run No.	**1**	**2**	**3**	**4**	**5**	**6**
Material	YM-1	YM-1	YM-1	YM-2	YM-2	YM-2
Temperature (°C)	400	450	500	400	450	500

Product Type (wt. %):						
Liquid	28.0	37.6	38.9	32.1	49.0	56.6
Gas	3.0	11.1	9.7	8.7	14.8	11.6
Solid	69.0	51.3	51.4	59.2	36.2	31.8

Example 2

Co-Pyrolysis of Waste Materials with PVC

[0033] The various waste materials YM-1, YM-2, and AS were pyrolyzed or co-pyrolyzed with YM-3 (comprising PVC) at 400°C according to the general procedure described above to yield the mix of liquid, solid, and gas products as shown in Table 2 and graphically illustrated in FIG. 4 (YM-1/YM-3), FIG. 5 (YM-2/YM-3), and FIG. 6 (AS/YM-3). All of the values shown are an average of three runs. When waste plastics (YM-1 or YM-2) or organic feedstock (AS) were co-pyrolyzed with the PVC-containing material (YM-3), higher yields of liquid product were observed than were predicted based on pyrolysis yields of the individual materials as shown in Table 3.

Table 2. Product Mix from Co-Pyrolysis of Waste Materials with PVC

Run No.	**7**	**8**	**9**	**10**	**11**
Material	AS	1:1 AS/YM-3	1:1 YM-1/YM-3	1:1 YM-2/YM-3	YM-3
Temperature (°C)	400	400	400	400	400
Product Type (wt. %):					
Oil	49.6	52.5	35.7	41.4	37.7
Gas	6.5	8.0	17.8	18.8	18.2
Solid Residue	43.9	39.6	46.5	39.8	44.1

Table 3. Liquid Yields from Co-Pyrolysis of Waste Materials with PVC (YM-3)

Liquid Yield (wt. %)	1:1 YM-1 / YM-3	1:1 YM-2 / YM-3	1:1 AS / YM-3
Predicted	32.8	34.9	43.6
Actual	35.7 ± 2.3	41.4 ± 3.5	52.5 ± 2.1

Example 3

Rejuvenation Performance of Depolymerized Liquids from Waste Plastics

[0034] A depolymerization liquid was prepared by the co-pyrolysis of 1:1 YM-1/YM-3 at 400°C according to the general procedure as in Run 9 of Example 2 above. A sample of "aged" asphalt binder was prepared from a virgin bitumen material ("Virgin") via standard laboratory accelerated aging procedures in a rolling thin film oven pressure vessel to a 10-year field aged equivalent material ("Aged"). Samples of rejuvenated asphalt binder were prepared by blending the aged bitumen material with (i) 10% by weight of the inventive depolymerization liquid ("Rejuvenated (I)") and (ii) 10% by weight of a standard commercial rejuvenating material Reclamite® (Tricor Refining, LLC) ("Rejuvenated (R)") as a reference material. Standard linear amplitude sweep (LAS) testing method AASHTO T 391-20 was run (FIG. 7) to determine the various asphalt binders' resistance to fatigue damage by means of cyclic loading employing systematic, linearly increasing load amplitudes. This test is commonly used to simulate field durability. Generally speaking, the LAS curves of each binder give a visual estimate of the load bearing performance when compared to one another. An ideal binder's modulus (y axis) should stay relatively stable across all levels of deformation. However, in reality, a binder will often yield with a sudden decrease of modulus, which is generally ascribed to development of significant cracks in the testing material. As seen in FIG. 7, the virgin asphalt binder (Virgin) did not yield during testing and had a softer modulus in general. The curve for the Aged material, which would be highly oxidized, shows a much higher modulus (stiffer material) that yields early on during the LAS testing as the material cracks. The curves for the rejuvenated samples prepared from the depolymerization liquid of the present invention, Rejuvenated (I), and from the reference commercial material, Rejuvenated (R), both show good performance. In fact, in terms of reducing the aged binder modulus and increasing flexibility, the inventive depolymerization liquid out-performed the commercial product.

INDUSTRIAL APPLICABILITY

[0035] This invention may be industrially applied to the development, manufacture, and use of an asphalt modifier that is environmentally friendly with low greenhouse gas (GHG), produced by using solid plastic materials, alone or in conjunction with other organic feedstocks, to prepare carbon-efficient asphalt formulations and end-products.

What is claimed is:

1. A method for forming an asphalt modifier comprising a depolymerized liquid material, the method comprising:
   (a) selecting a solid polymeric material, or a mixture of solid polymeric materials;
   (b) heating the solid polymeric material or mixture of solid polymeric materials in a vaporization reactor at a vaporization temperature under an inert gas stream or an applied vacuum such that the solid polymeric material or mixture of solid polymeric materials turns into a vaporized material;
   (c) transporting the vaporized material with the inert gas stream or the vacuum environment to a depolymerization reactor at a depolymerization temperature sufficient to effect a thermal depolymerization reaction of the vaporized material and form a depolymerized vapor stream comprising a mixture of depolymerization products; and
   (d) transporting the depolymerized vapor stream through a condenser at a lower temperature, or through a series of condensers at sequentially lower temperatures, to produce one or more depolymerized liquid materials and a gaseous product stream.

2. The method of claim 1, wherein a catalyst is utilized to facilitate the thermal depolymerization reaction.

3. The method of claim 2, wherein the catalyst comprises a zeolite or alumina.

4. The method of claim 2, wherein the catalyst comprises biochar derived from biomass.

5. The method of claim 2, wherein the catalyst comprises activated carbon.

6. The method of claim 2, wherein the catalyst comprises a metal or metal oxide or a combination thereof.

7. The method as in any of claims 1-6, wherein the depolymerization temperature is greater

than 550°C and a typical molecule in the depolymerized liquid material comprises aromatic rings interconnected with one another directly and/or aromatic rings connected by aliphatic species.

8. The method as in any of claims 1-6, wherein said depolymerization process further employs a fractionation method.

9. The method of claim 8, wherein the fractionation method employs heating the mixture.

10. The method of claim 8, wherein the fractionation method employs solvent.

11. The method as in any of claims 1-6, wherein the vaporization reactor and the depolymerization reactor are a single reaction chamber.

12. The method as in any of claims 1-6, wherein the vaporization temperature and the depolymerization temperature are different.

13. The method as in any of claims 1-6, wherein the vaporization temperature and the depolymerization temperature are the same.

14. The method as in any of claims 1-6, wherein the solid polymeric materials comprise waste plastics or a mixture of waste plastics.

15. The method as in any of claims 1-6, wherein other organic materials are combined with the solid polymeric material or mixture of solid polymeric materials.

16. The method as in claim 15, wherein the depolymerized liquid material contains polar oxygen-containing and/or nitrogen-containing compounds.

17. A method for forming an asphalt modifier comprising a depolymerized liquid material, the method comprising:

(a) selecting an organic material, or a mixture of organic materials;

(b) heating the organic material or mixture of organic materials in a vaporization reactor at a vaporization temperature under an inert gas environment or a vacuum environment such that the organic material or mixture of organic materials turns into a vaporized material;

(c) transporting the vaporized material with the inert gas to a depolymerization reactor at a depolymerization temperature sufficient to effect a thermal depolymerization reaction of the vaporized material and form a depolymerized vapor stream comprising a mixture of depolymerization products; and

(d) transporting the depolymerized vapor stream through a condenser at a lower temperature, or through a series of condensers at sequentially lower temperatures, to produce one or more depolymerized liquid materials and a gaseous product stream.

18. The asphalt modifier of any of claims 1-6.

19. The asphalt modifier of claim 7.

20. The asphalt modifier of claim 16.

21. The asphalt modifier of claim 17.

22. The asphalt modifier of claim 18 further compromising an additive selected from the group consisting of an elastomer, plastomer, wax, poly phosphoric acid, sulfuric acids, amines, amide-diamine, phosphate esters, hydrolene aromatic oil, extender oils, vegetable oils, rerefined motor oil bottoms, asphalt sand, bio-based oils, pyrolytic rubber oil or wax, aromatic extract, naturally occurring bitumens or combinations thereof.

23. The asphalt modifier of claim 19 further compromising an additive selected from the group consisting of an elastomer, plastomer, wax, poly phosphoric acid, sulfuric acids, amines, amide-diamine, phosphate esters, hydrolene aromatic oil, extender oils, vegetable oils, rerefined motor oil bottoms, asphalt sand, bio-based oils, pyrolytic rubber oil or wax,

aromatic extract, naturally occurring bitumens or combinations thereof.

24. The asphalt modifier of claim 20 further compromising an additive selected from the group consisting of an elastomer, plastomer, wax, poly phosphoric acid, sulfuric acids, amines, amide-diamine, phosphate esters, hydrolene aromatic oil, extender oils, vegetable oils, rerefined motor oil bottoms, asphalt sand, bio-based oils, pyrolytic rubber oil or wax, aromatic extract, naturally occurring bitumens or combinations thereof.

25. The asphalt modifier of claim 21 further compromising an additive selected from the group consisting of an elastomer, plastomer, wax, poly phosphoric acid, sulfuric acids, amines, amide-diamine, phosphate esters, hydrolene aromatic oil, extender oils, vegetable oils, rerefined motor oil bottoms, asphalt sand, bio-based oils, pyrolytic rubber oil or wax, aromatic extract, naturally occurring bitumens or combinations thereof.

26. The asphalt modifier of claim 16, added to an asphalt binder to produce a modified asphalt binder.

27. The asphalt modifier of claim 16, added to an asphalt concrete mixture to produce a modified asphalt concrete mixture.

28. The asphalt modifier of claim 16, added to a recycled or partially recycled asphalt concrete mixture to produce a modified asphalt concrete mixture.

29. The asphalt modifier of claim 16 further compromising an emulsifier and water to produce an emulsified mixture used as asphalt pavement surface treatment.

30. The asphalt modifier of claim 17, added to an asphalt binder to produce a modified asphalt binder.

31. The asphalt modifier of claim 17, added to an asphalt concrete mixture to produce a modified asphalt concrete mixture.

32. The asphalt modifier of claim 17, added to a recycled or partially recycled asphalt concrete mixture to produce a modified asphalt concrete mixture.

33. The asphalt modifier of claim 17 further compromising an emulsifier and water to produce an emulsified mixture used as asphalt pavement surface treatment.

34. A method to rejuvenate a RAP material comprising treating the RAP material with the asphalt modifier of claim 16.

35. A method to rejuvenate a RAP material comprising treating the RAP material with the asphalt modifier of claim 17.

36. The method as in any of claims 1-6 wherein the gaseous product stream is utilized as fuel to heat the vaporization reactor and/or the depolymerization reactor.

37. A method for producing a modified asphalt binder comprising mixing asphalt binder with the asphalt modifier of claim 16 in a wet process.

38. A method for producing a modified asphalt binder comprising mixing asphalt binder with the asphalt modifier of claim 17 in a wet process.

39. A method for producing an asphalt concrete mixture comprising mixing asphalt binder, the asphalt modifier of claim 16, and one or more filler materials selected from the group consisting of aggregate, RAP, and RAS in a dry process.

40. A method for producing an asphalt concrete mixture comprising mixing asphalt binder, the asphalt modifier of claim 17, and one or more filler materials selected from the group consisting of aggregate, RAP, and RAS in a dry process.

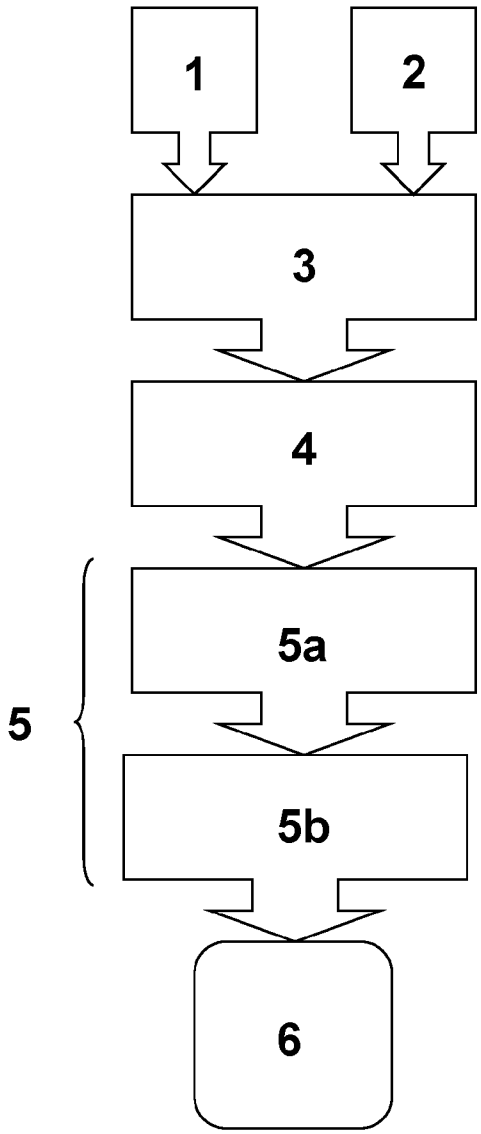

FIG. 1

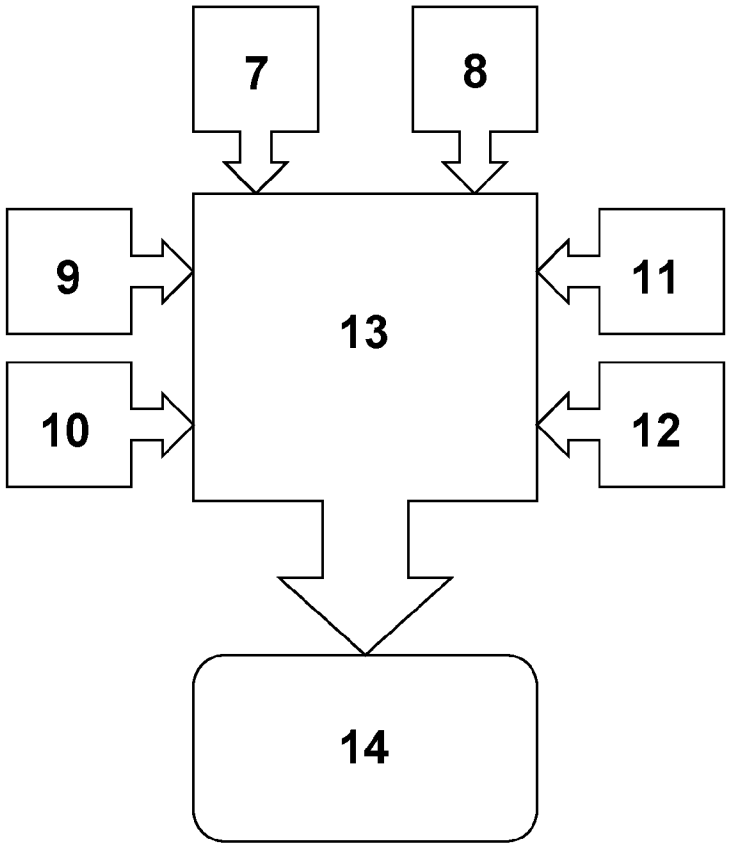

FIG. 2

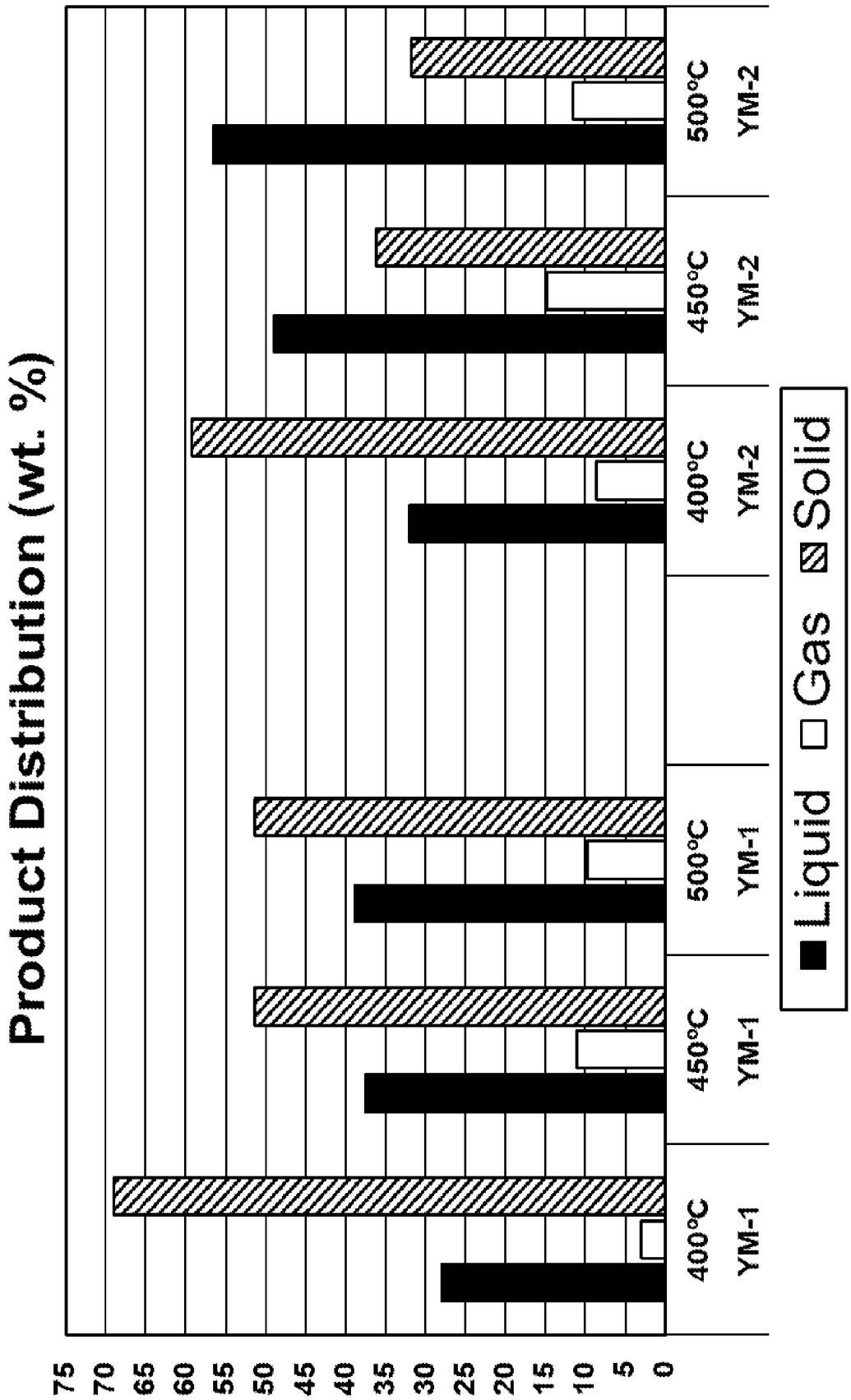
Product Distribution (wt. %)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
400°C
YM-1
450°C
YM-1
500°C
YM-1
400°C
YM-2
450°C
YM-2
500°C
YM-2
Liquid
Gas
Solid

FIG. 3

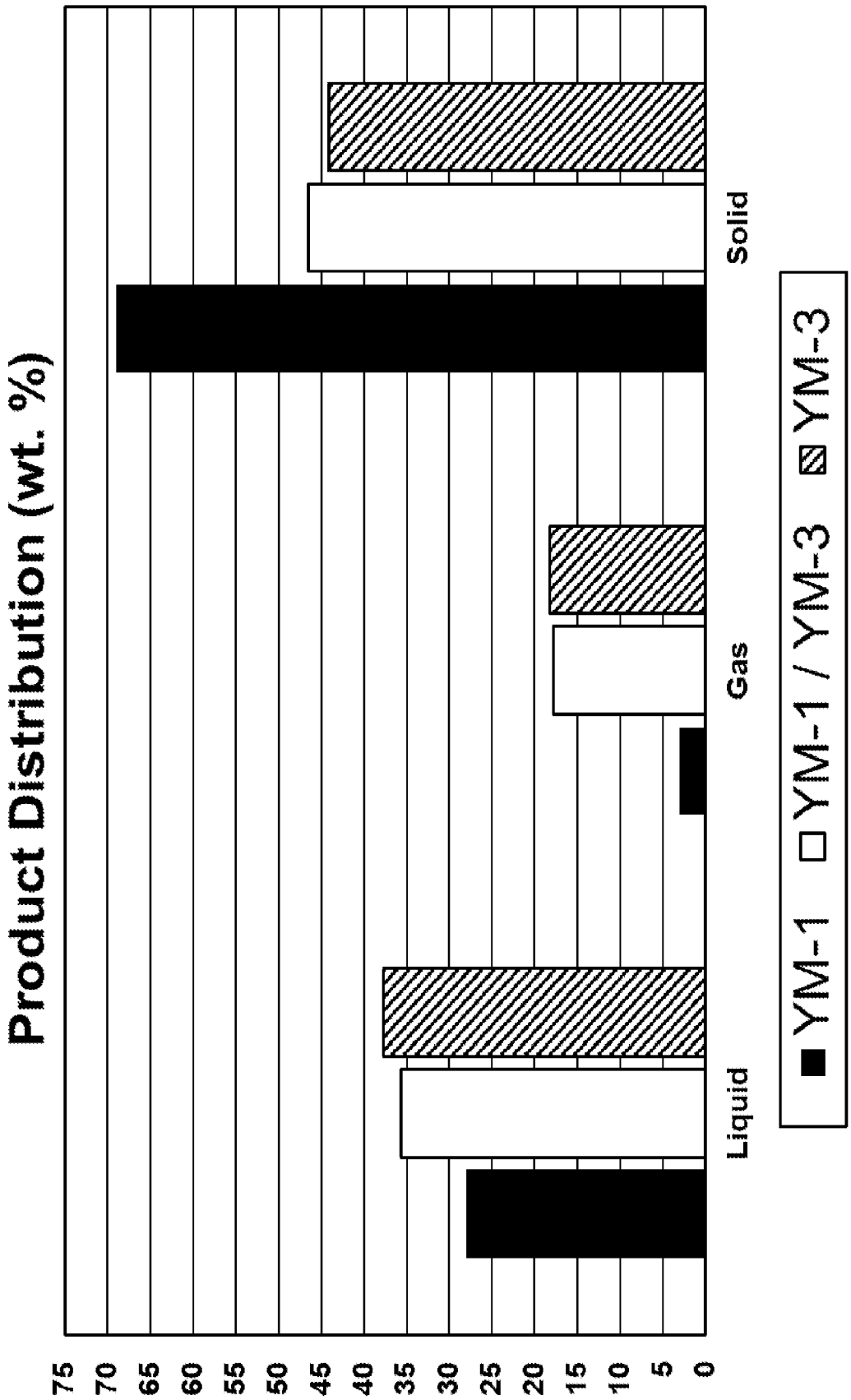
Product Distribution (wt. %)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Liquid
Gas
Solid
YM-1
YM-1 / YM-3
YM-3

FIG. 4

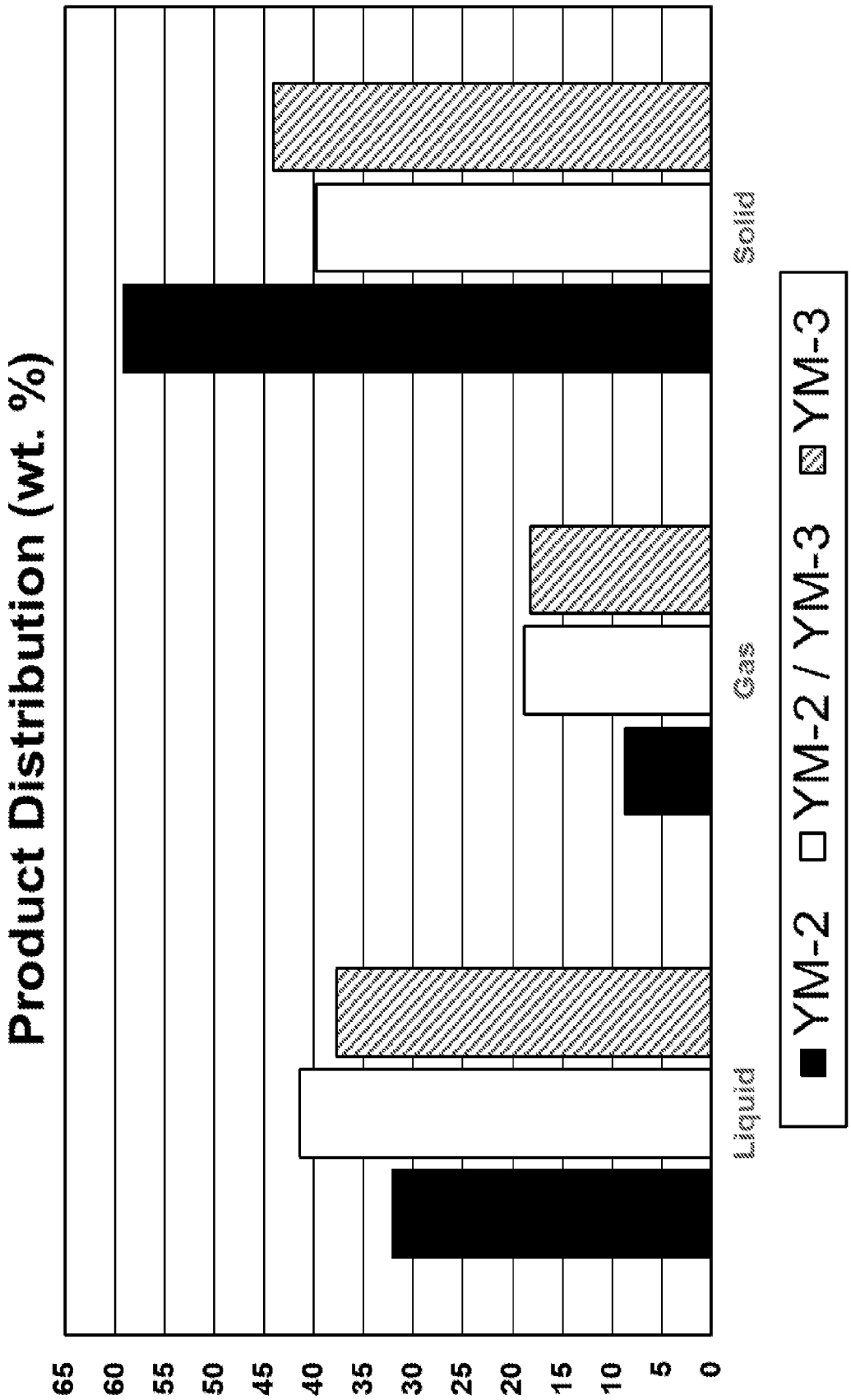
Product Distribution (wt. %)
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Liquid
Gas
Solid
YM-2
YM-2 / YM-3
YM-3

FIG. 5

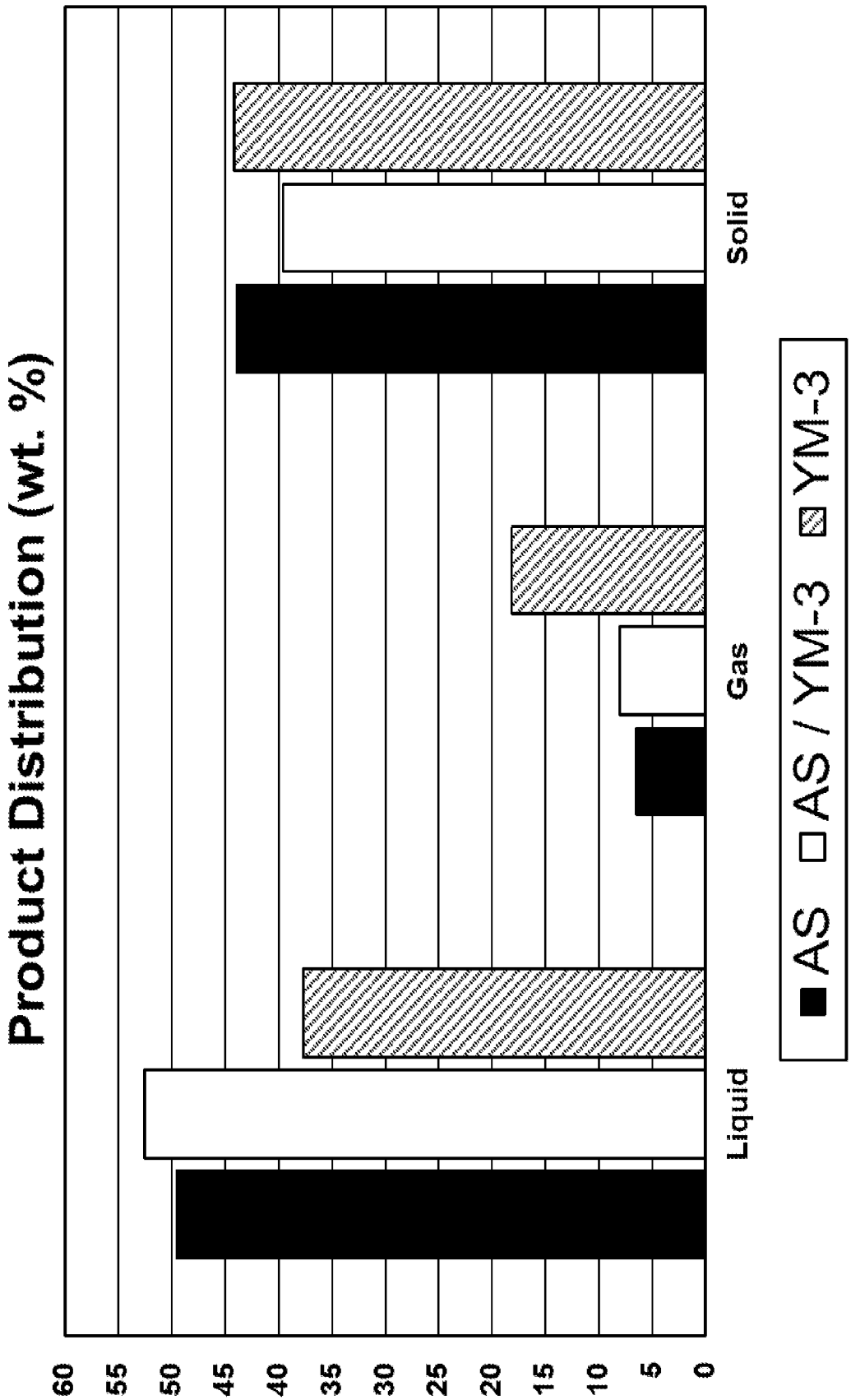
Product Distribution (wt. %)
60
55
50
45
40
35
30
25
20
15
10
5
0
Liquid
Gas
Solid
AS
AS / YM-3
YM-3

FIG. 6

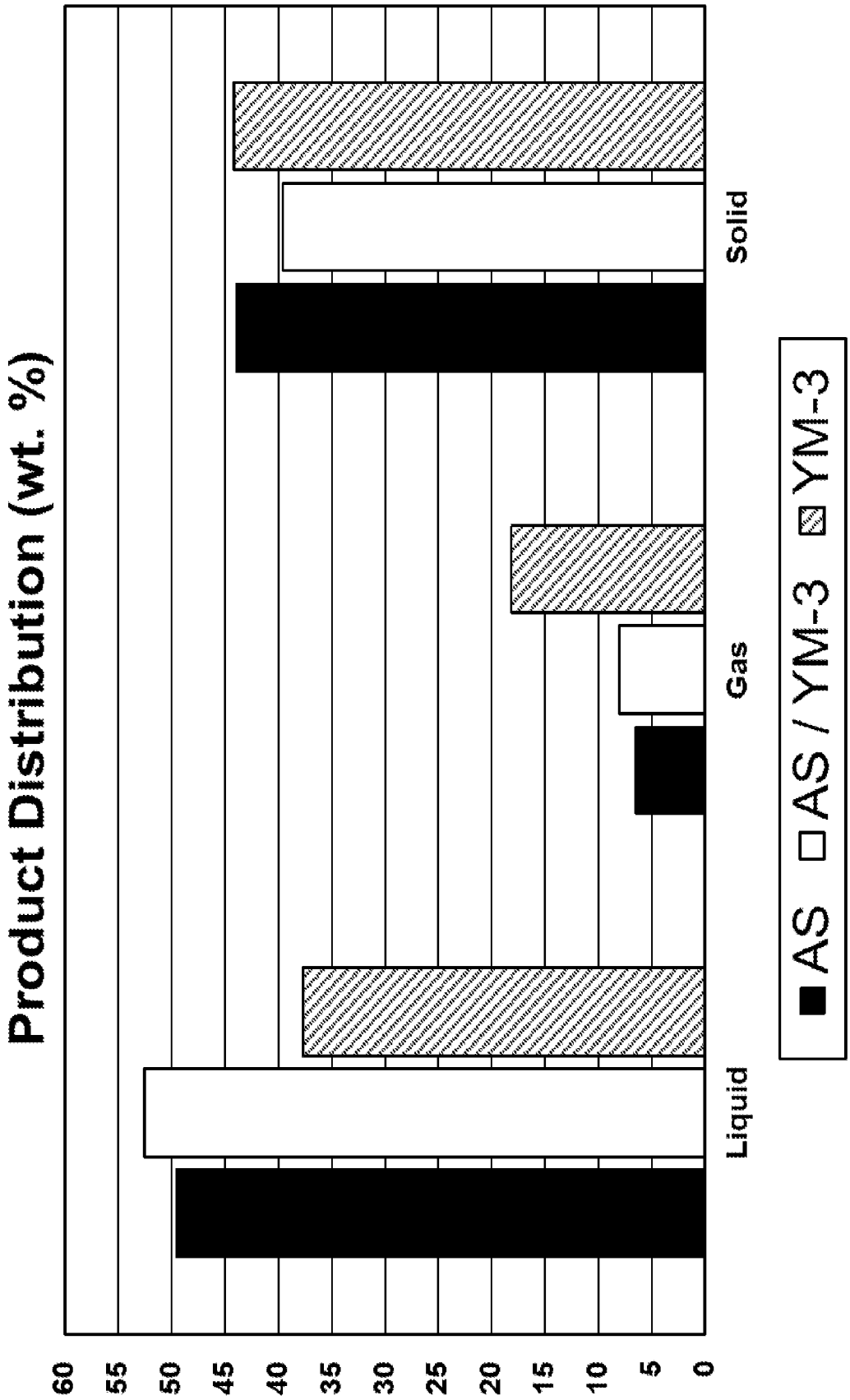
Product Distribution (wt. %)
60
55
50
45
40
35
30
25
20
15
10
5
0
Liquid
Gas
Solid
AS
AS / YM-3
YM-3

FIG. 7