



(51) International Patent Classification:

C07C 17/12 (2006.01) *C07C 25/02* (2006.01)
C07C 17/37 (2006.01) *C09K 8/34* (2006.01)

(21) International Application Number:

PCT/US2016/028310

(22) International Filing Date:

19 April 2016 (19.04.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/151,507 23 April 2015 (23.04.2015) US

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poration, 451 Florida Street, Baton Rouge, LA 70801-1765
(US).(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))*

(54) Title: PREPARATION OF MIXTURES OF BROMINATED BENZENES PREDOMINANT IN DIBROMOBENZENES AND TRIBROMOBENZENES

(57) Abstract: This invention provides a process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes. The process comprises forming and heating a reaction mixture to form an intermediate mixture, in which the catalyst is deactivated. The intermediate mixture is formed by heating the reaction mixture until a *meta*-dibromobenzene:*para*-dibromobenzene molar ratio of about 1.8: 1 or more is reached. The intermediate mixture is either i) cooled to a temperature of about 0°C or less, and the solid and liquid phases formed upon cooling are separated, or ii) monobromobenzene is removed from the intermediate mixture. The reaction mixture is formed from a Lewis acid catalyst and an aromatic substrate comprising (a) benzene and/or monobromobenzene, optionally in a mixture with partially brominated benzenes, or (b) 1,4-dibromobenzene optionally in a mixture with partially brominated benzenes; when the aromatic substrate is (a), formation of the reaction mixture includes feeding bromine into the mixture.



**PREPARATION OF MIXTURES OF BROMINATED BENZENES
PREDOMINANT IN DIBROMOBENZENES AND TRIBROMOBENZENES**

TECHNICAL FIELD

[0001] This invention relates to the preparation of mixtures of brominated benzenes predominant in dibromobenzenes and tribromobenzenes and their use.

BACKGROUND

[0002] Brominated benzenes (bromobenzenes) are useful intermediates in the preparation of aromatic compounds. Brominated organic compounds, including brominated benzenes and mixtures thereof, have been described as useful solids-free, non-aqueous wellbore fluids. See in this connection EP 247801 and EP 328279.

[0003] Methods for forming brominated benzenes are known in the art. Processes for the formation of mixtures of brominated benzenes, including mixtures of dibromobenzenes rich in the *meta* isomer, are known in the art. Such processes include isomerization of *para*-dibromobenzene; and bromination of benzene under specified conditions. See in this connection GB 886991 and U.S. 3,062,899.

[0004] A convenient way to obtain mixtures of brominated benzenes is to brominate benzene to form such mixtures. It would be useful to find processes that form mixtures of brominate benzenes with properties that are desirable for use in various applications, especially as wellbore fluids.

SUMMARY OF THE INVENTION

[0005] This invention provides mixtures of brominated benzenes, especially mixtures predominant in dibromobenzenes and tribromobenzenes, which can be obtained via processes that involve a catalyst, a brominating agent, and benzene. At least some of the mixtures of brominated benzenes provided by this invention are suitable for use as wellbore fluids and/or as components of wellbore fluids.

[0006] An embodiment of this invention is a process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes. The process comprises I) forming a liquid reaction mixture, heating at least a portion of the reaction mixture to form an intermediate mixture, deactivating the catalyst in the intermediate mixture; and II) either cooling at least a portion of the intermediate mixture

to a temperature of about 0°C or less, or removing at least a portion of the monobromobenzene from the intermediate mixture.

[0007] In these embodiments, the reaction mixture is formed from a Lewis acid catalyst and an aromatic substrate comprising (a) benzene, a mixture of benzene and partially brominated benzenes having a bromine number of about 3 or less, monobromobenzene, or a mixture of monobromobenzene and partially brominated benzenes having a bromine number of about 3 or less, by feeding bromine into the mixture, or from a Lewis acid catalyst and an aromatic substrate comprising (b) 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less. Ring-available bromine is provided in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate. When the aromatic substrate is (a), the bromine and aromatic substrate together provide ring-available bromine, and when the aromatic substrate is (b), the aromatic substrate provides ring-available bromine.

[0008] In these embodiments, the reaction mixture is heated until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed. When the aromatic substrate comprises (a), the heating is at one or more temperatures in the range of about 50°C to about 125°C, and when the aromatic substrate comprises (b), the heating is at one or more temperatures in the range of about 80°C to about 125°C.

[0009] These and other embodiments and features of this invention will be further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0010] As used throughout this document, the average bromine number is defined as the average number of bromine atoms per aromatic ring in a brominated benzene mixture. For example, the term "partially brominated benzene having a bromine number of about 3 or less" as used throughout this document means that the partially brominated benzene (mixture) contains an average of three bromine atoms or fewer as substituents on each aromatic ring.

[0011] The term "bromobenzenes" as used throughout this document means mixtures of brominated benzenes, which mixtures can include brominated benzenes having a different number of bromine atoms, and different isomers amongst those brominated benzenes

having the same number of bromine atoms. Similarly, the term "dibromobenzenes" as used throughout this document refers to mixtures of dibromobenzene isomers, and "tribromobenzenes" as used throughout this document refers to mixtures of tribromobenzene isomers.

[0012] Throughout this document, the phrase "aromatic substrate" refers to benzene, mixtures of benzene and partially brominated benzenes having a bromine number of about 3 or less, monobromobenzene, a mixture of monobromobenzene and partially brominated benzenes having a bromine number of about 3 or less, 1,4-dibromobenzene, or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less.

[0013] As used throughout this document, the term "ring-available bromine" refers to all of the bromine that is available to the aromatic rings, and includes the bromine atoms present on the aromatic rings of the 1,4-dibromobenzene and/or partially brominated benzenes (when included as part of the aromatic substrate) as well as the brominating agent fed during some of the processes of this invention. Elemental bromine provides one ring-available bromine atom per molecule of Br₂.

[0014] The term "subsurface" as used throughout this document denotes that the feed occurs below the surface of the liquid phase of the reaction mixture.

[0015] In some of the processes of this invention, benzene or a mixture of benzene and one or more partially brominated benzenes having a bromine number of about 3 or less, preferably about 2.5 or less, can be employed as the aromatic substrate. When a mixture of benzene and one or more partially brominated benzenes is used, the benzene is usually about 2 wt% or more of the mixture. Preferably, benzene is about 5 to about 75 wt%, more preferably about 20 wt% to about 40 wt%, of the aromatic substrate when benzene and one or more partially brominated benzenes are used as the aromatic substrate.

[0016] In other processes of this invention, monobromobenzene or a mixture of monobromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less, preferably about 2.5 or less, can be employed as the aromatic substrate. When a mixture of monobromobenzene and one or more partially brominated benzenes is used, the monobromobenzene is usually about 20 wt% or more of the mixture. Preferably, monobromobenzene is about 25 wt% to about 75 wt%, more preferably about 35 wt% to about 75 wt%, still more preferably about 40 wt% to about 60 wt%, of the aromatic substrate when monobromobenzene and one or more partially brominated benzenes are used as the aromatic substrate.

[0017] In other processes of this invention, 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less, preferably about 2.5 or less, can be employed as the aromatic substrate. When a mixture of 1,4-dibromobenzene and one or more partially brominated benzenes is used, the 1,4-dibromobenzene is usually about 20 wt% or more of the mixture. Preferably, 1,4-dibromobenzene is about 25 to about 90 wt%, more preferably 25 wt% to about 75 wt%, of the aromatic substrate when 1,4-dibromobenzene and one or more partially brominated benzenes are used as the aromatic substrate.

[0018] Preferred sources of partially brominated benzenes include monobromobenzene portions removed from intermediate mixtures formed in one or more processes of this invention, and portions of solid mixtures (solid at low temperature: *e.g.*, about 0°C or less) formed in one or more processes of this invention; or, more preferably, combinations thereof, which monobromobenzene portion(s) and/or solid mixture(s) (solid at *e.g.*, about 0°C or less) are recycled as at least part of the starting material.

[0019] When one or more partially brominated benzenes are part of the aromatic substrate, the aromatic substrate can be, for example, a mixture of benzene and monobromobenzene, a mixture of monobromobenzene and dibromobenzenes, or a mixture of benzene and dibromobenzenes. The one or more partially brominated benzenes can be from sources other than one or more previous processes of this invention.

[0020] Lewis acid catalysts are used in the practice of this invention. A large variety of Lewis acid catalysts can be employed in the practice of this invention provided that they have sufficient catalytic activity to provide for the desired amount of bromination. Preferred Lewis acid catalysts are iron-based catalysts, typically in the form of iron powder, FeCl₃, or FeBr₃; zirconium-containing catalysts, usually in the form of ZrCl₄ or ZrBr₄; and aluminum-based catalysts; mixtures of catalysts may also be used. Aluminum-based catalysts are preferred. When the catalyst is aluminum-based, the catalyst component as charged to the reaction mixture can be in the form of metallic aluminum such as in the form of aluminum foil, aluminum turnings, aluminum flakes, aluminum powder, or other subdivided forms of aluminum metal. Preferably, the aluminum-based catalyst component as charged to the reaction mixture can be in the form of an aluminum halide in which the halogen atoms are chlorine atoms, bromine atoms, or a combination of chlorine atoms and bromine atoms. More preferably, the aluminum-based catalyst is aluminum bromide and/or aluminum chloride. The iron-based and zirconium-containing catalysts can be used alone or in combination with one or more aluminum-based catalysts.

[0021] The aromatic substrates can act as both reagent and as solvent in the processes of this invention. A solvent is not necessary, but can be included if desired. Suitable solvents are inert organic solvents, and include halogenated hydrocarbons such as bromochloromethane, dibromomethane, dichloromethane, carbon tetrachloride, 1,2-dibromoethane, 1,2-dichloroethane, 1,1-dibromoethane, bromochloroethane, tribromomethane, tetrachloroethane, trichloroethylene, and the like. Mixtures of any two or more of the foregoing solvents may be used. The solvent or diluent can be added during the process if desired. To minimize degradation of the catalyst, the solvent preferably contains no more than 200 ppm of water, and more preferably no more than 100 ppm of water. Preferably, the process is conducted without a solvent.

[0022] Typically, the catalyst is in an amount in the range of about 1 wt% to about 10 wt% relative to the weight of the aromatic substrate. Preferably, the catalyst is in an amount of about 1 wt% to about 6 wt% relative to the weight of the aromatic substrate.

[0023] Due to the moisture sensitivity of the catalyst, the process is conducted under anhydrous conditions, up to the point where the catalyst is deactivated. As used throughout this document, "anhydrous" means that except for adventitious impurities, water is not present during, or introduced into, the processes of this invention until the *meta*-dibromobenzenes and *para*-dibromobenzenes are in a molar ratio of about 1.8:1 or more, preferably about 1.9:1 or more. To accomplish this, the processes of this invention are normally conducted under an inert atmosphere, usually argon, helium, or, preferably, nitrogen.

[0024] The aromatic substrate and the catalyst can be introduced to the reaction zone in any order or at the same time.

[0025] When the aromatic substrate is benzene or a mixture of benzene and one or more partially brominated benzenes having a bromine number of about 3 or less, or monobromobenzene or a mixture of monobromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less, a brominating agent is fed into the mixture comprising the catalyst and the aromatic substrate. The preferred brominating agent in the processes of this invention is elemental bromine, Br₂. Bromine is preferably used in liquid form, but can be used in gaseous form if desired. Although bromine is described throughout this document, it is understood that other brominating agents may be used instead.

[0026] It is preferred that the bromine used in the processes of this invention be essentially anhydrous, *i.e.*, contain about 100 ppm or less, preferably about 50 ppm or less,

of water, and contain about 100 ppm or less, preferably about 50 ppm or less, of organic impurities, *e.g.*, oil, grease, carbonyl containing hydrocarbons, and the like. Purification procedures for bromine are known; see for example U.S. Pat. No. 5,324,874.

[0027] When the aromatic substrate is 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less, a brominating agent is not used.

[0028] The molar ratio of ring-available bromine to aromatic rings in the aromatic substrate is about 1.5:1 to about 2.25:1, more preferably about 1.8:1 to 2.1:1, still more preferably about 1.9:1 to 2.1:1, even more preferably about 2:1. When benzene is the only component of the aromatic substrate, this is the molar ratio of elemental bromine to benzene. When 1,4-dibromobenzene is the aromatic substrate, and/or one or more partially brominated benzenes are part of the aromatic substrate, the molar ratio of ring-available bromine is relative to all of the aromatic rings, whether or not partially brominated (aromatic species), and is sometimes referred to herein as the "bromine to aromatic ratio." As described above, when monobromobenzene or a mixture of monobromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less are part of the aromatic substrate, and when 1,4-dibromobenzene and/or one or more partially brominated benzenes are part of the aromatic substrate, the ring-available bromine includes the bromine atoms present on their aromatic rings.

[0029] In performing processes according to this invention, it has been observed that decreasing the bromine to aromatic ratio decreases the amount of tribromobenzenes formed. Also, at lower molar ratios of ring-available bromine to aromatic rings than 1.8:1, the amount of monobromobenzene produced increases.

[0030] When the aromatic substrate is 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes, the mixture of the catalyst and the aromatic substrate is the reaction mixture. The reaction that occurs upon heating of these reaction mixtures is believed to be an isomerization of at least a portion of the 1,4-dibromobenzene in the reaction mixture to 1,3-dibromobenzene. For additional details, see GB 886991.

[0031] The reaction mixture is heated for a period of time at a temperature in the range of about 80°C to about 125°C, more preferably about 87°C to about 125°C. When a solvent is present, the maximum temperature is determined to some extent by the particular solvent used. Because the reaction mixture is liquid, when the aromatic

substrate comprises 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes, the 1,4-dibromobenzene is melted. When the aromatic substrate comprises 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes, the partially brominated benzenes are preferably combined with the 1,4-dibromobenzene before the 1,4-dibromobenzene is melted.

[0032] When the aromatic substrate is benzene or a mixture of benzene and partially brominated benzenes, or monobromobenzene or a mixture of monobromobenzene and one or more partially brominated benzenes having a bromine number of about 3 or less, the brominating agent is fed to the mixture of the catalyst and the aromatic substrate. The brominating agent is preferably fed subsurface to the mixture. This forms a reaction mixture. The reactions that occur in this type of reaction mixture include bromination of one or more sites on an aromatic ring of the aromatic substrate, and isomerization, presumably of 1,4-dibromobenzene to 1,3-dibromobenzene; the 1,4-dibromobenzene may be formed *in situ* or already present as at least part of the partially brominated benzenes, when the aromatic substrate is a mixture of benzene and partially brominated benzenes or a mixture of monobromobenzene and partially brominated benzenes.

[0033] The feed time and feed rate for bromine generally do not affect the products formed in the process. A fast feed rate may cause the reaction temperature to rise rapidly because the bromination of aromatic rings is exothermic, and cooling of the reaction mixture may be needed to maintain the desired temperature in the reaction mixture. During the feeding of the bromine to the reaction mixture, the reaction mixture is preferably maintained at a temperature of about 125°C or less, preferably in the range of about 50°C to about 125°C, more preferably about 60°C to about 110°C, still more preferably about 70°C to about 100°C.

[0034] At least part of the co-product hydrogen bromide produced by the bromination reaction is typically released from the bromination (reaction) mixture in part in the form of a vapor. It is desirable to collect the co-product hydrogen bromide such as by passing the vapors into a scrubbing system in which the hydrogen bromide is converted either to hydrobromic acid using water as the scrubbing liquid or into a bromide salt using an aqueous solution of a water-soluble inorganic base such as sodium hydroxide, potassium hydroxide, or sodium carbonate, or sodium bicarbonate as the scrubbing liquid.

[0035] The heating of the reaction mixture (of either type) continues until the molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene is about 1.8:1 or more, preferably about

1.9:1 or more; this is typically monitored via nuclear magnetic resonance (NMR) spectroscopy or gas chromatography (GC) analysis. For the aromatic substrates to which bromine is fed, achieving this ratio of *meta*-dibromobenzene to *para*-dibromobenzene usually occurs after cessation of HBr evolution from the reaction mixture. In this manner, an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, in which the *meta*-dibromobenzene and *para*-dibromobenzene are in a molar ratio of about 1.8:1 or more, preferably about 1.9:1 or more, is formed. Increasing the ratio of the *meta* isomer of dibromobenzene decreases the temperature at which solids form when the intermediate mixture or the polybrominated mixture is cooled, which is advantageous in certain applications.

[0036] Upon reaching a *meta:para* molar ratio for dibromobenzene of about 1.8:1 or more, preferably about 1.9 or more, the catalyst is deactivated, and the product is recovered. Catalyst deactivation can occur at room temperature, or preferably, at elevated temperatures, *e.g.*, about 35°C to about 55°C, preferably about 40°C to about 50°C. In a preferred method, the catalyst is deactivated by washing the intermediate mixture with a dilute aqueous acid solution, of, *e.g.*, hydrochloric acid. In another method, the catalyst is deactivated by contacting the intermediate mixture with water.

[0037] After catalyst deactivation, the product-containing organic layer (the intermediate mixture) is separated from the aqueous layer, and optionally and preferably, the intermediate mixture is then washed with water and/or an aqueous solution of a water-soluble inorganic base such as sodium hydroxide, potassium hydroxide, sodium or potassium carbonate or sodium bicarbonate. The intermediate mixture is the organic layer after washing.

[0038] In some embodiments, a polybrominated mixture is formed by removing monobromobenzene from the intermediate mixture after the catalyst deactivation, optional washing, and separation of the intermediate mixture (organic layer) from the aqueous layer. The removal of monobromobenzene is usually carried out by distillation, preferably under reduced pressure. The reduced pressures are typically about 10 torr to about 150 torr (about 1.33×10^3 to about 2.0×10^4 Pa). Reducing the monobromobenzene content to 0.5 wt% or less is preferable. For certain applications, the increased density and increased flash point attained by removal of monobromobenzene are preferred. The removed portion of the mixture contains monobromobenzene (typically about 25 wt% to about 99 wt%) and is sometimes referred to as monobromobenzene, although the removed portion

often contains 1,3-dibromobenzene, 1,4-dibromobenzene, and small or trace amounts of benzene and water.

[0039] It is preferred, after removal of monobromobenzene, to separate the polybrominated mixture of brominated benzenes into those which are solid (crystallize out) at temperatures of about 0°C or higher, preferably about -5°C or higher, more preferably about -10°C or higher, still more preferably about -15°C or higher, from those which remain in the liquid phase at these temperatures. This can be accomplished by cooling the polybrominated mixture to about 0°C or less, preferably at about -5°C or less, more preferably about -10°C or less, still more preferably at about -15°C, followed by separating the solid from the liquid at about 0°C or less, preferably about -5°C or less, more preferably about -10°C or less, still more preferably at about -15°C or less. Normally and preferably, the temperature to which the polybrominated mixture is cooled and the separation temperature are the same or nearly the same. Typical separation methods include filtration and centrifugation. The portion of the polybrominated mixture that is solid at low temperatures is referred to as the solid polybromobenzene mixture, although it is normally a liquid or slurry above 0°C. The portion of the polybrominated mixture that is liquid at low temperature is referred to as the liquid polybromobenzene mixture. The solid polybromobenzene mixture tends to contain a large amount of *para*-dibromobenzene relative to the amount of *para*-dibromobenzene in the liquid polybromobenzene mixture.

[0040] At least a portion of the monobromobenzene that was removed from the intermediate mixture and/or at least a portion of the solid polybromobenzene mixture, or preferably both, can be recycled, preferably to a process of the present invention.

[0041] In other embodiments, the intermediate mixture (which contains some monobromobenzene) is cooled to separate the brominated benzenes into those which are solid (crystallize out) at temperatures of about -5°C or higher, preferably about -10°C or higher, more preferably about -15°C or higher, from those which remain in the liquid phase at these temperatures. This can be accomplished as described above for the low temperature separation of the polybrominated mixture; temperatures and preferences therefor are the same. The portion of the intermediate mixture that is solid at low temperatures is referred to as the solid multibromobenzene mixture, although it is normally a liquid or slurry above 0°C. The portion of the intermediate mixture that is liquid at low temperature is referred to as the liquid multibromobenzene mixture. The presence of monobromobenzene makes these mixtures less dense and less viscous, which

is preferred for certain applications. If desired, at least a portion of the solid multibromobenzene mixture can be recycled, preferably to a process of the present invention.

[0042] The intermediate mixture generally contains monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (very small or trace amounts). Typically, the dibromobenzenes are predominant (about 45 wt% or more of the intermediate mixture), often 60 wt% or more of the intermediate mixture, and the monobromobenzene and tribromobenzenes form the large part of the remainder of the intermediate mixture. The monobromobenzene content of the intermediate mixture can vary from about 1 wt% or less to about 30 wt% or more of the intermediate mixture. The tribromobenzenes are usually about 3 wt% to about 50 wt% of the intermediate mixture.

[0043] The polybrominated mixture, which is also a brominated benzene composition of this invention, generally contains dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (very small or trace amounts). Typically, the dibromobenzenes are predominant (about 45 wt% or more of the mixture), and the tribromobenzenes form the large part of the remainder of the product mixture. For the dibromobenzenes, the *meta* isomer is the most abundant, and the *ortho* isomer is least abundant. For the tribromobenzenes, the 1,2,4– isomer is most abundant, with small amounts of the 1,3,5– and 1,2,3– isomers.

[0044] The polybrominated mixture usually contains about 50 wt% to about 85 wt% dibromobenzenes and about 14 wt% to about 47 wt% tribromobenzenes. Normally, there is about zero to about 4 wt% tetrabromobenzenes in the mixture. Preferably, the polybrominated mixture has about 60 wt% to about 85 wt% dibromobenzenes; and about 20 wt% to about 46 wt% tribromobenzenes.

[0045] In the polybrominated mixture, the isomer distribution for the dibromobenzenes is typically about 50% to about 80% *meta*, about 20% to about 50% *para*, and about 2.5% to about 10% of the *ortho* isomer. For the tribromobenzenes in the polybrominated mixture, the isomer distribution is typically about 85% to about 98% 1,2,4–, about 1% to about 10% 1,3,5–, and about 1% to about 5% of the 1,2,3– isomer.

[0046] After the cooling and separation of the polybrominated mixture at low temperature, the resultant solid polybromobenzene mixture usually contains dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (very small or trace amounts). Typically, the dibromobenzenes and the tribromobenzenes form the large part of the product mixture. For the dibromobenzenes, the *ortho* isomer is least abundant. For

the tribromobenzenes, the 1,2,4– isomer is usually the most abundant, with small amounts of the 1,3,5– and 1,2,3– isomers.

[0047] The solid polybromobenzene mixture, which is also a brominated benzene composition of this invention, generally contains about 50 wt% to about 95 wt% dibromobenzenes and about 5 wt% to about 40 wt% tribromobenzenes. This mixture typically contains about zero to about 15 wt% tetrabromobenzenes. Preferably, the solid polybromobenzene mixture has about 55 wt% to about 85 wt% dibromobenzenes, about 10 wt% to about 35 wt% tribromobenzenes, more preferably about 15% to about 35% tribromobenzenes, and about zero to about 12% tetrabromobenzenes.

[0048] In the solid polybromobenzene mixture, the isomer distribution for the dibromobenzenes is typically about 45% or more *para*, about 10% to about 60% *meta*, and about 0.5% to about 10% of the *ortho* isomer. Preferably, the isomer distribution for the dibromobenzenes in the solid polybromobenzene mixture is about 45% to about 75% *para*, and about 15% to about 55% *meta*. For the tribromobenzenes in this mixture, the isomer distribution is typically about 85% to about 98% 1,2,4–, about 1% to about 8% 1,3,5–, and about 1% to about 8% of the 1,2,3– isomer.

[0049] After the separation at low temperature, the resultant liquid polybromobenzene mixture, which is also a brominated benzene composition of this invention, usually contains dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (small or trace amounts). Typically, the dibromobenzenes are predominant (about 45 wt% or more of the mixture), and the tribromobenzenes form the large part of the remainder of the product mixture. For the dibromobenzenes, the *meta* isomer is most abundant, with an intermediate amount of the *para* isomer, and the *ortho* isomer is least abundant. For the tribromobenzenes, the 1,2,4– isomer is the most abundant, with small amounts of the 1,3,5– and 1,2,3– isomers.

[0050] The liquid polybromobenzene mixture generally contains about 45 wt% to about 90 wt% dibromobenzenes and about 5 wt% to about 55 wt% tribromobenzenes. Usually, this mixture also contains about zero to about 5 wt% tetrabromobenzenes. Preferably, the liquid polybromobenzene mixture has about 50 wt% to about 80 wt% dibromobenzenes, 15 wt% to about 55 wt% tribromobenzenes, and about 0.25 wt% to about 3 wt% tetrabromobenzenes. These mixtures may also contain small or trace amounts of monobromobenzene, benzene, and pentabromobenzene. Monobromobenzene is typically zero to about 1 wt% of the liquid polybromobenzene mixture; benzene is typically zero to about 0.1 wt%, preferably zero to about 0.01 wt% of the mixture; and pentabromobenzene

is generally about zero to about 0.1 wt%, preferably zero to about 0.01 wt% of the mixture.

[0051] In the liquid polybromobenzene mixture, the isomer distribution for the dibromobenzenes is typically about 55% to about 95% *meta*, about 35% or less *para*, and about 3% to about 15% of the *ortho* isomer. Preferably, the isomer distribution for the dibromobenzenes is about 65% to about 85% *meta*, about 10% to about 35% *para*, and about 5% to about 10% of the *ortho* isomer. For the tribromobenzenes in this mixture, the isomer distribution is typically about 85% to about 98% 1,2,4–, about 1% to about 12% 1,3,5–, and about 1% to about 5% of the 1,2,3– isomer. Preferably, the isomer distribution for the tribromobenzenes in this mixture is about 90% to about 97% 1,2,4–, about 1.5% to about 10% 1,3,5–, and about 1.5% to about 4% of the 1,2,3– isomer.

[0052] The polybrominated mixtures, solid polybromobenzene mixtures, and liquid polybromobenzene mixtures may also contain small or trace amounts of monobromobenzene, benzene, and/or pentabromobenzene. In the polybrominated mixture, solid polybromobenzene mixture, and liquid polybromobenzene mixture, the monobromobenzene content is about 1 wt% or less.

[0053] After the cooling and separation of an intermediate mixture at low temperature, the resultant solid multibromobenzene mixture usually contains monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (very small or trace amounts). Typically, the dibromobenzenes form the large part of the product mixture. For the dibromobenzenes, the *ortho* isomer is least abundant. For the tribromobenzenes, the 1,2,4– isomer is usually the most abundant, with small amounts of the 1,3,5– and 1,2,3– isomers.

[0054] The solid multibromobenzene mixture, which is also a brominated benzene composition of this invention, generally contains more than about 1 wt% (typically about 1 wt% to about 20 wt%) monobromobenzene, about 50 wt% to about 95 wt% dibromobenzenes and about 0.5 wt% to about 10 wt% tribromobenzenes. These mixtures generally contain about zero to about 1 wt% tetrabromobenzenes. Preferably, the solid multibromobenzene mixture has about 5 wt% to about 15 wt% monobromobenzene, about 60 wt% to about 90 wt% dibromobenzenes, and about 1 wt% to about 5 wt% tribromobenzenes. More preferably, the solid multibromobenzene mixture has about 70 wt% to about 90 wt% dibromobenzenes.

[0055] In the solid multibromobenzene mixture, the isomer distribution for the dibromobenzenes is typically about 50% or more *para*, about 40% or less *meta*, and about

0.5% to about 10% of the *ortho* isomer. Preferably, the isomer distribution for the dibromobenzenes in the solid multibromobenzene mixture is about 60% to about 90% *para*, about 5% to about 40% *meta*, more preferably about 10% to about 30% *meta*. For the tribromobenzenes in this mixture, the isomer distribution is typically about 85% to about 98% 1,2,4–, about 1% to about 8% 1,3,5–, and about 1% to about 8% of the 1,2,3– isomer.

[0056] After the separation at low temperature, the resultant liquid multibromobenzene mixture which is also a brominated benzene composition of this invention, usually contains monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes (small or trace amounts). Typically, the dibromobenzenes are predominant (about 45 wt% or more of the mixture). For the dibromobenzenes, the *meta* isomer is most abundant, with an intermediate amount of the *para* isomer, and the *ortho* isomer is least abundant. For the tribromobenzenes, the 1,2,4– isomer is the most abundant, with small amounts of the 1,3,5– and 1,2,3– isomers.

[0057] The liquid multibromobenzene mixture generally contains more than about 1 wt% monobromobenzene, about 45 wt% to about 85 wt% dibromobenzenes, about 1 wt% to about 20 wt% tribromobenzenes, The mixture typically contains about zero to about 2 wt% tetrabromobenzenes. Preferably, the liquid multibromobenzene mixture has about 10 wt% to about 40 wt% monobromobenzene, more preferably about 15 wt% to about 35 wt% monobromobenzene, about 50 wt% to about 80 wt% dibromobenzenes; and about 5 wt% to about 15 wt% tribromobenzenes. Benzene is typically zero to about 0.1 wt%, preferably zero to about 0.01 wt% of the mixture; and pentabromobenzene is generally about zero to about 0.1 wt%, preferably zero to about 0.01 wt% of the mixture.

[0058] In the liquid multibromobenzene mixture, the isomer distribution for the dibromobenzenes is typically about 60% to about 85% *meta*, about 35% or less *para*, and about 3% to about 15% of the *ortho* isomer. Preferably, the isomer distribution for the dibromobenzenes is about 60% to about 80% *meta*, about 10% to about 35% *para*, and about 4% to about 10% of the *ortho* isomer. For the tribromobenzenes in this mixture, the isomer distribution is typically about 70% to about 98% 1,2,4–, about 1% to about 15% 1,3,5–, and about 1% to about 5% of the 1,2,3– isomer. Preferably, the isomer distribution for the tribromobenzenes in this mixture is about 75% to about 95% 1,2,4–, and about 5% to about 15% of the 1,3,5– isomer.

[0059] The solid multibromobenzene mixtures and the liquid multibromobenzene mixtures may also contain small or trace amounts of benzene and/or pentabromobenzene.

[0060] Brominated benzene compositions of this invention, preferably the product mixtures that are liquid at low temperature (liquid multibromobenzene mixtures and liquid polybromobenzene mixtures), can be used as non-aqueous, solids-free wellbore fluids, alone or in combination with other substances. Examples of wellbore fluids include, but are not limited to, packer fluids, completion fluids, drill-in fluids, fracturing fluids, workover fluids, perforating fluids, gravel packing fluids, and sustained casing pressure abatement fluids (kill fluids). For wellbore fluids, densities in the range of about 7.5 pounds per gallon (ppg; 0.9 kg/L) to about 20 ppg (2.40 kg/L) are desirable, and densities in the range of about 12.5 ppg (1.50 kg/L) to about 19.5 (2.34 kg/L) ppg are preferred. Particularly preferred for use as sustained casing pressure abatement fluids are at least portions of the product mixtures that are liquid at low temperature, especially the liquid polybromobenzene mixtures, which are introduced into an annulus of a wellbore when used as at least part of a sustained casing pressure abatement fluid.

[0061] Properties of the compositions of this invention which are advantageous for wellbore fluids include high density, high stability, low corrosion, and high flash point. The liquid polybromobenzene mixtures also have low solidification temperatures. Mixtures of bromobenzenes containing both dibromobenzenes and tribromobenzenes have higher densities than mixtures of dibromobenzenes alone. If the dibromobenzenes in the mixture of dibromobenzenes and tribromobenzenes are rich in the *meta* isomer and low in the *para* isomer, the solidification temperature of the overall fluid mixture is minimized. It is recommended and preferred to minimize the amount of monobromobenzene in such mixtures to increase the density and to decrease the flash point of the overall fluid mixture. Although the mixture can contain small amounts of tetrabromobenzenes, the amount of tetrabromobenzenes is preferably minimized to reduce the solidification temperature of the overall fluid mixture.

[0062] In certain wellbore applications, it may be advantageous to blend portions of liquid polybromobenzene mixtures produced via processes of this invention after monobromobenzene removal with fluids with which they are miscible to achieve desired physical properties such as density and/or viscosity.

[0063] The processes of this invention also include introducing at least a portion of one or more intermediate mixtures, one or more polybrominated mixtures, and/or one or more liquid polybromobenzene mixtures into an annulus of a wellbore.

[0064] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention.

EXAMPLE 1

[0065] A mixture of benzene (204.4 g; 2.62 mol) and aluminum chloride (12.3 g; 6 wt% relative to benzene) was prepared under nitrogen at room temperature, and with stirring, was treated over 155 minutes with bromine (831.2 g; 5.2 mol; 2 equiv. relative to benzene). The reaction mixture reached a temperature of 49.6°C after adding the first equivalent of bromine, and reached 59.3°C after adding the second equivalent of bromine. After bromine addition was complete, the reaction mixture was heated to 90°C and stirred at that temperature for 2 hours, at which time the ratio of *meta*-dibromobenzene to *para*-dibromobenzene was 1.9:1, as determined by ¹H NMR analysis.

[0066] The reaction mixture was allowed to cool to 45°C and then transferred to 600 g of a 0.4 wt% HCl solution. After stirring for 15 minutes, the organic layer was separated and washed with 300 g of water. Via distillation, 25.7 g (0.16 mol) of monobromobenzene were removed over a 10-plate Older-Shaw column at a reduced pressure of 30 mm of Hg (4.0x10³ Pa). The stirred distillation residue was cooled to -5°C for 20 minutes and 210.6 g of precipitated solids were removed via filtration at -5°C. An orange filtrate (267.8 g) was collected, and found to have a density of about 17.0 pounds per gallon (2.04 kg/L).

[0067] Both the precipitated solids and the orange filtrate were analyzed by ¹H NMR spectroscopy. Table 1 shows the bromination product and isomer distribution for the sample after distillation to remove monobromobenzene, but before the low temperature separation; the average bromine number of this sample was 2.25. Table 1 also shows the bromination product and isomer distribution for the solids and filtrate after separation at low temperature. The orange filtrate had an average bromine number of 2.336, and the solids had an average bromine number of 2.237. Results of the ¹H NMR analyses are summarized in Table 1 below.

TABLE 1

Sample	Brominated product	Amount	Isomers and amounts
Distillation residue ¹	dibromobenzenes	72.4 wt%	62.1% 1,3-dibromobenzene 32.7% 1,4-dibromobenzene 4.95% 1,2-dibromobenzene
	tribromobenzenes	26.7 wt%	93.5% 1,2,4-tribromobenzene 4.15% 1,3,5-tribromobenzene 2.4% 1,2,3-tribromobenzene
	tetrabromobenzenes	1.0 wt%	not determined

Solids ² (at -5°C)	dibromobenzenes	77.1 wt%	50.1% 1,4-dibromobenzene 46.2% 1,3-dibromobenzene 3.7% 1,2-dibromobenzene
	tribromobenzenes	22.1 wt%	92.6% 1,2,4-tribromobenzene 4.9% 1,3,5-tribromobenzene 2.5% 1,2,3-tribromobenzene
	tetrabromobenzenes	0.8 wt%	not determined
Filtrate ³	dibromobenzenes	67.6 wt%	77.9% 1,3-dibromobenzene 15.2% 1,4-dibromobenzene 6.9% 1,2-dibromobenzene
	tribromobenzenes	31.2 wt%	94.3% 1,2,4-tribromobenzene 3.4% 1,3,5-tribromobenzene 2.3% 1,2,3-tribromobenzene
	tetrabromobenzenes	1.2 wt%	not determined

¹A polybrominated mixture (values were calculated from the results for the solids);

²a solid polybromobenzene mixture; ³a liquid polybromobenzene mixture.

EXAMPLE 2

[0068] Several runs were performed on a larger scale. In Run 1, benzene was the only aromatic compound; in Runs 2-6, partially brominated benzenes (comprised of mixtures of distillate and the portion that was solid at low temperature) from a previous run were recycled and included with benzene as the aromatic substrate.

[0069] In all of these runs, the bromine was added in two portions. The first half of the bromine charge was added over 2 hours while cooling the reactor to maintain a temperature below 50°C and while collecting the evolved HBr overhead in an aqueous scrubber. After the HBr was visually observed to have stopped off-gassing, the second half of the bromine charge was added over an additional 2 hours while cooling the reactor to maintain a temperature below 70°C and while collecting the evolved HBr overhead in an aqueous scrubber. In these reactions, the size of the HBr scrubber required the bromine addition to take place in two portions. If a large enough scrubber were available, the bromine addition could take place in one portion. After the addition of bromine was complete, the reactor was heated to 90°C and stirred at that temperature until the ratio of *meta*-dibromobenzene to *para*-dibromobenzene was at least 1.9:1 as determined by ¹H NMR or GC analysis (usually at least 2 hours). Specific conditions and reagent amounts are summarized for each run in Table 2.

[0070] Once a 1.9:1 *meta:para* molar ratio for dibromobenzene was reached, the reaction mixture was cooled to 50°C and then transferred into an HCl solution (aq., 0.4 wt%). After stirring for 30 minutes at 50°C and allowing the solution to separate, the organic layer was removed and washed with a dilute sodium bicarbonate solution (aq., ~0.5 wt%). Most of the monobromobenzene was removed via distillation under vacuum. The distillate contained monobromobenzene (ranging from 26.3 wt% to 58.6 wt%); the majority of the remaining components were 1,3-dibromobenzene and 1,4-dibromobenzene. The distillation residue was cooled over 2 hours to -5°C, kept at that temperature for 30 minutes, and filtered at -5°C to remove precipitated solids. Results of ¹H NMR analyses on the distillation residue, the mixture that was solid at -5°C, and the orange-to-brown colored filtrate (liquid polybromobenzene mixture) for the runs are summarized in Tables 3A-3C.

TABLE 2

Run	1	2	3
AlCl ₃	498 g	501 g	501 g
Benzene	7.82 kg	4.665 kg	3.831 kg
Recycled aromatic distillate	0	2.641 kg	4.285 kg
Recycled solids	0	7.382 kg	7.354 kg
Br ₂	33.12 kg	18.20 kg	15.36 kg
bromine:aromatic molar ratio	2.07:1	1.95:1	1.88:1
Br ₂ feed rate	7.5 kg/hr	6.2 kg/hr	5.5 kg/hr
Distillation pressure	16 torr (2.13x10 ³ Pa)	16 torr (2.13x10 ³ Pa)	38 torr (5.07x10 ³ Pa)
Filtrate density*	17.37 ppg (2.08 kg/L)	17.02 ppg (2.04 kg/L)	16.78 ppg (2.01 kg/L)
Run	4	5	6
AlCl ₃	555 g	201 g	309 g
Benzene	5.58 kg	3.999 kg	4.40 kg
Recycled aromatic distillate	4.246 kg	4.469 kg	3.211 kg
Recycled solids	5.047 kg	7.631 kg	7.756 kg
Br ₂	25.08 kg	17.70 kg	17.53 kg

bromine:aromatic molar ratio	2.00:1	1.99:1	1.90:1
Br ₂ feed rate	6.4 kg/hr	4.1 kg/hr	4.5 kg/hr
Distillation pressure	17 torr (2.26x10 ³ Pa)	40 torr (5.33x10 ³ Pa)	100 torr (1.33x10 ⁴ Pa)
Filtrate density *	17.07 ppg (2.05 kg/L)	17.00 ppg (2.04 kg/L)	16.95 ppg (2.03 kg/L)

* The abbreviation "ppg" stands for pounds per gallon.

TABLE 3A

Distillation bottoms (polybrominated mixture)			
Run	1	2	3
dibromobenzenes	66.82 wt% 62.68% <i>meta</i> 32.12% <i>para</i> 5.20% <i>ortho</i>	78.60 wt% 62.48% <i>meta</i> 32.40% <i>para</i> 5.12% <i>ortho</i>	84.40 wt% 62.34% <i>meta</i> 32.37% <i>para</i> 5.29% <i>ortho</i>
tribromobenzenes	31.70 wt% 94.16% 1,2,4- 2.03% 1,2,3- 3.81% 1,3,5-	20.46 wt% 92.13% 1,2,4- 2.02% 1,2,3- 5.85% 1,3,5-	14.97 wt% 92.69% 1,2,4- 1.81% 1,2,3- 5.50% 1,3,5-
tetrabromobenzenes	1.43 wt%	0.54 wt%	0.27 wt%
monobromobenzene	0.05 wt%	0.40 wt%	0.36 wt%
Run	4	5	6
dibromobenzenes	75.79 wt% 62.34% <i>meta</i> 32.37% <i>para</i> 5.29% <i>ortho</i>	74.88 wt% 62.06% <i>meta</i> 31.50% <i>para</i> 6.57% <i>ortho</i>	79.77 wt% 62.06% <i>meta</i> 31.74% <i>para</i> 6.20% <i>ortho</i>
tribromobenzenes	23.32 wt% 90.82% 1,2,4- 1.84% 1,2,3- 7.33% 1,3,5-	23.77 wt% 91.22% 1,2,4- 2.84% 1,2,3- 5.94% 1,3,5-	19.68 wt% 90.05% 1,2,4- 3.54% 1,2,3- 6.41% 1,3,5-
tetrabromobenzenes	0.67 wt%	0.69 wt%	0.41 wt%
monobromobenzene	0.22 wt%	0.67 wt%	0.14 wt%

TABLE 3B

Solids (at -5°C)	(solid polybromobenzene mixture)		
Run	1	2	3
dibromobenzenes	74.94 wt% 42.28% <i>meta</i> 54.09% <i>para</i> 3.63% <i>ortho</i>	88.57 wt% 29.30% <i>meta</i> 68.54% <i>para</i> 2.16% <i>ortho</i>	92.55 wt% 25.52% <i>meta</i> 72.39% <i>para</i> 2.08% <i>ortho</i>
tribromobenzenes	24.01 wt% 95.25% 1,2,4- 2.18% 1,2,3- 2.56% 1,3,5-	11.08 wt% 90.35% 1,2,4- 1.82% 1,2,3- 7.83% 1,3,5-	7.33 wt% 88.09% 1,2,4- 2.35% 1,2,3- 9.56% 1,3,5-
tetrabromobenzenes	1.01 wt%	0.24 wt%	0.12 wt%
monobromobenzene	0.04 wt%	0.11 wt%	0.00
Run	4	5	6
dibromobenzenes	90.29 wt% 20.06% <i>meta</i> 78.00% <i>para</i> 1.94% <i>ortho</i>	83.33 wt% 37.19% <i>meta</i> 59.06% <i>para</i> 3.75% <i>ortho</i>	87.13 wt% 35.00% <i>meta</i> 61.50% <i>para</i> 3.50% <i>ortho</i>
tribromobenzenes	9.47 wt% 92.50% 1,2,4- 2.01% 1,2,3- 5.49% 1,3,5-	15.76 wt% 90.47% 1,2,4- 2.88% 1,2,3- 6.65% 1,3,5-	12.41 wt% 91.36% 1,2,4- 3.31% 1,2,3- 5.34% 1,3,5-
tetrabromobenzenes	0.24 wt%	0.44 wt%	0.26 wt%
monobromobenzene	0.00	0.46 wt%	0.19 wt%

TABLE 3C

Filtrate (liquid polybromobenzene mixture)			
Run	1	2	3
dibromobenzenes	61.73 wt% 78.06% <i>meta</i> 15.66% <i>para</i> 6.28% <i>ortho</i>	74.98 wt% 78.48% <i>meta</i> 14.46% <i>para</i> 7.06% <i>ortho</i>	80.42 wt% 79.13% <i>meta</i> 14.25% <i>para</i> 6.62% <i>ortho</i>
tribromobenzenes	36.57 wt% 93.33% 1,2,4- 2.50% 1,2,3- 4.17% 1,3,5-	24.00 wt% 92.53% 1,2,4- 2.00% 1,2,3- 5.47% 1,3,5-	18.81 wt% 90.41% 1,2,4- 2.51% 1,2,3- 7.09% 1,3,5-
tetrabromobenzenes	1.61 wt%	0.59 wt%	0.35 wt%
monobromobenzene	0.09 wt%	0.43 wt%	0.42 wt%
Run	4	5	6
dibromobenzenes	71.95 wt% 77.83% <i>meta</i> 15.09% <i>para</i> 7.07% <i>ortho</i>	71.44 wt% 77.39% <i>meta</i> 14.71% <i>para</i> 7.91% <i>ortho</i>	76.23 wt% 77.66% <i>meta</i> 14.76% <i>para</i> 7.57% <i>ortho</i>
tribromobenzenes	27.00 wt% 92.04% 1,2,4- 2.44% 1,2,3- 5.52% 1,3,5-	26.89 wt% 90.47% 1,2,4- 3.10% 1,2,3- 6.43% 1,3,5-	23.15 wt% 91.54% 1,2,4- 2.99% 1,2,3- 5.46% 1,3,5-
tetrabromobenzenes	0.83 wt%	0.82 wt%	0.5 wt%
monobromobenzene	0.22 wt%	0.84 wt%	0.12 wt%

EXAMPLE 3

[0071] Two runs were performed using 1,4-dibromobenzene as the starting material. In Run A, 1,4-dibromobenzene was the only aromatic compound; in Run B, partially brominated benzenes (comprised of mixtures of distillate and the portion that was solid at low temperature) from Run A were recycled and included with the 1,4-dibromobenzene as the aromatic substrate.

[0072] In Run A, 1,4-dibromobenzene and aluminum chloride were added to a flask, and the flask was heated under nitrogen to melt the 1,4-dibromobenzene. In Run B, 1,4-dibromobenzene, aluminum chloride, and recycled partially brominated benzenes were added to a flask, and the flask was heated under nitrogen to melt the 1,4-dibromobenzene. After the melting was complete, the reactor was heated to 90°C and stirred at that

temperature until the ratio of *meta*-dibromobenzene to *para*-dibromobenzene was at least 1.9:1 as determined by ^1H NMR or GC analysis.

[0073] From this point, the procedure is the same as described in Example 2 (catalyst deactivation, washes, distillation, and separation of solids and liquids at -5°C). Reaction parameters and results, including ^1H NMR analyses on the filtrate of each run, are summarized in Table 4.

TABLE 4

Run		A	B
AlCl_3		493 g	480 g
1,4-dibromobenzene		23.6 kg	15.98 kg
Recycled distillate		0	1.895 kg
Recycled solids		0	4.13 kg
bromine:aromatic molar ratio		2.00:1	1.99:1
Distillation pressure		16 torr (2.13×10^3 Pa)	16 torr (2.13×10^3 Pa)
Filtrate density ¹		17.01 ppg (2.04 kg/L)	16.88 ppg (2.02 kg/L)
Distillation bottoms ²	dibromobenzenes	76.63 wt% 62.06% <i>meta</i> 31.55% <i>para</i> 6.40% <i>ortho</i>	78.42 wt% 62.06% <i>meta</i> 26.32% <i>para</i> 5.21% <i>ortho</i>
	tribromobenzenes	22.66 wt% 92.13% 1,2,4- 3.07% 1,2,3- 4.80% 1,3,5-	21.07 wt% 93.22% 1,2,4- 1.81% 1,2,3- 4.97% 1,3,5-
	tetrabromobenzenes	0.55 wt%	0.40 wt%
	monobromobenzene	0.16 wt%	0.11 wt%
Solids (at -5°C) ³	dibromobenzenes	90.02 wt% 21.50% <i>meta</i> 76.36% <i>para</i> 2.13% <i>ortho</i>	92.32 wt% 19.78% <i>meta</i> 78.77% <i>para</i> 1.45% <i>ortho</i>
	tribromobenzenes	9.75 wt% 90.56% 1,2,4- 4.36% 1,2,3- 5.08% 1,3,5-	7.55 wt% 94.37% 1,2,4- 2.95% 1,2,3- 2.68% 1,3,5-
	tetrabromobenzenes	0.23 wt%	0.13 wt%
	monobromobenzene	0.00	0.00

Filtrate ⁴	dibromobenzenes	72.77 wt% 76.50% <i>meta</i> 15.58% <i>para</i> 7.92% <i>ortho</i>	76.56 wt% 78.58% <i>meta</i> 14.94% <i>para</i> 6.48% <i>ortho</i>
	tribromobenzenes	26.39 wt% 91.54% 1,2,4- 2.99% 1,2,3-5.46% 1,3,5-	22.84 wt% 91.54% 1,2,4- 2.99% 1,2,3-5.46% 1,3,5-
	tetrabromobenzenes	0.68 wt%	0.49 wt%
	monobromobenzene	0.16 wt%	0.12 wt%

¹The abbreviation "ppg" stands for pounds per gallon; ²a polybrominated mixture;

³a solid polybromobenzene mixture; ⁴a liquid polybromobenzene mixture.

EXAMPLE 4

[0074] A mixture of benzene (49.96 g; 0.64 mol) and aluminum chloride (2.4 g; 4.8 wt% relative to benzene) was prepared under nitrogen at room temperature, and with stirring, was treated over 1 hour with bromine (153.4 g; 0.96 mol; 1.5 equiv. relative to benzene). The reaction temperature increased from 16°C to 45°C during the bromine addition. After the bromine addition was complete, the reactor was heated to 90°C and stirred at that temperature for 2 hours, at which time the ratio of *meta*-dibromobenzene to *para*-dibromobenzene was 2.03 to 1 as determined by ¹H NMR analysis.

[0075] The reaction mixture was cooled to 50°C and then transferred to 125 g of an aqueous HCl solution (0.4 wt%). After stirring for 10 minutes, the organic layer was separated and then washed with 125 g of an aqueous sodium hydroxide solution (0.5 wt%). The reaction mixture was cooled over 48 minutes to −5°C, kept at that temperature for 20 minutes, and 16.13 g of tan solids were removed via filtration at −5°C. An orange-colored filtrate (110.62 g) was collected, and had a density of 14.92 ppg (1.79 kg/L). The mixture that was solid at −5°C and the filtrate were analyzed by ¹H NMR spectroscopy. Results of the ¹H NMR analyses are summarized in Table 5 below.

TABLE 5

Sample	Solids ¹ (at -5°C)	Filtrate ²
dibromobenzenes	88.84 wt% 18.13% <i>meta</i> 80.58% <i>para</i> 1.28% <i>ortho</i>	62.98 wt% 73.02% <i>meta</i> 21.07% <i>para</i> 5.91% <i>ortho</i>
tribromobenzenes	1.98 wt% 88.38% 1,2,4- 5.05% 1,2,3- 6.57% 1,3,5-	8 wt% 86.63% 1,2,4- 3.00% 1,2,3- 10.38% 1,3,5-
tetrabromobenzenes	< 0.1 wt%	< 0.1 wt%
monobromobenzene	9.23 wt%	28.54 wt%
benzene	< 0.1 wt%	0.38 wt%

¹A solid multibromobenzene mixture; ²a liquid multibromobenzene mixture.

EXAMPLE 5

[0076] A mixture of benzene (49.99 g; 0.64 mol) and aluminum chloride (3.246 g; 6.3 wt% relative to benzene) was prepared under nitrogen at room temperature, and with stirring, was treated over 83 minutes with bromine (225.0 g; 1.41 mol; 2.2 equiv. relative to benzene). The reaction temperature increased from 23°C to 59°C during the bromine addition. After the bromine addition was complete, the reactor was heated to 90°C and stirred at that temperature for 2 hours, at which time the ratio of *meta*-dibromobenzene to *para*-dibromobenzene was 1.998 to 1 as determined by ¹H NMR analysis.

[0077] The reaction mixture was cooled to 50°C and then transferred to 170 g of an aqueous HCl solution (0.4 wt%). After stirring for 10 minutes, the organic layer was separated and then washed with 170 g of an aqueous sodium bicarbonate solution (0.5 wt%). Most of the monobromobenzene was removed by distillation over a 5 inch (12.7 cm) Vigreux column at a reduced pressure of 30 mm of Hg (4.0x10³ Pa). The monobromobenzene content was reduced from 1.33 wt% to 0.14 wt% via the distillation; 5.15 g of distillate were collected. The distillation bottoms mixture was cooled over 36 minutes to 0°C, kept at that temperature or slightly below that temperature for 50 minutes, and 24.12 g of light tan solids were removed via filtration at 0°C. An orange-colored filtrate (105.83 g) was collected, and had a density of 17.82 ppg (2.14 kg/L). The

distillation bottoms, the mixture that was solid at 0°C, and the filtrate were analyzed by ¹H NMR spectroscopy. Results of the ¹H NMR analyses are summarized in Table 6 below.

TABLE 6

Sample	Distillation bottoms ¹	Solids ² (at 0°C)	Filtrate ³
dibromobenzenes	50.02 wt% 61.88% <i>meta</i> 32.55% <i>para</i> 5.58% <i>ortho</i>	54.18 wt% 36.16% <i>meta</i> 60.61% <i>para</i> 3.23% <i>ortho</i>	49.08 wt% 68.34% <i>meta</i> 25.55% <i>para</i> 6.11% <i>ortho</i>
tribromobenzenes	45.87 wt% 92.15% 1,2,4- 2.44% 1,2,3- 5.41% 1,3,5-	34.38 wt% 92.35% 1,2,4- 2.71% 1,2,3- 4.94% 1,3,5-	48.53 wt% 91.98% 1,2,4- 2.78% 1,2,3- 5.23% 1,3,5-
tetrabromobenzenes	3.96 wt%	11.38 wt%	2.29 wt%
monobromobenzene	0.14 wt%	< 0.1 wt%	0.11 wt%
benzene	< 0.1 wt%	< 0.1 wt%	< 0.1 wt%

¹A polybrominated mixture; ²a solid polybromobenzene mixture; ³a liquid polybromobenzene mixture.

EXAMPLE 6

[0078] A mixture of monobromobenzene (108.18 g; 0.689 mol) and aluminum bromide (2.68 g; 2.5 wt% relative to monobromobenzene) was prepared under nitrogen with stirring. Bromine (99.4 g; 0.619 mol) was added over 158 minutes while the temperature of the mixture was maintained between 49 and 55°C. After the bromine addition was complete, an additional amount of aluminum bromide (2.72 g; 2.5 wt% relative to monobromobenzene) was added to the reaction mixture, which was then stirred for an additional 20 minutes at 50°C.

[0079] The reaction mixture was cooled to ambient temperature before being transferred to 51 g of an aqueous solution of sulfuric acid (0.12 wt%). After stirring for 10 minutes, the organic layer was separated and then washed four times with water, using a total of 236 g of water. The washed mixture (intermediate mixture) was analyzed by ¹H NMR spectroscopy and found to consist of 75.2 wt% dibromobenzenes (55.8% *meta*, 39.0% *para*, 5.2% *ortho*), 9.46 wt% tribromobenzenes (96.6% 1,2,4-; 1.27% 1,2,3-; 2.11% 1,3,5-), 2.37 wt% tetrabromobenzene, and 12.75 wt% monobromobenzene.

[0080] Further embodiments of this invention include, without limitation:

[0081] AA) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a mixture from a Lewis acid catalyst and an aromatic substrate comprising benzene or a mixture of benzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the bromine and aromatic substrate together provide ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate,
- ii) feeding bromine into the mixture, to form a liquid reaction mixture;
- iii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 50°C to about 125°C,
- iv) deactivating the catalyst in the intermediate mixture; and
- v) cooling at least a portion of the intermediate mixture to a temperature of about 0°C or less, forming a solid multibromobenzene mixture and a liquid multibromobenzene mixture, and separating the solid multibromobenzene mixture from the liquid multibromobenzene mixture.

[0082] BB) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a mixture from a Lewis acid catalyst and an aromatic substrate comprising benzene or a mixture of benzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the bromine and aromatic substrate together provide ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate,
- ii) feeding bromine into the mixture, to form a liquid reaction mixture;
- iii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 50°C to about 125°C,
- iv) deactivating the catalyst in the intermediate mixture; and

- v) removing at least a portion of the monobromobenzene from the intermediate mixture to form a polybrominated mixture.

[0083] CC) A process as in BB) which further comprises cooling at least a portion of the polybrominated mixture to a temperature of about 0°C or less, which forms a solid polybromobenzene mixture and a liquid polybromobenzene mixture, and separating the solid polybromobenzene mixture from the liquid polybromobenzene mixture.

[0084] DD) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a mixture from a Lewis acid catalyst and an aromatic substrate comprising monobromobenzene or a mixture of monobromobenzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the bromine and aromatic substrate together provide ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate,
- ii) feeding bromine into the mixture, to form a liquid reaction mixture;
- iii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 50°C to about 125°C,
- iv) deactivating the catalyst in the intermediate mixture; and
- v) cooling at least a portion of the intermediate mixture to a temperature of about 0°C or less, forming a solid multibromobenzene mixture and a liquid multibromobenzene mixture, and separating the solid multibromobenzene mixture from the liquid multibromobenzene mixture.

[0085] EE) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a mixture from a Lewis acid catalyst and an aromatic substrate comprising monobromobenzene or a mixture of monobromobenzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the bromine and aromatic substrate together provide ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate,

- ii) feeding bromine into the mixture, to form a liquid reaction mixture;
- iii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 50°C to about 125°C,
- iv) deactivating the catalyst in the intermediate mixture; and
- v) removing at least a portion of the monobromobenzene from the intermediate mixture to form a polybrominated mixture.

[0086] FF) A process as in EE) which further comprises cooling at least a portion of the polybrominated mixture to a temperature of about 0°C or less, which forms a solid polybromobenzene mixture and a liquid polybromobenzene mixture, and separating the solid polybromobenzene mixture from the liquid polybromobenzene mixture.

[0087] GG) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a liquid reaction mixture from a Lewis acid catalyst and an aromatic substrate comprising 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the aromatic substrate provides ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate;
- ii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 80°C to about 125°C;
- iii) deactivating the catalyst in the intermediate mixture; and
- iv) cooling at least a portion of the intermediate mixture to a temperature of about 0°C or less, forming a solid multibromobenzene mixture and a liquid multibromobenzene mixture, and separating the solid multibromobenzene mixture from the liquid multibromobenzene mixture.

[0088] HH) A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises

- i) forming a liquid reaction mixture from a Lewis acid catalyst and an aromatic substrate comprising 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the aromatic substrate provides ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate;
- ii) heating at least a portion of the reaction mixture formed in ii) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein the heating is at one or more temperatures in the range of about 80°C to about 125°C;
- iii) deactivating the catalyst in the intermediate mixture;
- iv) removing at least a portion of the monobromobenzene from the intermediate mixture to form a polybrominated mixture.

[0089] JJ) A process as in HH) which further comprises cooling at least a portion of the polybrominated mixture to a temperature of about 0°C or less, which forms a solid polybromobenzene mixture and a liquid polybromobenzene mixture, and separating the solid polybromobenzene mixture from the liquid polybromobenzene mixture.

[0090] KK) A brominated benzene composition which is solid at about 0°C or less, the composition comprising about 50 wt% to about 95 wt% dibromobenzenes, about 0.5 wt% to about 10 wt% tribromobenzenes, further comprising about zero to about 1 wt% tetrabromobenzenes and/or about 1 wt% to about 20 wt% monobromobenzene.

[0091] LL) A composition as in KK) wherein the dibromobenzenes have an isomer distribution comprised of about 50% or more of *para*-dibromobenzene.

[0092] MM) A brominated benzene composition which is liquid at about 0°C or less, the composition comprising about 45 wt% to about 85 wt% dibromobenzenes, about 1 wt% to about 20 wt% tribromobenzenes, further comprising about zero to about 2 wt% tetrabromobenzenes and/or about 10 wt% to about 40 wt% monobromobenzene.

[0093] NN) A composition as in MM) wherein the dibromobenzenes have an isomer distribution comprised of about 35% or less of *para*-dibromobenzene.

[0094] PP) A brominated benzene composition which comprises about 50 wt% to about 85 wt% dibromobenzenes, about 14 wt% to about 47 wt% tribromobenzenes, and about zero to about 4 wt% tetrabromobenzenes.

[0095] QQ) A brominated benzene composition which is solid at about 0°C or less, the composition comprising about 50 wt% to about 95 wt% dibromobenzenes, about 5 wt% to about 47 wt% tribromobenzenes, and about zero to about 15 wt% tetrabromobenzenes.

[0096] RR) A composition as in QQ) wherein the dibromobenzenes have an isomer distribution comprised of about 45% or more of *para*-dibromobenzene.

[0097] SS) A brominated benzene composition which is liquid at about 0°C or less, the composition comprising about 45 wt% to about 90 wt% dibromobenzenes, about 5 wt% to about 55 wt% tribromobenzenes, and about zero to about 5 wt% tetrabromobenzenes.

[0098] TT) A composition as in SS) wherein the dibromobenzenes have an isomer distribution comprised of which about 35% or less of *para*-dibromobenzene.

[0099] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

[0100] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0101] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real

world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0102] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0103] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A process for preparing a mixture of brominated benzenes predominant in dibromobenzenes and tribromobenzenes, which process comprises
 - I) A) i) forming a mixture from a Lewis acid catalyst and an aromatic substrate comprising (a) benzene, a mixture of benzene and partially brominated benzenes having a bromine number of about 3 or less, monobromobenzene, or a mixture of monobromobenzene and partially brominated benzenes having a bromine number of about 3 or less,
 - ii) feeding bromine into the mixture, to form a liquid reaction mixture, wherein the bromine and aromatic substrate together provide ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate;
 - or
 - B) forming a liquid reaction mixture from a Lewis acid catalyst and an aromatic substrate comprising (b) 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less, wherein the aromatic substrate provides ring-available bromine in an amount of about 1.5 to about 2.25 moles per mole of aromatic rings present in the aromatic substrate;
 - and
 - C) i) heating at least a portion of the reaction mixture formed in I) until an intermediate mixture comprising monobromobenzene, dibromobenzenes, tribromobenzenes, and tetrabromobenzenes, and having a molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene of about 1.8:1 or more is formed, wherein when the aromatic substrate comprises (a), said heating is at one or more temperatures in the range of about 50°C to about 125°C, and when the aromatic substrate comprises (b), said heating is at one or more temperatures in the range of about 80°C to about 125°C, and
 - ii) deactivating the catalyst in the intermediate mixture; and
 - II) A) cooling at least a portion of the intermediate mixture to a temperature of about 0°C or less, forming a solid multibromobenzene mixture and a liquid

multibromobenzene mixture, and separating the solid multibromobenzene mixture from the liquid multibromobenzene mixture; or

B) removing at least a portion of the monobromobenzene from the intermediate mixture to form a polybrominated mixture.

2. A process as in Claim 1 which further comprises cooling at least a portion of the polybrominated mixture formed in II) B) to a temperature of about 0°C or less, which forms a solid polybromobenzene mixture and a liquid polybromobenzene mixture, and separating the solid polybromobenzene mixture from the liquid polybromobenzene mixture.

3. A process as in Claim 1 wherein in II) A) the temperature is about -5°C or less.

4. A process as in Claim 2 wherein the temperature is about -5°C or less.

5. A process as in Claim 1 wherein the Lewis acid catalyst is an iron-based catalyst, a zirconium-containing catalyst, and/or an aluminum-based catalyst.

6. A process as in any of Claims 1-5 wherein the Lewis acid catalyst is metallic aluminum or an aluminum halide having halogen atoms which are chlorine atoms, bromine atoms, or a combination of chlorine atoms and bromine atoms.

7. A process as in any of Claims 1-5 wherein the Lewis acid catalyst is aluminum bromide and/or aluminum chloride.

8. A process as in any of Claims 1-5 wherein in I), the ring-available bromine is in an amount of about 1.9 to about 2.1 moles per mole of aromatic rings.

9. A process as in any of Claims 1-5 wherein in I), the aromatic substrate comprises benzene or a mixture of benzene and partially brominated benzenes having a bromine number of about 3 or less, and the one or more temperatures in C) are in the range of about 60°C to about 110°C.

10. A process as in any of Claims 1-5 wherein in I), the aromatic substrate comprises monobromobenzene or a mixture of monobromobenzene and partially

brominated benzenes having a bromine number of about 3 or less, and the one or more temperatures in C) are in the range of about 60°C to about 110°C.

11. A process as in any of Claims 1-5 wherein in I), the aromatic substrate comprises 1,4-dibromobenzene or a mixture of 1,4-dibromobenzene and partially brominated benzenes having a bromine number of about 3 or less, and the one or more temperatures in C) are in the range of about 87°C to about 125°C.

12. A process as in any of Claims 1-5 wherein in I) C), the molar ratio of *meta*-dibromobenzene to *para*-dibromobenzene is about 1.9:1 or more.

13. A process as in any of Claims 1-5 wherein a solvent is included.

14. A process as in Claim 1 wherein at least a portion of the monobromobenzene removed from the intermediate mixture in II) B) is recycled to I).

15. A process as in Claim 1 wherein at least a portion of the solid multibromobenzene mixture separated from the liquid multibromobenzene mixture is recycled to I).

16. A process as in Claim 2 wherein at least a portion of the solid polybromobenzene mixture separated from the liquid polybromobenzene mixture is recycled to I).

17. A process as in Claim 1 wherein the solid multibromobenzene mixture comprises about 50 wt% to about 95 wt% dibromobenzenes and about 0.5 wt% to about 10 wt% tribromobenzenes.

18. A process as in Claim 1 wherein the liquid multibromobenzene mixture comprises about 45 wt% to about 85 wt% dibromobenzenes and about 1 wt% to about 20 wt% tribromobenzenes.

19. A process as in Claim 1 wherein the polybrominated mixture comprises about 50 wt% to about 85 wt% dibromobenzenes and about 14 wt% to about 47 wt% tribromobenzenes.

20. A process as in Claim 2 wherein the solid polybromobenzene mixture comprises about 50 wt% to about 95 wt% dibromobenzenes and about 5 wt% to about 40 wt% tribromobenzenes.

21. A process as in Claim 2 wherein the liquid polybromobenzene mixture comprises about 45 wt% to about 90 wt% dibromobenzenes and about 15 wt% to about 55 wt% tribromobenzenes.

22. A process as in any of Claims 18, 19, or 21 further comprising introducing at least a portion of the liquid multibromobenzene mixture, polybrominated mixture, or liquid polybromobenzene mixture into an annulus of a wellbore.

23. A brominated benzene composition which is solid at about 0°C or less, the composition comprising about 50 wt% to about 95 wt% dibromobenzenes and about 0.5 wt% to about 10 wt% tribromobenzenes.

24. A brominated benzene composition which is liquid at about 0°C or less, the composition comprising about 45 wt% to about 85 wt% dibromobenzenes and about 1 wt% to about 20 wt% tribromobenzenes.

25. A brominated benzene composition which comprises about 50 wt% to about 85 wt% dibromobenzenes and about 14 wt% to about 47 wt% tribromobenzenes.

26. A brominated benzene composition which is solid at about 0°C or less, the composition comprising about 50 wt% to about 95 wt% dibromobenzenes and about 5 wt% to about 47 wt% tribromobenzenes.

27. A brominated benzene composition which is liquid at about 0°C or less, the composition comprising about 45 wt% to about 90 wt% dibromobenzenes and about 5 wt% to about 55 wt% tribromobenzenes.

28. A wellbore fluid comprising a composition as in Claim 24 or 25 wherein the wellbore fluid is a packer fluid, completion fluid, drill-in fluid, fracturing fluid, workover fluid, perforating fluid, gravel packing fluid, or a sustained casing pressure abatement fluid.

29. A wellbore fluid comprising a composition as in Claim 27, wherein the wellbore fluid is a packer fluid, completion fluid, drill-in fluid, fracturing fluid, workover fluid, perforating fluid, gravel packing fluid, or a sustained casing pressure abatement fluid.

30. A wellbore fluid as in Claim 29 wherein the wellbore fluid is a sustained casing pressure abatement fluid.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/028310

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/12 C07C17/37 C07C25/02 C09K8/34
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C09K

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A-J LEROY M: "Sur les benzines bromées", BULLETIN DE LA SOCIÉTÉ CHIMIQUE DE PARIS : COMPRENANT LE PROCÈS-VERBAL DES SÉANCES, LES MÉMOIRES PRÉS. À LA SOC., L'ANALYSE DES TRAVAUX DE CHIMIE PURE ET APPLIQUÉE PUBL. EN FRANCE ET À L'ÉTRANGER - SERIE 3, SOCIÉTÉ CHIMIQUE, FRANCE, vol. 2, 1 January 1887 (1887-01-01), pages 210-216, XP008181374, ISSN: 0991-6504 the whole document	1-21, 23-27
X	US 3 062 899 A (SAX KARL J) 6 November 1962 (1962-11-06) cited in the application claims; examples ----- -/-	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 August 2016

Date of mailing of the international search report

07/09/2016

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Zervas, Brigitte

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/028310

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 247 801 A2 (BRITISH PETROLEUM CO PLC [GB]) 2 December 1987 (1987-12-02) cited in the application claims; examples -----	22,28-30
X,P	WO 2015/100004 A1 (ALBEMARLE CORP [US]) 2 July 2015 (2015-07-02) page 13, line 9 - line 13; claims; example 8; table 8 -----	23-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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