(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
02 December 2021 (02.12.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/237342 A1

(51) International Patent Classification:
C08J 11/04 (2006.01) *B29B 17/00* (2006.01)
A62D 3/40 (2007.01) *C07B 63/02* (2006.01)
B01D 53/68 (2006.01) *C08J 11/12* (2006.01)
B09B 3/00 (2006.01)

(21) International Application Number:
PCT/CA2021/050700

(22) International Filing Date:
25 May 2021 (25.05.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/029,693 25 May 2020 (25.05.2020) US

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(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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).

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) Title: PROCESS FOR RECYCLING CONTAMINATED SOLID MATERIALS AND PURIFICATION OF GASES

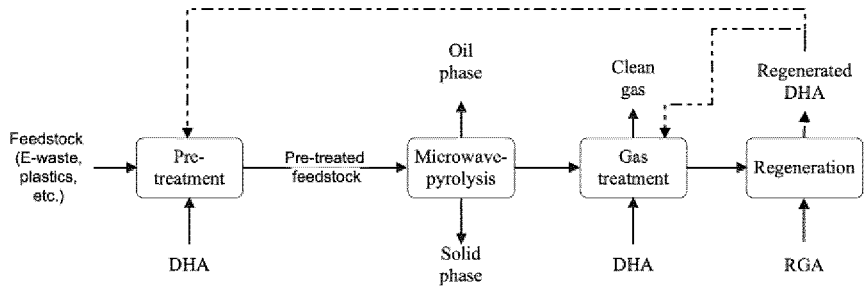

Figure 1

(57) Abstract: A process for recycling contaminated solid material is provided. The process comprises heating the material yielding a solid phase, an oil phase, and a gas phase. Prior to being heated, the material is subjected to a pre-treatment involving a dehalogenation agent (DHA). The gas phase obtained is further subjected to a purification treatment. The DHA agent used is regenerated using a regeneration agent (RGA) and further re-used in the process.

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TITLE OF THE INVENTION

PROCESS FOR RECYCLING CONTAMINATED SOLID MATERIALS AND PURIFICATION OF GASES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application No. 63/029,693, filed on May 25, 2020, the content of which is incorporated herein in its entirety by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for recycling contaminated solid materials including plastic materials such as electronic waste (E-waste) plastic materials. More specifically, the invention relates to such a process that uses a microwave-pyrolysis and that is environmental-friendly. The invention also relates to a process for purifying a gas emission.

BACKGROUND OF THE INVENTION

[0003] Owing to the industrialization, economic expansion and growing global population, the electric and electronic product manufacturing sector is expanding worldwide, which leads to a dramatic increase in the amount of electronic waste (E-waste), from 44.75 Mt in 2016 to 53.6 Mt in 2020 according to the UN Global E-waste Monitor 2020 report. In the circumstance of the generation of an abundant amount of E-waste, only 17.4% of E-waste is appropriately collected and recycled, and the remaining 82.6% of E-waste is either dumped in landfills or traded through illegal market (Forti et al., 2020 [1]).

[0004] Consequently, finding ways to properly recycle of E-waste has become a serious environmental issue worldwide. Most of the current recycling strategies focus on the recovery of valuable metals present in E-wastes such as gold, silver, and copper; and the plastic fraction of E-waste is usually either incinerated or discarded (Das et al., 2021 [2]).

[0005] Plastic fraction accounts for 25-30% of the E-wastes, and this plastic material is typically composed of high-quality polymers such as polycarbonate (PC), polypropylene (PP), high impact polystyrene (HIPS), and acrylonitrile butadiene styrene (ABS) (Das et al., 2021 [2]). However, the plastic material in E-waste usually also contains highly toxic substances including heavy metals (e.g., Pb, Hg, and Cd) and brominated flame retardants (BFRs)

(Damrongsiri et al., 2016 [3]; Dehnath et al., 2018 [4]). For instance, the concentration of Pb in cathode-ray tubes (CRTs) and printing wiring boards was reported to be 429-9,900 mg/kg and 18,060-400,560 mg/kg, respectively, amounts which significantly exceed the permissible limit of 10 µg/L (Olubanjo et al., 2015 [6]).

[0006] Flame retardants (FRs) are considered key components of electric and electronic products; they are often added to the products in order to meet the fire safety standards. Among commercially available FRs such as nitrogen- and phosphorous-based FRs, brominated FRs are the most commonly used. However, they are persistent, bio-accumulative and toxic in nature (Kefeni et al., 2011 [5]). The broadly used BFRs in the plastics of electric and electronic products include: tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), hexabromocyclo dodecane (HBCD), and polybrominated biphenyls (PBB); among which TBBPA represents around 60% of the total volume of BFRs (Ortuño et al., 2014 [7]).

[0007] Upon thermal degradation of BFR-containing E-waste plastics, a wide range of hazardous pollutants such as HBr and brominated aromatic compounds can be emitted. Brominated aromatic compounds are precursors to polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzo furans (PBDF), which are known to present serious environmental problems (Wong et al., 2007 [8]) and to have harmful impacts on human health (Lilienthal et al., 2009 [9]).

[0008] Conventional E-waste plastics recycling generally consists of mechanical, chemical, and thermal processes. In the mechanical recycling, the approaches typically include grinding, washing, separation, drying, re-granulation, extrusion, and compounding where the recycled material can be further processed into secondary products such as 3D printer filaments (Mohammed et al., 2017 [10]). The mechanical recycling of E-waste plastics into secondary products is often determined by the purity of the E-waste plastics. However, the presence of heavy metals and BFRs negatively affects the purity of the E-waste plastics and thus leads to a shift towards chemical and thermal recycling approaches. In contrast to mechanical recycling, chemical, and thermal recycling technologies (e.g., incineration, hydrothermal treatment, and pyrolysis) generally convert heterogeneous and contaminated E-waste plastics into value-added chemicals and fuels.

[0009] Incineration can significantly reduce the volume of waste (i.e., 90-99% reduction in volume) being landfill and produce electricity at the same time (Arvanitoyannis, 2013 [11]). However, the high cost of the necessary installation and the emission of hazardous substances limit the widescale implementation of incineration for E-waste plastics. Emitted toxic substances include volatile and semi-volatile organic compounds (VOCs, e.g., chlorobenzene, bromobenzene, tribromomethane, bromomethane, and dibromomethane), dioxins, other halogenated compounds (e.g., HBr, HCl), and common flue gas components (Stewart et al., 2003 [12]).

[0010] Hydrothermal treatment is an effective approach to remove BFRs from E-waste plastics and convert them into value-added fuels and chemicals (Yin et al., 2011 [13]). For example, Zhao et al. (2019, [14]) hydrothermally treated E-waste plastics in subcritical water and converted them into 81.4-97.6 wt.% of organic product containing styrene, bisphenol A, caprolactam and other valuable compounds that can be reused to produce polymer or other chemicals. Aside from this organic product, solid product with a microstructure was also generated from the hydrothermal treatment of E-waste plastics, which demonstrates the potential to be used as absorbent. However, factors such as high installation cost, requirement for a high-pressure resistant reactor and handling of a pressurized reactor, limit the large-scale application of E-waste plastics recycling by hydrothermal treatment (Das et al., 2021 [2]).

[0011] Pyrolysis is a thermochemical recycling approach that can convert E-waste plastics into oil, solid and gas phases in an oxygen-free condition. Even though pyrolysis is effective in diverting E-waste plastics from landfill by their conversion into valuable products, the generation of wax during the process and the formation of halogenated gases such as HBr and HCl make pyrolysis less suitable for recycling contaminated E-waste plastics (Zhang et al., 2021 [15]). A catalyst has been introduced into pyrolysis in order to limit the formation of brominated components; however, issues such as occurrence of catalyst deactivation caused by Br fixation and coke formation, remain to be addressed before any widescale utilization of catalytic pyrolysis (Liu et al., 2014 [16]; Hall et al., 2008 [17]).

[0012] There is a need for environmental-friendly, efficient, and cost-effective processes for recycling E-waste plastic materials. Also, there is a need for such processes which can be performed at industrial level.

SUMMARY OF THE INVENTION

[0013] The inventors have designed and performed an environmental-friendly process for recycling contaminated solid materials including plastic materials such as electronic waste (E-waste) plastic materials. More specifically, the invention relates to such a process that uses a heating process including microwave-pyrolysis, and also uses a dehalogenation agent (DHA). The process according to the invention yields a solid phase, an oil phase, and a gas phase. The gas phase is further subjected to a purification treatment. The gas purification treatment according to the invention may be adapted for the purification of gases emitted from other processes.

[0014] In embodiments of the invention, the process comprises pre-treating a raw contaminated solid material then submitting the pre-treated material to a heating process such as microwave-pyrolysis for example yielding a solid phase, an oil phase, and a gas phase. The gas phase is further treated such as to remove unwanted components including acidic gases (halogenated gases), volatile organic compounds (VOCs), and sulfur-containing compounds such as sulfur oxides (SOx). Accordingly, the process of the invention leads to the production of a clean solid, an oil phase, and a purified gas phase.

[0015] In embodiments of the invention, each of the pre-treatment of the raw contaminated solid material and the purification treatment of the gas emitted during the heating process is performed using a dehalogenation agent (DHA) comprising an organophosphorus (OP) compound. The DHA agent used these two processes may be the same or different.

[0016] In embodiments of the invention, the DHA agent used is regenerated using a regeneration agent (RGA) and further re-used in the process.

[0017] In embodiments of the invention, the pre-treated material is mixed with a microwave absorber prior to performing the microwave-pyrolysis. The microwave absorber assists in the melting of the plastic material. In other embodiments of the invention, the melting process is preformed prior to the microwave-pyrolysis.

[0018] The process of the invention can be readily scaled up and performed in an industrial facility.

[0019] The invention thus provides the following in accordance with aspects thereof:

(1) A process for recycling contaminated solid material, comprising heating the material yielding a solid phase, an oil phase, and a gas phase, wherein the material is subjected to a pre-treatment involving a dehalogenation agent (DHA) prior to the heating.

(2) A process according to (1), wherein the heating is performed using a technique which is microwave-pyrolysis, ultrasound, electromagnetic waves at other frequencies than microwave frequencies, electric field, magnetic field, plasma, or a combination thereof.

(3) A process according to (1) or (2), further comprising subjecting the gas phase to a purification treatment involving a further dehalogenation agent yielding a purified gas and a reacted dehalogenation agent.

(4) A process according to (3), further comprising subjecting the reacted dehalogenation agent to a regeneration process yielding a regenerated dehalogenation agent.

(5) A process according to (4), wherein the regeneration process involves use of a regeneration agent comprising an acid compound or proton donor; optionally the acidic compound is an inorganic acid (HCl or H_2SO_4) or an organic acid.

(6) A process according to (4) or (5), wherein the regenerated dehalogenation agent is directed for re-use in the pre-treatment of the material and/or in the purification treatment of the gas phase.

(7) A process according to any one of (1) to (6), further comprising cleaning the contaminated solid material prior to the pre-treatment.

(8) A process according to any one of (1) to (7), wherein the pre-treatment of the material is conducted at ambient temperature or a higher temperature.

(9) A process according to (3), wherein the DHA used in the pre-treatment step and the further DHA used in the gas purification are the same or are different. In other words, in embodiments of the invention, a first DAH is used in the pre-treatment step and a second DHA agent is used

in the gas purification step; and the first DHA and the second DHA may be the same or different.

(10) A process according to any one of (1) to (9), wherein the pre-treated material comprises reduced amounts of compounds containing Br, Cl, F, Co, and Pb when compared to an untreated material.

(11) A process according to (3), wherein the purified gas is substantially free of chemicals of concern (CoCs) including acidic gases, volatile organic compounds (VOCs), and sulfur-containing compounds; optionally the acidic gases are halogenated gases including HCl, HBr, and HF; optionally the VOCs are propylene, 1,3-butadiene, chloromethane, bromomethane, chloroethane, and vinyl chloride; optionally the sulfur-containing compounds are sulfur oxides (SOx).

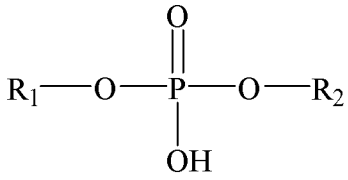
(12) A process according to any one of (1) to (11), wherein the oil phase comprises monomers of degraded raw materials, which are classified into low boiling point oils such as gasoline (optionally in an amount of about 63.68%) and medium boiling point oils such as diesel (optionally in an amount of about 20.08%).

(13) A process for recycling a contaminated plastic material, comprising the steps of: (a) subjecting the material to a pre-treatment involving a dehalogenation agent (DHA) to yield a pre-treated material; (b) subjecting the pre-treated material to a heating process to yield a solid phase, an oil phase, and a gas phase; (c) separating the solid phase, the oil phase, and the gas phase; (d) subjecting the gas phase to a purification treatment involving a further dehalogenation agent (DHA) to yield a purified gas and a reacted DHA; (e) separating the purified gas and the reacted DHA; (f) subjecting the reacted DHA to a regeneration process to yield a regenerated DHA; and (g) directing the regenerated DHA for use at steps (a) and/or step (d).

(14) A process according to (13), wherein the DHA at step (a) and the further DHA at step (d) are the same or are different. In other words, in embodiments of the invention, a first DAH is used at step (a) and a second DHA agent is used at step (d); and the first DHA and the second DHA may be the same or different.

(15) A process according to any one of (1) to (14), wherein the dehalogenation agent comprises an organophosphorus compound.

(16) A process according to any one of (1) to (15), wherein the dehalogenation agent comprises a phosphoric acid ester of general formula **I** below

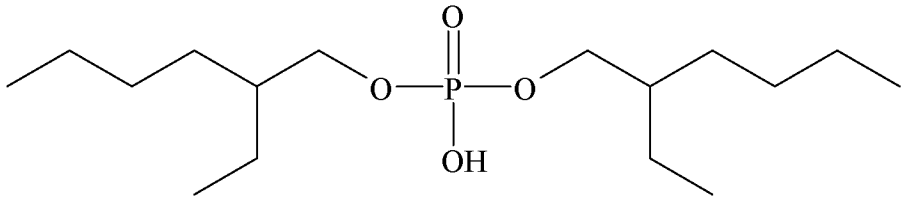


I

wherein R_1 and R_2 are each independently C_1 to C_{20} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

(17)A process according to (16), wherein R_1 and R_2 are each independently a C_8 to C_{20} or a C_8 to C_{16} or a C_{16} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

(18) A process according to any one of (1) to (17), wherein the dehalogenation agent comprises di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined below



DEHPA or HDEHP

(19) A process according to any one of (1) to (17), wherein the dehalogenation agent comprises a compound selected from the group consisting of: di-(2-ethylhexyl) phosphoric acid, bis(2-ethylhexyl) hydrophosphoric acid, di-(2-ethylhexyl) orthophosphoric acid, O,O-

bis(2-ethylhexyl)phosphoric acid, orthophosphoric acid 2-ethylhexyl alcohol, phosphoric acid di(2-ethylhexyl) ester, and Hostarex PA 216™.

(20) A process according to any one of (1) to (19), which yields a clean solid material, an oil comprising monomers of the raw material, and a purified gas substantially free of acidic gases, volatile organic compounds, and sulfur-containing compounds.

(21) A process according to any one of (1) to (20), wherein the contaminated solid material is a contaminated plastic material.

(22) A process according to any one of (1) to (20), wherein the contaminated solid material is an electronic waste (E-waste) plastic material.

(23) A process according to any one of (1) to (20), wherein the heating is performed using microwave-pyrolysis.

(24) A process for recycling contaminated solid material, comprising subjecting the material to a microwave-pyrolysis yielding a solid phase, an oil phase, and a gas phase, wherein the material is subjected to a pre-treatment involving a dehalogenation agent (DHA) prior to the microwave-pyrolysis.

(25) A process according to (24), wherein a microwave absorber is added to the material prior to performing the microwave-pyrolysis; optionally the microwave absorber is a carbon-based compound such as SiC or carbon.

(26) A process according to (25), wherein the microwave absorber and the material are melted prior to performing the microwave-pyrolysis; optionally, melting is performed using a technique which is microwave heating, conventional heating, extrusion, or a combination thereof.

(27) A process according to any one of (24) to (26), wherein the contaminated solid material is a contaminated plastic material.

(28) A process according to any one of (24) to (26), wherein the contaminated solid material is an electronic waste (E-waste) plastic material.

(29) A process for purifying a gas emission, comprising allowing the gas emission to react with a dehalogenation agent (DHA) yielding a purified gas and a reacted DHA, and separating the purified and reacted DHA.

(30) A process according to claim, further comprising subjecting the reacted DHA to a regeneration process to yield a regenerated DHA.

(31) A process according to (30), further comprising re-using the regenerated DHA in the process.

(32) A process according to any one of (29) to (31), wherein the gas emission is from a facility for combustion of E-waste, organic waste, oil, or coal.

(33) A process according to any one of (29) to (31), wherein the gas emission is from a facility for recycling contaminated solid materials such as contaminated plastic material and contaminated electronic waste (E-waste) plastic materials.

(34) A system adapted to perform the process as defined in any one of (1) to (33).

(35) An industrial facility embodying the system as defined in (34).

[0020] Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of specific embodiments thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] In the appended drawings:

[0022] **Figure 1**: Schematic diagram outlining the process according to the invention.

[0023] **Figure 2**: Flow chart outlining the experimental procedure applied in the pre-treatment.

[0024] Figure 3: Flow chart outlining the experimental procedure used in the microwave-pyrolysis and the gas purification step.

[0025] Figure 4: Image showing the regenerated DHA floating on the surface of the liquid.

[0026] Figure 5: SEM band characterization of the untreated heavy fraction plastic. Note: The Lithium band is associated with the X-ray detector window.

[0027] Figure 6: FT-IR spectrum of the untreated feedstock.

[0028] Figure 7: SEM images of (**A**) untreated feedstock; (**B**) pre-treated feedstock obtained from pre-treatment using DHA at 25°C; (**C**) pre-treated feedstock obtained from pre-treatment using DHA at 60°C; (**D**) pre-treated feedstock obtained from pre-treatment using toluene-DHA.

[0029] Figure 8: Investigation on the removal efficiency of chemicals of concern with different pre-treatment conditions. (**A**) untreated feedstock (solid); (**B**) pre-treated feedstock obtained from pre-treatment using DHA at 25°C (dotted); (**C**) pre-treated feedstock obtained from pre-treatment using DHA at 60°C (dashdot); (**D**) pre-treated feedstock obtained from pre-treatment using toluene-DHA (longdash).

[0030] Figure 9: FT-IR spectra of untreated (solid), pre-treated with ECOC (emulsion-containing organophosphoric compound) at 25°C (dotted), and pre-treated with ECOC at 60°C (dotdash) for 6 hours in the range of 650-1000 cm^{-1}.

[0031] Figure 10: FT-IR spectra of untreated (solid), treated with DHA for 2 hours (dotted), for 4 hours (dotdash), and for 6 hours (longdash) at 60°C in the range of 650-1000 cm^{-1}.

[0032] Figure 11: FT-IR spectrum of untreated (solid), treated with ECOC for 2 hours (dotted), for 4 hours (dotdash), and for 6 hours (longdash) at 60°C in the range of 1100-1700 cm^{-1}.

[0033] Figure 12: FT-IR spectra of unreacted and reacted ECOC obtained from pre-treatment at various reaction conditions.

[0034] Figure 13: The boiling point distribution of liquid oil obtained from microwave pyrolysis of E-waste plastics.

[0035] Figure 14: FT-IR spectra of untreated (solid) and reacted (longdash) DHA obtained from DHA-assisted gas purification from 1600-600 cm^{-1}.

[0036] Figure 15: FT-IR spectra of unreacted (solid) and reacted (longdash) DHA in the range of 1600-900 cm^{-1}.

[0037] Figure 16: FT-IR spectrum of regenerated DHA.

[0038] Figure 17: FT-IR spectrum of fresh DHA (Millipore Sigma, 2021 [36]).

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0039] Before the present invention is further described, it is to be understood that the invention is not limited to the particular embodiments described below, as variations of these embodiments may be made and still fall within the scope of the appended claims. It is also to be understood that the terminology employed is for the purpose of describing particular embodiments; and is not intended to be limiting. Instead, the scope of the present invention will be established by the appended claims.

[0040] In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure pertains.

[0041] Use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one”, but it is also consistent with the meaning of “one or more”, “at least one”, and “one or more than one”. Similarly, the word “another” may mean at least a second or more.

[0042] As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”) or “containing” (and any form of containing, such as “contain” and “contains”), are inclusive or open-ended and do not exclude additional, unrecited elements or process steps.

[0043] As used herein when referring to numerical values or percentages, the term “about” includes variations due to the methods used to determine the values or percentages, statistical

variance and human error. Moreover, each numerical parameter in this application should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0044] As used herein, the term "dehalogenation agent" (DHA) refers to a chemical agent suitable for removing halogens and/or halogen-containing compounds from a material. In embodiments of the invention, the dehalogenation agent comprises an organophosphorus compound. In the present disclosure, term "emulsion-containing organophosphoric compound" (ECOC) is also used to designate the dehalogenation agent.

[0045] As used herein, the term "microwave-pyrolysis" refers to a pyrolysis process using a microwave heating technique.

[0046] As used herein, the term "microwave absorber" refers to material that absorbs microwaves and becomes heated. Such material is used in the microwave-pyrolysis and transfers its heat to the plastic material, thus assisting in the melting of the plastic material. Accordingly, a microwave absorber is used when the raw contaminated solid material contains plastic. Use of a microwave absorber may not be necessary when the raw material itself is a microwave absorber. The microwave absorber used is a carbon-based material such as for example SiC or carbon itself.

[0047] As used herein, the term "contaminated solid material" refers to the raw material used in the invention. The material may consist of any solid material that is contaminated and contains chemicals of concern (CoC) as defined herein below. Such solid materials include plastic materials and electronic waste plastic materials as defined herein below.

[0048] As used herein, the term "electronic waste (E-waste) plastic material" or "E-waste plastics" refers to the raw material used in this invention. The material consists of waste from various electronic equipment and contains chemicals of concern as defined herein above.

[0049] As used herein, the term "gas emission" refers to a gas stream emitted during the process of the invention. In particular, the gas emitted during the microwave-pyrolysis. The gas emission also refers to a gas emitted during any other process such as for example the combustion of E-waste, organic waste, oil or coal. It is to be understood that the gas

purification treatment according to the invention may be applied to gases emitted during other processes.

[0050] As used herein, the term "chemicals of concern" (CoC) refers to chemicals present in the raw material used in the process of the invention. It is generally not desirable to have such chemicals present in solid materials discarded in the nature. Such chemicals are generally harmful to the nature or the health of humans. As indicated herein above, chemicals of concern comprise for example: acidic gases including halogenated gases such as HCl, HBr, and HF; volatile organic compounds (VOCs) including propylene, 1,3-butadiene, chloromethane, bromomethane, chloroethane, and vinyl chloride; and sulfur-containing compounds including sulfur oxides (SOx).

[0051] As used herein, the term "regeneration agent" (RGA) refers to a chemical used in the process of the invention to retrieve the dehalogenation agent (DHA) after use. The regeneration agent comprises a proton donor such as an acid. The acid may be inorganic (HCl, H_2SO_4) or organic.

[0052] The inventors have designed and performed a process for recycling contaminated solid materials including plastic materials such as electronic waste (E-waste) plastic materials. More specifically, the invention relates to such a process that uses a heating process including but not limited to microwave-pyrolysis. The process also uses a dehalogenation agent (DHA). The process according to the invention yields a solid phase, an oil phase, and a gas phase. The gas phase is further subjected to a purification treatment. The gas purification treatment according to the invention may be adapted for the purification of gases emitted from other processes.

[0053] The present invention is illustrated in further details in the Experiment Work section below. The section includes non-limiting examples.

[0054] To tackle the E-waste plastic recycling problems as discussed herein above, the inventors have developed an environmental-friendly and energy-sufficient recycling approach consisting of a pre-treatment with an effective dehalogenation agent (DHA), a microwave-assisted pyrolysis, a gas purification with DHA, and a regeneration process. The end products obtained from this developed process include: the purified gas that meet the environmental regulation, the valuable monomers-containing oil phase, and the precious metals-containing

solid phase. The schematic diagram of this proposed recycling solution for contaminated E-waste plastics is depicted in **Figure 1**.

Example 1 – Pre-treatment

[0055] Due to the presence of debris on the raw feedstock, the feedstock initially underwent washing by water (if needed) and then dried, and then cut into pieces having a dimension of about 5 about. DHA solution was prepared by mixing an organophosphorus (OP) compound and distilled water. The DHA solution is also referred to herein as emulsion-containing organophosphoric compound (ECOC). In the experiments conducted, di-(2-ethylhexyl) phosphoric acid was used as OP. The OP dosage is between about 0.1 to 30 vol.%, preferably between about 1 to 10 vol.%, most preferably between about 1 to 5 vol.%. To evaluate the performance of DHA in removing chemical of concern (CoC) from E-waste plastics, another pre-treatment solution containing toluene and OP was prepared as the reference. This reference pre-treatment solution is referred to herein as toluene-ECOC. Indeed, it is suggested in the prior art that toluene is a common extracting agent used in the treatment of contaminated E-waste plastics (Evangelopoulos et al., 2019 [18]; Mnim et al., 2003 [19]; Schlummer et al., 2005 [20]).

[0056] The flow chart for the experimental procedure used in the pre-treatment step is illustrated in **Figure 2**. For a typical pre-treatment test, feedstock was mixed with pre-treatment solutions (ECOC or toluene-DHA) under constant stirring at 25°C or 60°C for a certain time, for example 2, 4, and 6 hours. At the end of the experiment, the solid and liquid fraction were separated. The liquid fraction, referred to herein as reacted ECOC, which was collected and stored for further analyses. The solid fraction was subjected to washing to remove any traces of ECOC, followed by drying.

Example 2 – Microwave-pyrolysis and gas purification

[0057] The flow chart for the experimental procedure used in the microwave pyrolysis and the gas purification is illustrated in **Figure 3**Erreur ! Source du renvoi introuvable.. This is performed after on the pre-treated feedstock obtained from the pre-treatment. The microwave pyrolysis and subsequent gas purification were also performed on the untreated feedstock as reference.

[0058] Prior to the experiment, an inert gas such as nitrogen gas was purged into the reactor to remove any remaining oxygen inside the reactor thereby creating an environment which is substantially oxygen-free.

[0059] For a typical run, the feedstock and SiC were added into the reactor. A microwave with a maximum power of and frequency of 2.45 GHz was used for the pyrolysis experiments. The pyrolytic products were then passed through a series of condensers and the liquid oil was condensed and collected. The non-condensable gases also referred to herein as untreated gas were passed through a column containing ECOC to remove toxic substances including halogenated gases (HBr, HCl, and HF), VOCs and SOx. The duration of the microwave pyrolysis depends on the amount of material loaded. The duration may be about 5 minutes.

Example 3 – Regeneration

[0060] The regeneration process for the reacted DHA obtained from the pre-treatment and also from the gas purification was carried out using a regeneration agent (RGA) which a proton donor such as an acid. The amount of RGA used was chosen to be equivalent to the amount of the DHA such as to ensure regeneration of a maximum amount of DHA. The RGA dosage is between about 0.1 to 30 vol.%, preferably between about 1 to 10 vol.%, most preferably between about 1 to 5 vol.%; and the duration of the regeneration process is about 1 to 30 minutes.

[0061] A known amount of the RGA was added to the reacted ECOC after treatment process. The mixture was then exposed to stirring to ensure the complete separation of the DHA from the contaminants. Once the exchange reaction was completed, separating the DHA is easily performed due to its immiscibility with water as can be seen in **Figure 4**. The regenerated agent was then separated from the liquid and sent for analyzed.

Analysis

[0062] A series of analytical techniques were applied to fully characterized the main products and by-products at each stage of the process according to the invention. **Table 1** below summarizes the analytical techniques applied for the characterizations.

[0063] Table 1. Summary of the analytical techniques used at each step.

Products and by-products	Analytical techniques
Raw feedstock	NAA; SEM-EDX; FT-IR
Pre-treatment	
Pre-treated feedstock	SEM-EDX; FT-IR
Reacted DHA	FT-IR
Microwave-pyrolysis	
Oil phase	GC-MS; TGA
Untreated gas phase	FT-IR; Acidic gases; GC-MS (VOCs)
Gas purification	
Clean gas	FT-IR; Acidic gases; GC-MS (VOCs)
Reacted DHA	FT-IR
Regeneration	
Regenerated DHA	FT-IR

Feedstock – NAA Analysis

[0064] The elemental composition of the untreated feedstock or raw feedstock identified by neutron activation analysis (NAA) is presented in **Table 2** below**Table 2**. As can be seen,**Erreur ! Source du renvoi introuvable.** a high content of silicon was observed in the feedstock, which could be due to the presence of glass fiber substrates. It can also be seen that a high concentration of bromine in the feedstock, this might be attributed to the presence of BFRs in the E-waste. This feedstock also shows a high content of Na, Al, S, Cl, Fe, and Zn. The presence of glass fibers could cause the high concentration of Al and Fe since the preparation of glass fibers requires the addition of Al_2O_3 and SiO_2. In addition, some trace elements were identified in the feedstock including F, Mg, K, Ca, Sc, Ti, V, Cr, Mn, Co, Cu, As, Se, Rb, Zr, Mo, Ag, Cd, In, Sn, Sb, I, Cs, Ba, La, Au, and Hg. Among these elements, the presence of elements such as Ca, Mg, and Ba could be attributed to the fiber glass present in the feedstock (Gao et al., 2021 [21]). A low concentration of Sb was also detected in the feedstock. Indeed, this element is sometimes used as additive in the plastic matrix to enhance the effectiveness of flame retardants (Zhan et al., 2020 [22]).

[0065] Table 2. The elemental composition of the raw feedstock used in this project as determined by NAA analysis.

Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)
F	<920	Fe	2,000 ± 300	Sn	<50
Na	2,050 ± 80	Co	37 ± 2	Sb	10.2 ± 0.4
Mg	600 ± 200	Ni	<100	I	<0.6
Al	32,000 ± 1,000	Cu	898 ± 50	Cs	<0.8
Si	27,000 ± 7,000	Zn	1,940 ± 80	Ba	100
Si	<15,000	As	<0.6	La	7.1 ± 0.3
Cl	2,500 ± 100	Br	1,090 ± 80	Hf	<1
K	<770	Rb	<20	W	<0.7
Ca	<140	Zr	<470	Au	<0.02
Sc	<2	Mo	<3	Hg	<0.5
Ti	900 ± 100	Ag	<510	Mn	1.9 ± 0.2
V	10 ± 1	Cd	<4		
Cr	14 ± 5	In	<0.07		

Feedstock – SEM-EDX Analysis

[0066] For SEM-EDX analysis of raw feedstock, two prominent peaks corresponding to C and O were detected; see **Figure 5**. A weak peak that can be ascribed to N was found, which could be due to the fact the feedstock contains ABS polymer and this is further supported by the FT-IR analysis of raw material described herein below. Additionally, strong peaks representing Br and Cl were observed in the feedstock, as evidenced by the results obtained from NAA analysis. Other strong peaks corresponding to Si and Na were identified, owing to the presence of glass fiber in the feedstock. Except for these strong peaks, the peaks that can be ascribed to F, Co, Mg, and Pb were also observed.

Feedstock – FT-IR Analysis

[0067] FT-IR analysis of the raw feedstock was performed, the resulting spectrum is shown in **Figure 6**. The peaks at 3693, 3647, and 3618 cm^{-1} could be related to the O-H stretching. It was also found that the peaks at 2935 cm^{-1}, 2920 cm^{-1}, and 2851 cm^{-1} were identified in the feedstock, which could be due to the aliphatic C-H. A peak that is attributed to the presence of C≡N bond can be observed at 2237 cm^{-1}, suggesting the presence of ABS polymer in the feedstock (Truc et al., 2017 [23]; Zhang et al., 2012 [24]). Besides, it was found that a peak corresponding to C=O stretching was observed at 1692 cm^{-1}. A strong peak at 1599 cm^{-1} can be ascribed to the aromatic C=C vibration and a peak representing was found at 966 cm^{-1}. Together, these results could imply the presence of HIPS polymer in the feedstock (Truc et al., 2017 [23]). The peaks at 1467 cm^{-1} and 1377 cm^{-1} representing methylene group and methyl group, respectively, which are reported to be the characteristics bonds of PP (Zhang et al., 2012 [25]; Wagner et al., 2020 [26]). A strong peak was identified at 1303 cm^{-1} and this could be ascribed to the C-F stretching (Limcharoen et al., 2013 [27]). Another peak at 1182 cm^{-1} corresponding to C-O of esters can be identified in the feedstock, which implies the feedstock might contain PC (Annamalai et al., 2020 [28]). The peaks at 1080 cm^{-1} and 667 cm^{-1} could be ascribed to the presence of BFR in the feedstock (Grigorescu et al., 2020 [29]). A strong peak of epoxy group was found at 829 cm^{-1} in the feedstock (Shen et al., 2018 [30]). Several peaks at 686 cm^{-1} and 752 cm^{-1} can be due to the presence of Pb-O-Pb and C-Cl bond in the feedstock, respectively.

Pre-treatment – SEM-EDX Analysis

[0068] The SEM images of pre-treated feedstock obtained at different conditions are shown in **Figure 7**. The presence of a relatively lower chemical contrast in the pre-treated feedstock could indicate the removal of higher atomic number contaminants in the plastic matrix, such as Pb, Cd, Hg, Br, and Cl.

[0069] **Figure 8** shows a reduction in the peak areas for all CoCs including F, Co, Br, Pb, and Cl in the pre-treated feedstock obtained from pre-treatment using DHA solution (ECOC) at 25 or 60°C. On the contrary, no significant difference was found in the peak area of F, Br, and Pb of the pre-treated feedstock obtained from pre-treatment using toluene-DHA, and only a decrease in the peak area of Cl was found. Thus, it can be inferred that the removal efficiency of CoCs (i.e., F, Co, Br, Pb, and Cl) obtained from pre-treatment using ECOC was higher than that obtained from pre-treatment using toluene-DHA.

[0070] As illustrated in **Table 3** below, the effect of reaction temperature on the removal efficiency of Co, F, Pb, and Br was insignificant. In contrast, the removal efficiency of Cl was proportional to the reaction temperature.

[0071] Table 3. Effect of reaction temperature on the removal efficiency of Co, F, Pb, and Br

Temperature	Br	Cl	F	Co	Pb
25°C	77	72	43	32	72
60°C	77	95	42	31	75

[0072] Clearly, as shown in **Table 4** below, the pre-treatment removal efficiencies of Br, Cl, F, and Pb obtained from pre-treatment using DHA were higher compared to those obtained from pre-treatment using toluene-DHA. However, it was observed that the pre-treatment using toluene-DHA led to a higher removal efficiency of Co than that obtained using DHA at 25°C but lower than that obtained using DHA at 60°C.

[0073] Table 4. Removal Efficiency of various chemicals of concern for different pre-treatment conditions.

Element	Removal Efficiency (%)		
	DHA, 25°C	DHA, 60°C	Toluene-DHA
Br	73	74	0
Cl	94	93	71
F	43	42	28
Co	9	31	15
Pb	76	68	9

Pre-treatment – FT-IR Analysis

[0074] The FT-IR spectra of untreated feedstock and pre-treated feedstock obtained at 25°C for 6 hours and 60°C for 6 hours in the range of 650-1000 cm^{-1} are depicted in **Figure 9**.

[0075] The intensity of the peak at 667 cm^{-1} representing C-Br of feedstock reduced after pre-treatment using DHA. A peak at 957 cm^{-1} was observed in the untreated feedstock and pre-treated feedstock, which could be related to the methylic C-Br stretching. Together with the reduced intensity of C-Br at 957 cm^{-1}, it can be stated that the DHA-assisted pre-treatment is

helpful for removing Br from the contaminated E-waste plastics. This is supported by the SEM-EDX analysis where the Br removal obtained at DHA-assisted pre-treatment at 25°C and 60°C was 73% and 74%, respectively (**Table 4**). Another peak at 686 cm^{-1} was detected in the untreated feedstock, which could be ascribed to the presence of Pb-O-Pb in the raw material. After DHA-assisted pre-treatment, it was found that the intensity of Pb-O-Pb bond reduced. Again, as indicated in **Table 4**, the Pb removal efficiency achieved by DHA-based pre-treatment was 68-76%. In addition, the peak corresponding to C-Cl bond was identified at 752 cm^{-1}, and its intensity was found to reduce after pre-treatment, which is consistent with the results obtained from SEM-EDX analysis. The peak of epoxy group was found at 829 cm^{-1} in the untreated feedstock was stronger than that identified in the pre-treated feedstock. This lower intensity of epoxide group after pre-treatment could be due to the ring opening of epoxide in the acidic aqueous solution since the agent used is an acid. It is well known that epoxy resin is used to provide the protection for the electrical components against dust, moisture and short circuits.

[0076] The effect of reaction time on the CoC removal efficiency obtained from pre-treatment using DHA was investigated at 60°C for 2, 4, and 6 hours. As shown in **Figure 10**, no significant difference was observed between the spectrum of pre-treated feedstock obtained at 60°C for 2 hours and untreated feedstock; however, a significant difference was found in the FT-IR spectrum of pre-treated feedstock when extending the processing time till 4 hours and 6 hours. The peak identified at 957 cm^{-1} can be ascribed to the C-Br stretching, and its intensity was found to be reduced after pre-treatment, especially at 4 hours and 6 hours. A stronger peak of epoxy group was found at 829 cm^{-1} in the untreated feedstock when compared with that of pre-treated feedstock obtained at 4 hours and 6 hours, which could be related to the ring-opening of epoxide in the pre-treatment. A similar observance was observed in the intensity of the C-Cl at 752 cm^{-1} and Pb-O-Pb at 686 cm^{-1}.

[0077] The FT-IR spectra of the untreated and pre-treated feedstock obtained at 60°C for 2 hours, 4 hours, and 6 hours in the range of 1100-1700 cm^{-1} are presented in **Figure 11**. As shown in **Figure 12(a)**, a weaker peak at 1303 cm^{-1} representing C-F stretching was found in the pre-treated feedstock obtained at 4 hours and 6 hours compared to that in the untreated feedstock, implying the F was removed during the pre-treatment. This can be supported by a F removal efficiency of 42% was obtained at 60°C for 6 hours (**Table 4**).

Pre-treatment – Reacted DHA

[0078] FT-IR spectra of unreacted DHA and reacted DHA are presented in **Figure 12**. No big difference can be observed in the FT-IR spectra of various reacted DHAs. A peak corresponding to C-F bond at 1040 cm^{-1} was only found in the reacted DHA, indicating the occurrence of the reaction between DHA and F-containing compounds during the pre-treatment. It was found that a peak at 880 cm^{-1} was absent in the unreacted DHA, which can be ascribed to C-Br bond. This phenomenon could suggest the reaction between DHA and Br-containing compounds during the pre-treatment, thereby reducing the Br concentration in the feedstock (**Table 4**). The peak representing C-O bond at 1084 cm^{-1} was absent in the unreacted DHA. In addition, a strong peak representing O-H stretching was observed at 1637 cm^{-1}, which has been reported to be a main characteristic peak of DHA (de Silva et al., 2019 [31]). No significant difference was found in this peak before and after DHA-assisted pre-treatment, which may imply the high stability of DHA.

[0079] According to the FT-IR and SEM-EDX analyses of the pre-treated feedstock, it can be observed that DHA pre-treatment showed a positive role in removing Br, Cl, F, Co, and Pb from the contaminated E-waste plastics. In addition, based on the results obtained from the effect of temperature on the CoC removal efficiency obtained from DHA pre-treatment, this pre-treatment performed at room temperature led to a similar pre-treatment efficiency with that performed at higher temperatures (i.e., 60°C). From the FT-IR analysis of reacted DHA, the high stability of DHA during the pre-treatment can be observed.

Microwave-pyrolysis – GC-MS

[0080] The organic compounds in the pyrolysis oil were analyzed by GC-MS equipped with a HP-5MS capillary column. The main components of pyrolysis oil (with a relative peak area > 1%) are summarized in **Table 5** below. The components are classified in the table based on the structure characteristics (i.e., phenols, aromatic hydrocarbons excluding phenols, N-containing compounds, and others including compounds difficult to classify). It should be noted that only volatile compounds having a boiling point lower than 300°C can be detected by the GC-MS. In general, a number of organic compounds can be detected in the pyrolysis oil from E-waste plastics, and some compounds can be utilized to produce other chemicals after separation. The results showed that no brominated compound was identified in the pyrolysis oil obtained. This can be explained as follows: the higher temperature was achieved

in the microwave pyrolysis, leading to the decomposition of the brominated compounds such as 2-bromophenol and phenol 2,4-dibromo- which could be decomposed into small molecules such as bromomethane. The absence of the bromine-containing compounds ensures the low toxicity of the oil products.

[0081] Table 5. A summary of the main chemical compounds in the oil phase obtained from microwave pyrolysis of BFR-containing E-waste plastics.

RT (min)	Area Percentage (%)	Compound	Formula
Aromatic hydrocarbons			
2.96	2.05	o-Xylene	C_8H_{10}
3.33	2.49	Styrene	C_8H_8
4.16	1.09	Benzene, 1,2,3-trimethyl-	C_9H_{12}
16.33	1.31	Benz[a]anthracene, 7-methyl-	$C_{19}H_{14}$
22.98	1.63	5H-Tribenzo[a,f,k]trindene, 10,15-dihydro-	$C_{27}H_{18}$
Phenols			
4.46	12.13	Phenol	C_6H_6O
5.47	11.63	Phenol, 2-methyl-	C_7H_8O
5.90	2.09	p-Cresol	C_7H_8O
6.20	14.22	Phenol, 2,6-dimethyl-	$C_8H_{10}O$
6.92	12.65	Phenol, 2,4-dimethyl-	$C_8H_{10}O$
7.18	2.30	Phenol, 3,5-dimethyl-	$C_8H_{10}O$
N-containing compounds			
18.77	2.23	Pyrrole-2-carboxaldehyde, 1-[1-(1-adamantyl)ethyl]-	$C_{17}H_{23}NO$
22.89	4.23	Purin-2,6-dione, 1,3-dimethyl-8-[2-[3,4-dimethoxyphenyl]ethenyl]-	$C_{17}H_{18}N_4O_4$
Others			
16.72	1.37	9,10-Anthracenedione, 1,2,6-trihydroxy-	$C_{14}H_8O_5$
17.67	1.49	Benzoic acid, 2-(4-methylphenoxy)-	$C_{14}H_{12}O_3$
18.08	2.72	(3-Methoxyphenyl) methanol, 2-methylbutyl ether	$C_{13}H_{20}O$
18.42	2.19	4,4'-Dimethoxybenzophenone	$C_{15}H_{14}O_3$
20.10	2.57	Triphenyl phosphate	$C_{18}H_{15}O_4P$

Microwave pyrolysis – TGA

[0082] TGA analysis of oil obtained from microwave-pyrolysis of contaminated E-waste plastics was conducted to estimate its boiling point distribution. A simulated boiling point graph of the oil is shown in **Figure 13** and six distinct boiling point ranges including: 0-150°C, 150-200°C, 200-250°C, 250-300°C, 300-350°C, and ≥350°C were identified.

[0083] With microwave pyrolysis, the fraction with a boiling point below 150°C (40.36%), 150-200°C (23.32%), and above 350°C (16.24%), represented as the main components identified in the liquid oil from E-waste plastics. In a comparison, Ye et al. (2018) [33] performed the pyrolysis of waste printed circuit board using conventional heating, and a higher fraction of heavy oil (32.30%) with a boiling point >350°C was observed. **Figure 13** shows the two fractions of oil was 63.68% and 20.08%, which indicates the high value of the E-waste plastics-derived liquid oil obtained using microwave heating. In another previous study, the oil fraction with a boiling point lower than 200°C obtained from conventional pyrolysis with the use of Al_2O_3 was significantly lower than that obtained by microwave pyrolysis without a catalyst (Wang et al., 2015 [32]). Thus, the effectiveness of microwave heating in terms of producing light oil fraction from E-waste plastics can be verified.

Gas purification

[0084] As indicated herein above, the untreated gas phase obtained from the microwave-pyrolysis of contaminated E-waste plastics was purified using DHA to remove or eliminate halogenated gases (e.g., HCl, HBr, and HF), VOCs, sulfur-containing compounds, and others.

Acidic gases – Analyses

[0085] The removal efficiency of HCl, HBr, and HF obtained from DHA-assisted gas purification was measured using NIOSH 7907 and 7906. The results are summarized in **Table 6** below. Previous studies suggested that HBr is a common toxic gas generated from the thermal degradation of E-waste plastics ([8], [11], [26]). As indicated in **Table 6**Erreur ! Source du renvoi introuvable., the concentration of HBr before and after the gas purification was lower than the detection limit of 0.15 ppm, which is considerably lower than the emission limit of 2.4 ppm. One possible reason could be the majority of Br existed in the form of bromomethane

rather than HBr, as evidenced by the VOCs analysis. The results also showed that the concentration of HCl decreased from 2.2 ppm to <0.36 ppm after the gas purification treatment, and significantly lower than the emission limit of 18 ppm. Additionally, a sharp reduction in the HF concentration from 18 ppm to 0.74 ppm was observed after gas purification.

[0086] Table 6. Concentration of HF, HCl, and HBr before and after gas purification.

Gases	Untreated gas (ppm)	Treated gas (ppm)	Limit (ppm)
HF	18	0.74	2.4
HCl	2.2	<0.36	18
HBr	<0.15	<0.15	2.4

VOCs – Analyses

[0087] The concentration of VOCs before and after gas purification was determined by EPA TO-15 and the results are shown in **Table 7** below. As can be seen, the concentration of propylene decreased from 1,030,000 ppb to 4,240 ppb with a removal efficiency of 99.59%. Additionally, 1,3-butadiene which is one of the toxic substances and is a probable carcinogen in humans, had its concentration reduced dramatically from 255,000 ppb to 10,900 ppb with a removal efficiency of 95.73%. The chlorinated gases including CH_3Cl, C_2H_5Cl, and C_2H_3Cl were almost removed in the gas purification stage. In addition, a removal efficiency of 98.25% was observed for CH_3Br where the concentration reduced from 10,800 ppb to 189 ppb. This result could indicate that the Br from the gas phase obtained from microwave pyrolysis is likely to exist in the form of CH_3Br rather than HBr, which could be used to explain a very low concentration of HBr in the untreated gas (<0.15 ppm), as shown in **Table 6**.

[0088] Table 7. The removal efficiency of selected VOCs obtained from DHA-assisted gas purification.

VOCs	Untreated gas (ppb)	Treated gas (ppb)	Removal efficiency (%)
Propylene	1,030,000	4,240	99.59
1,3-Butadiene	255,000	10,900	95.73
Chloromethane	152,000	81	99.95

Bromomethane	10,800	189	98.25
Chloroethane	1,580	13	99.21
n-Hexane	890	500	43.82
Vinyl chloride	390	7.7	98.03

DHA – FT-IR Analysis

[0089] FT-IR analysis of unreacted and reacted DHA was performed, and the resulting spectra are presented in **Figure 14**. The sharp peaks at 728 cm^{-1} and 695 cm^{-1} were observed in the reacted DHA, which could be attributed to the presence of C-Cl and C-Br, respectively; while these peaks were absent in the fresh or unreacted DHA. This result could suggest the reaction between DHA and Cl- and Br-containing compounds in the gas purification, thereby leading to a reduction in the concentration of CH_3Br and CH_3Cl (**Table 7**).

[0090] As can be seen in **Figure 15**, the intensities of peaks centered at 1229 cm^{-1} and 1033 m^{-1} of unreacted and reacted DHA were similar. As suggested by Cortina et al. (1997, [34]) and Cheraghi et al. (2015, [35]), they are characteristic peaks of DHA, which are attributed to the presence of P=O stretching vibration at 1229 cm^{-1} and P-O-H or P-O-C stretching vibration at 1033 m^{-1}. Therefore, the high stability of DHA during the gas purification is observed.

[0091] The regenerated DHA was characterized using FT-IR analysis, and compared with the FT-IR spectrum of fresh DHA. As can be seen in **Figure 16** and **Figure 17**, the FT-IR spectrum of regenerated and fresh DHA was similar, indicating the effectiveness of the regeneration step.

[0092] As will be understood by a skilled person, the present invention provides an alternative and environmental-friendly recycling approach for contaminated E-waste plastics. The process according to the invention comprises a pre-treatment of the raw feedstock, a microwave-pyrolysis of the pre-treated feedstock, gas purification. The pretreatment and the gas purification comprise use of a dehalogenation agent which can be regenerated and re-used in the process. With the implementation of the present invention, emission of halogenated gases, VOCs and sulfur-containing compounds which are commonly observed in the thermal degradation of E-waste plastics can meet the environmental regulations.

[0093] The removal efficiency of chemicals of concern (CoC) obtained from DHA-assisted pre-treatment was found to be substantially higher than conventional approach (i.e., approaches using toluene). The pre-treatment using DHA resulted in higher removal efficiencies of Br, Cl, F, Co, and Pb. Indeed, the values obtained were respectively 73-74%, 93-94%, 42-43%, 9-31%, and 68-76% which are higher than those obtained using toluene-DHA (Br: 0%; Cl: 71%; F: 28%; Co: 15%; and Pb: 9%).

[0094] According to the invention, it is possible to conduct DHA pre-treatment at room temperature without negatively affecting the CoC removal efficiency.

[0095] The major fractions of oil product obtained from the microwave-pyrolysis of E-waste plastics according to the invention were classified into low boiling point oils such as gasoline (63.68%) and medium boiling point oils such as diesel (20.08%).

[0096] DHA-assisted gas purification reduced the amounts of HF and HCl, from 18 ppm to 0.74 ppm and from 2.2 ppm to <0.36 ppm, respectively; and the concentration of HBr was below 0.15 ppm. Accordingly, the gas purification according to the invention is effective in removing acidic gases including HF, HCl, and HBr.

[0097] Regarding VOCs removal efficiency, the DHA-assisted gas purification according to the invention led to removal efficiencies of 95.73%, 99.95%, 98.25%, 99.21%, and 98.03% for 1,3-butadiene, chloromethane, bromomethane, chloroethane, and vinyl chloride, respectively.

[0098] In embodiments of the invention, the microwave may be applied at a frequency range between about 915 MHz to about 2450 GHz. As will be understood by a skilled person, other heating techniques than microwave may be used in the process. Such heating techniques may be for example induction heating, ultrasound, electromagnetic waves at other frequencies than microwave frequencies, electric field, magnetic field, plasma, or combinations thereof.

[0099] The process according to the invention embodies a system for performing the process and may be readily scaled up and integrated in an industrial facility. As will be understood by a skilled person, such system and facility are within the scope of the present invention.

[00100] In embodiments of the invention, the process may be batch operated, semi-batch operated, continuous flow operated, or combinations thereof. Also, in embodiments of the

invention, the process may be s small scale, medium scale, large scale, or combinations thereof.

[00101] The scope of the claims should not be limited by the preferred embodiments set forth in the examples; but should be given the broadest interpretation consistent with the description as a whole.

[00102] The present description refers to a number of documents, the content of which is herein incorporated by reference in their entirety.

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CLAIMS:

1. A process for recycling contaminated solid material, comprising heating the material yielding a solid phase, an oil phase, and a gas phase, wherein the material is subjected to a pre-treatment involving a dehalogenation agent (DHA) prior to the heating.

2. A process according to claim 1, wherein the heating is performed using a technique which is microwave-pyrolysis, ultrasound, electromagnetic waves at other frequencies than microwave frequencies, electric field, magnetic field, plasma, or a combination thereof.

3. A process according to claim 1 or 2, further comprising subjecting the gas phase to a purification treatment involving a further dehalogenation agent yielding a purified gas and a reacted dehalogenation agent.

4. A process according to claim 3, further comprising subjecting the reacted dehalogenation agent to a regeneration process yielding a regenerated dehalogenation agent.

5. A process according to claim 4, wherein the regeneration process involves use of a regeneration agent comprising an acid compound or proton donor; optionally the acidic compound is an inorganic acid (HCl or H_2SO_4) or an organic acid.

6. A process according to claim 4 or 5, wherein the regenerated dehalogenation agent is directed for re-use in the pre-treatment of the material and/or in the purification treatment of the gas phase.

7. A process according to any one of claims 1 to 6, further comprising cleaning the contaminated solid material prior to the pre-treatment.

8. A process according to any one of claims 1 to 7, wherein the pre-treatment of the material is conducted at ambient temperature or a higher temperature.

9. A process according to claim 3, wherein the DHA used in the pre-treatment step and the further DHA used in the gas purification are the same or are different.

10. A process according to any one of claims 1 to 9, wherein the pre-treated material comprises reduced amounts of compounds containing Br, Cl, F, Co, and Pb when compared to an untreated material.

11. A process according to claim 3, wherein the purified gas is substantially free of chemicals of concern (CoCs) including acidic gases, volatile organic compounds (VOCs), and sulfur-containing compounds; optionally the acidic gases are halogenated gases including HCl, HBr, and HF; optionally the VOCs are propylene, 1,3-butadiene, chloromethane, bromomethane, chloroethane, and vinyl chloride; optionally the sulfur-containing compounds are sulfur oxides (SOx).

12. A process according to any one of claims 1 to 11, wherein the oil phase comprises monomers of degraded raw materials, which are classified into low boiling point oils such as gasoline (optionally in an amount of about 63.68%) and medium boiling point oils such as diesel (optionally in an amount of about 20.08%).

13. A process for recycling a contaminated plastic material, comprising the steps of:

(a) subjecting the material to a pre-treatment involving a dehalogenation agent (DHA) to yield a pre-treated material;

(b) subjecting the pre-treated material to a heating process to yield a solid phase, an oil phase, and a gas phase;

(c) separating the solid phase, the oil phase, and the gas phase;

(d) subjecting the gas phase to a purification treatment involving a further dehalogenation agent (DHA) to yield a purified gas and a reacted DHA;

(e) separating the purified gas and the reacted DHA;

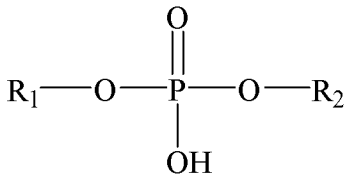
(f) subjecting the reacted DHA to a regeneration process to yield a regenerated DHA; and

(g) directing the regenerated DHA for use at steps (a) and/or step (d).

14. A process according to claim 13, wherein the DHA at step (a) and the further DHA at step (d) are the same or are different.

15. A process according to any one of claims 1 to 14, wherein the dehalogenation agent comprises an organophosphorus compound.

16. A process according to any one of claims 1 to 15, wherein the dehalogenation agent comprises a phosphoric acid ester of general formula **I** below

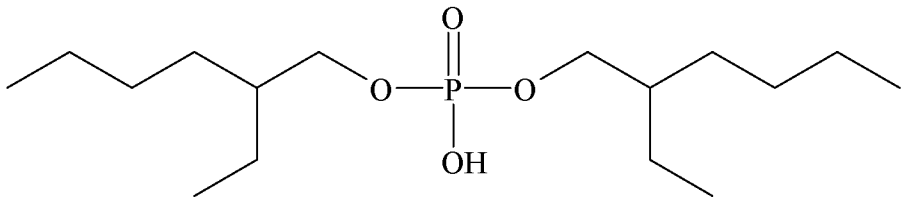


I

wherein R_1 and R_2 are each independently C_1 to C_{20} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

17. A process according to claim 16, wherein R_1 and R_2 are each independently a C_8 to C_{20} or a C_8 to C_{16} or a C_{16} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

18. A process according to any one of claims 1 to 17, wherein the dehalogenation agent comprises di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined below



DEHPA or HDEHP

19. A process according to any one of claims 1 to 17, wherein the dehalogenation agent comprises a compound selected from the group consisting of: di-(2-ethylhexyl) phosphoric acid, bis(2-ethylhexyl) hydrophosphoric acid, di-(2-ethylhexyl) orthophosphoric acid, O,O-

bis(2-ethylhexyl)phosphoric acid, orthophosphoric acid 2-ethylhexyl alcohol, phosphoric acid di(2-ethylhexyl) ester, and Hostarex PA 216™.

20. A process according to any one of claims 1 to 19, which yields a clean solid material, an oil comprising monomers of the raw material, and a purified gas substantially free of acidic gases, volatile organic compounds, and sulfur-containing compounds.

21. A process according to any one of claims 1 to 20, wherein the contaminated solid material is a contaminated plastic material.

22. A process according to any one of claims 1 to 20, wherein the contaminated solid material is an electronic waste (E-waste) plastic material.

23. A process according to any one of claims 1 to 20, wherein the heating is performed using microwave-pyrolysis.

24. A process for recycling contaminated solid material, comprising subjecting the material to a microwave-pyrolysis yielding a solid phase, an oil phase, and a gas phase, wherein the material is subjected to a pre-treatment involving a dehalogenation agent (DHA) prior to the microwave-pyrolysis.

25. A process according to claim 24, wherein a microwave absorber is added to the material prior to performing the microwave-pyrolysis; optionally the microwave absorber is a carbon-based compound such as SiC or carbon.

26. A process according to claim 25, wherein the microwave absorber and the material are melted prior to performing the microwave-pyrolysis; optionally, melting is performed using a technique which is microwave heating, conventional heating, extrusion, or a combination thereof.

27. A process according to any one of claims 24 to 26, wherein the contaminated solid material is a contaminated plastic material.

28. A process according to any one of claims 24 to 26, wherein the contaminated solid material is an electronic waste (E-waste) plastic material.

29. A process for purifying a gas emission, comprising allowing the gas emission to react with a dehalogenation agent (DHA) yielding a purified gas and a reacted DHA, and separating the purified and reacted DHA.

30. A process according to claim, further comprising subjecting the reacted DHA to a regeneration process to yield a regenerated DHA.

31. A process according to claim 30, further comprising re-using the regenerated DHA in the process.

32. A process according to any one of claims 29 to 31, wherein the gas emission is from a facility for combustion of E-waste, organic waste, oil, or coal.

33. A process according to any one of claims 29 to 31, wherein the gas emission is from a facility for recycling contaminated solid materials such as contaminated plastic material and contaminated electronic waste (E-waste) plastic materials.

34. A system adapted to perform the process as defined in any one of claims 1 to 33.

35. An industrial facility embodying the system as defined in claim 34.

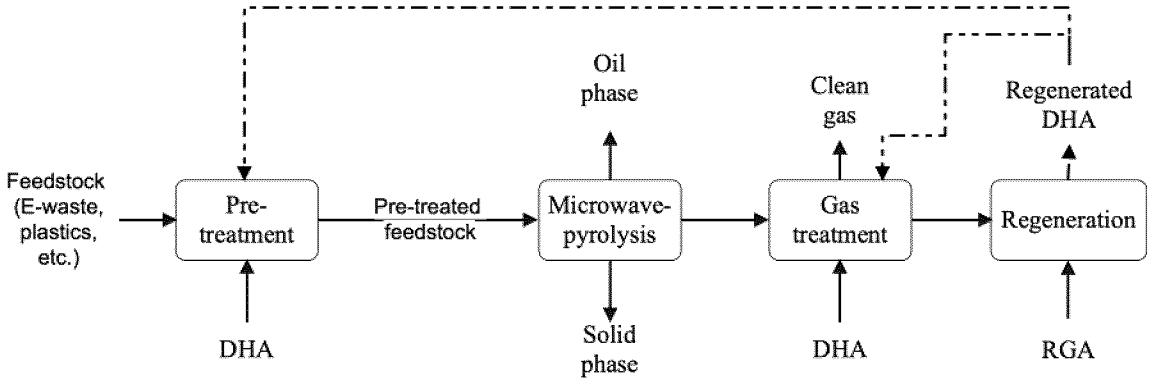


Figure 1

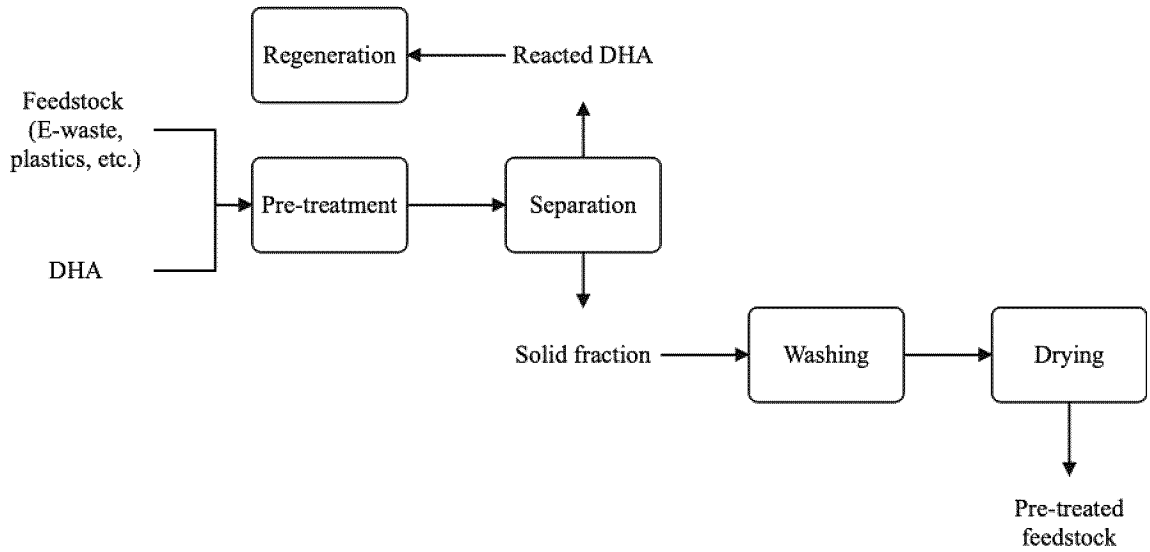


Figure 2

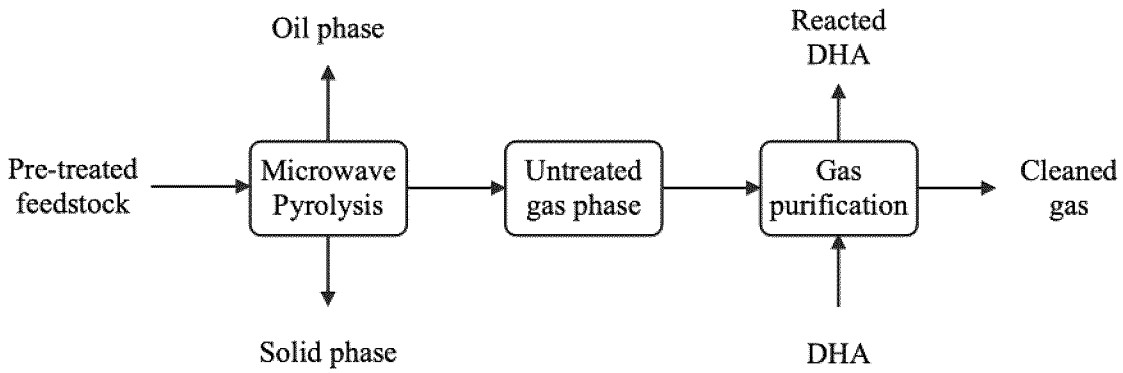


Figure 3

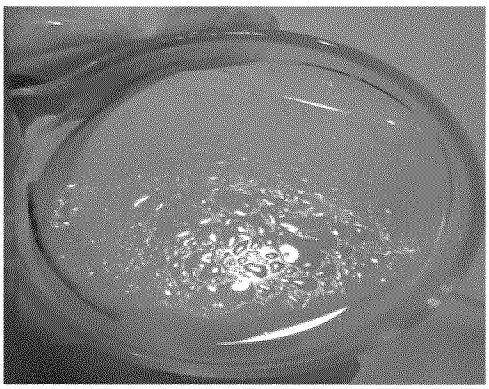


Figure 4

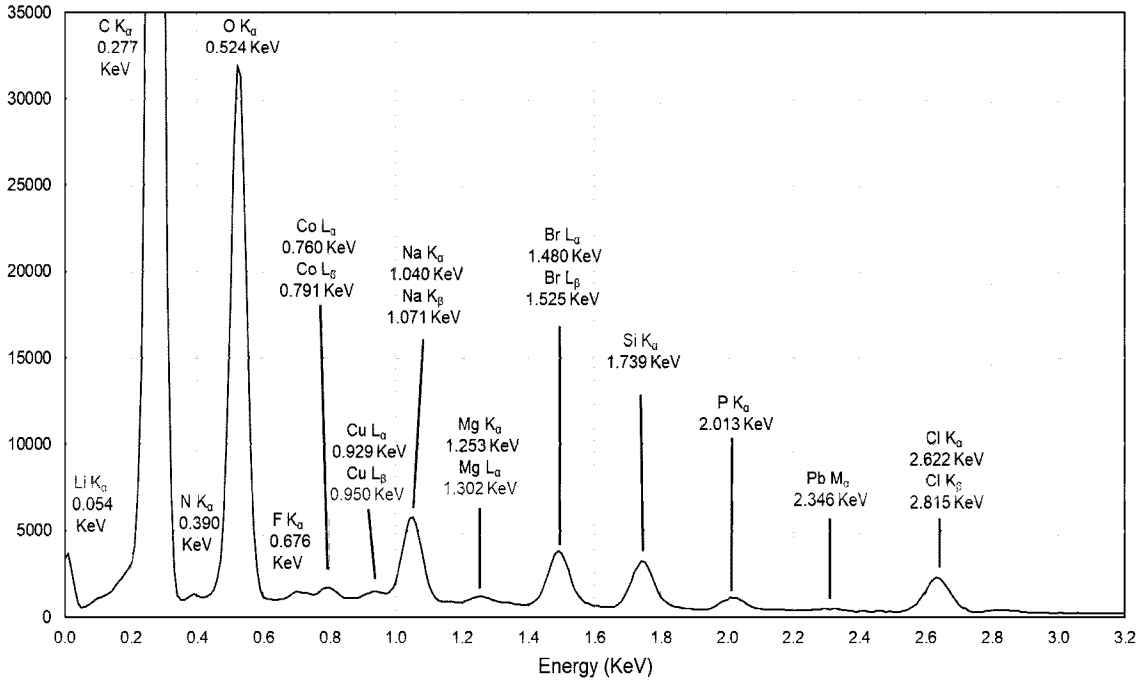


Figure 5

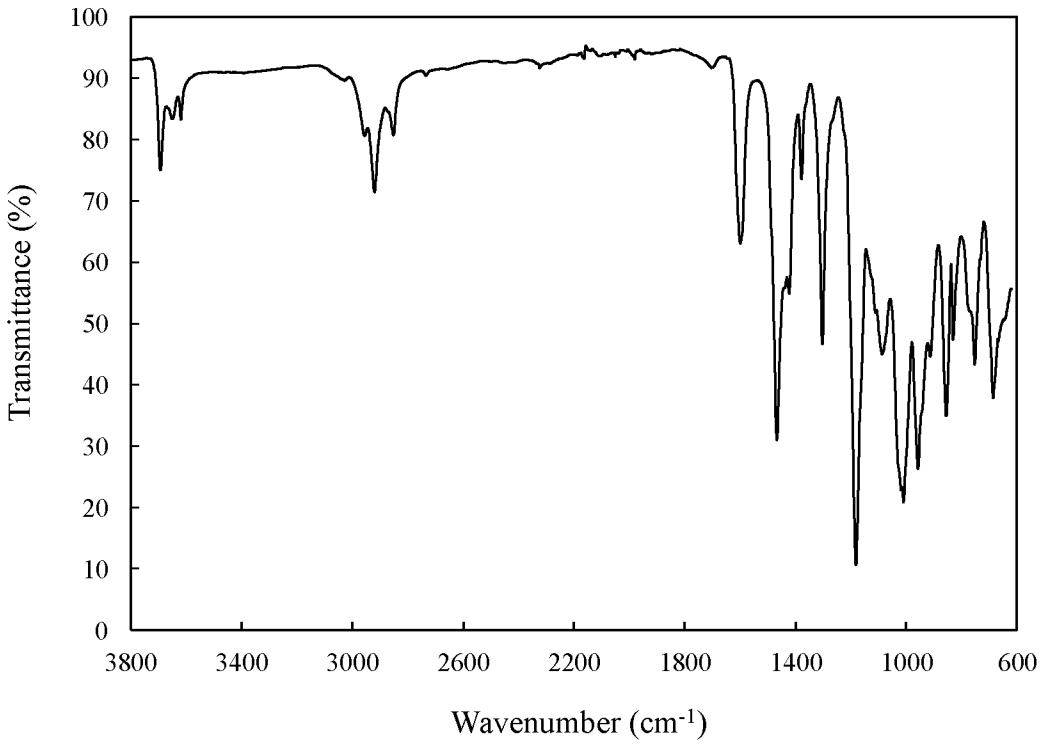


Figure 6

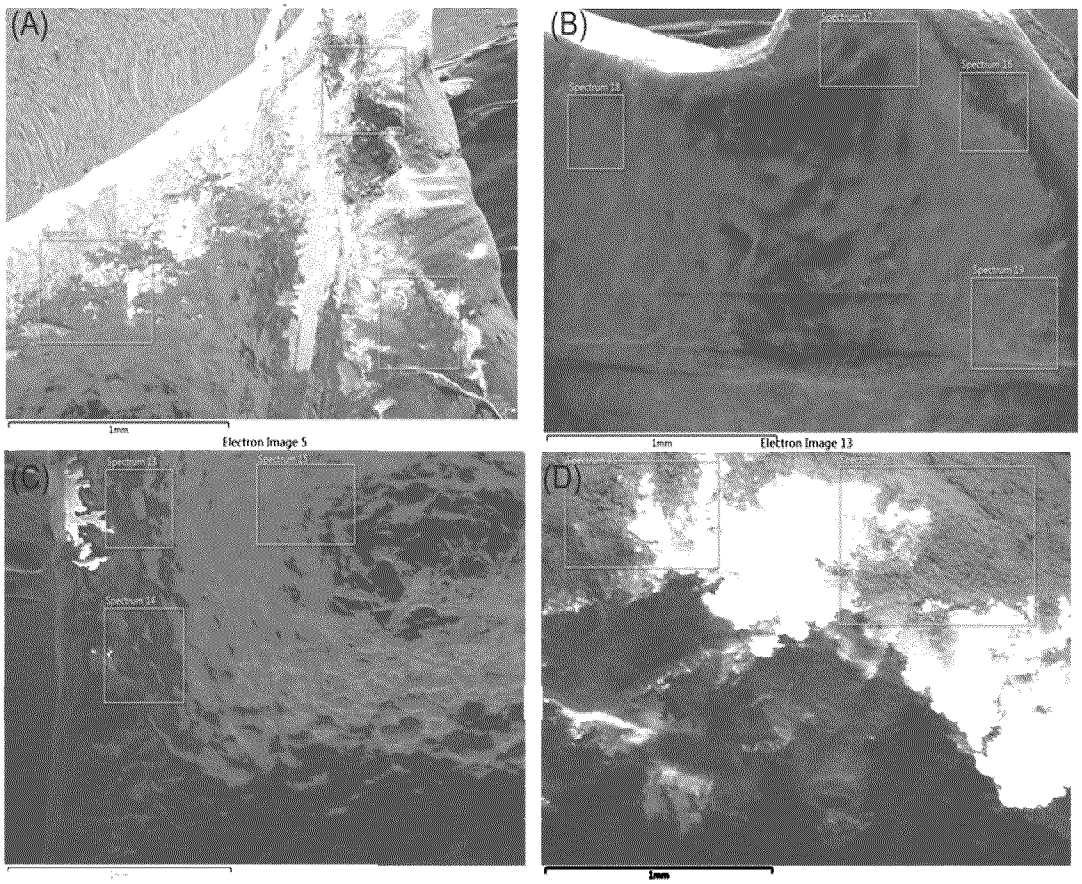


Figure 7

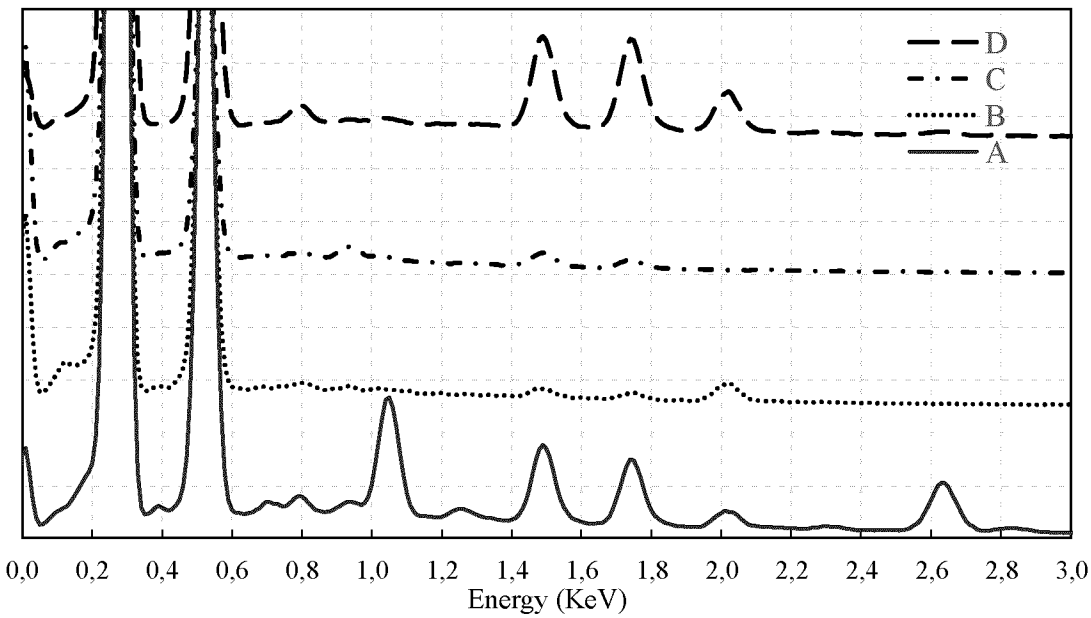


Figure 8

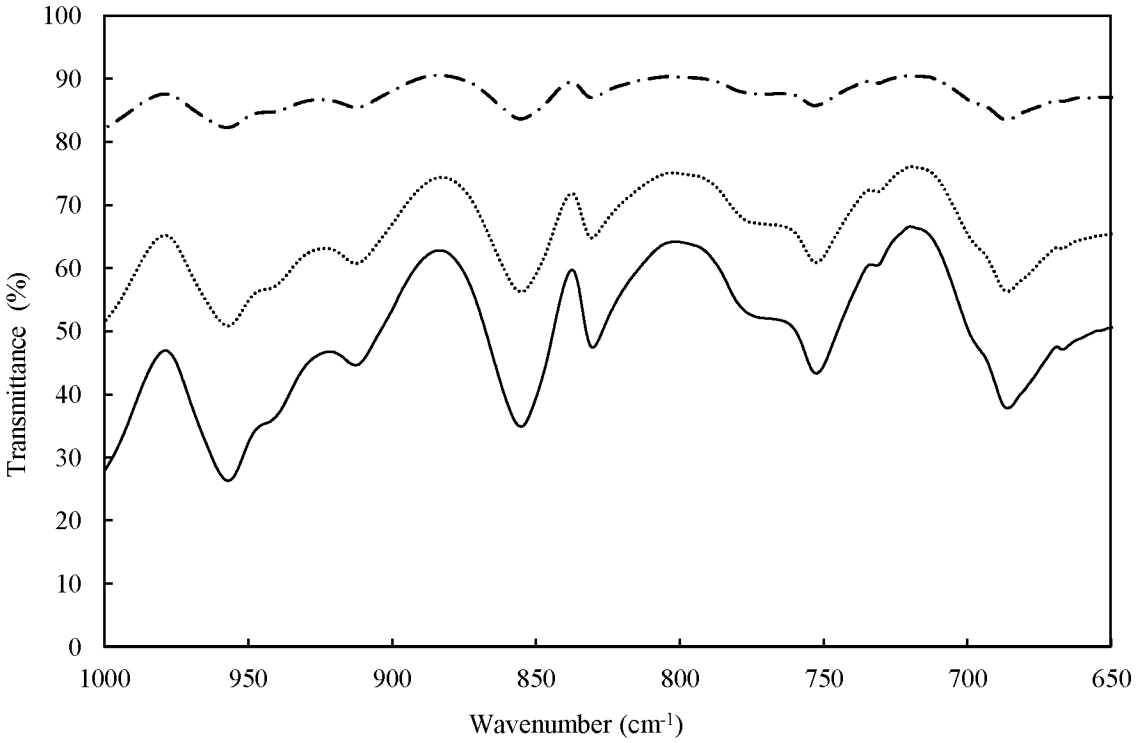


Figure 9

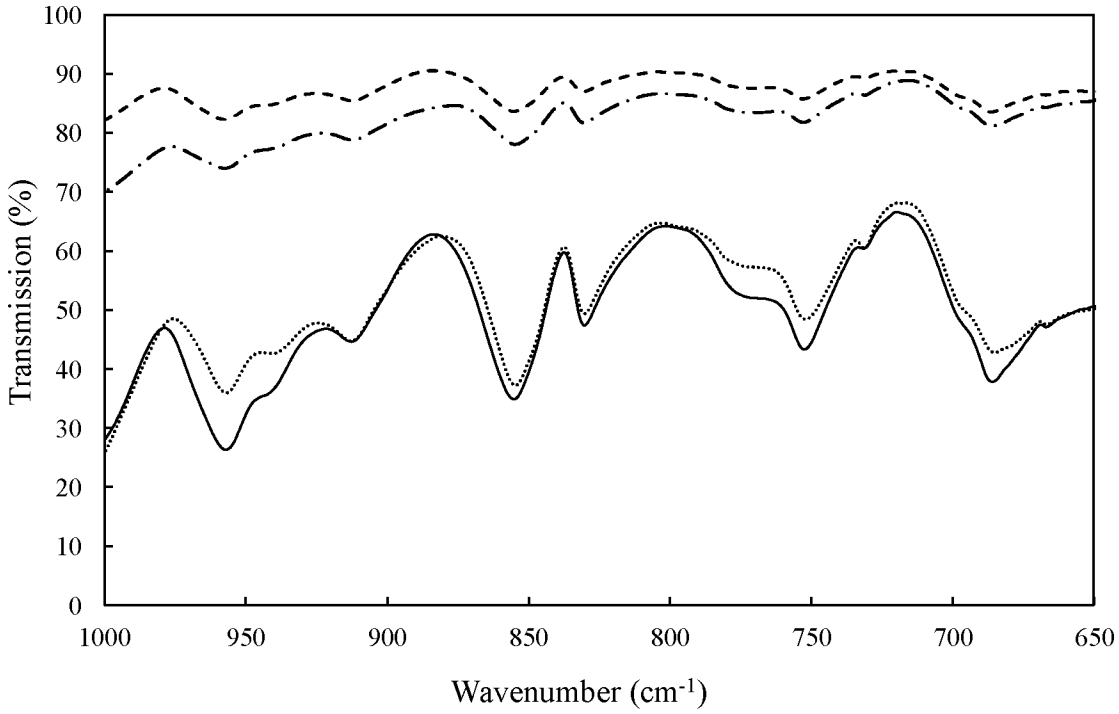


Figure 10

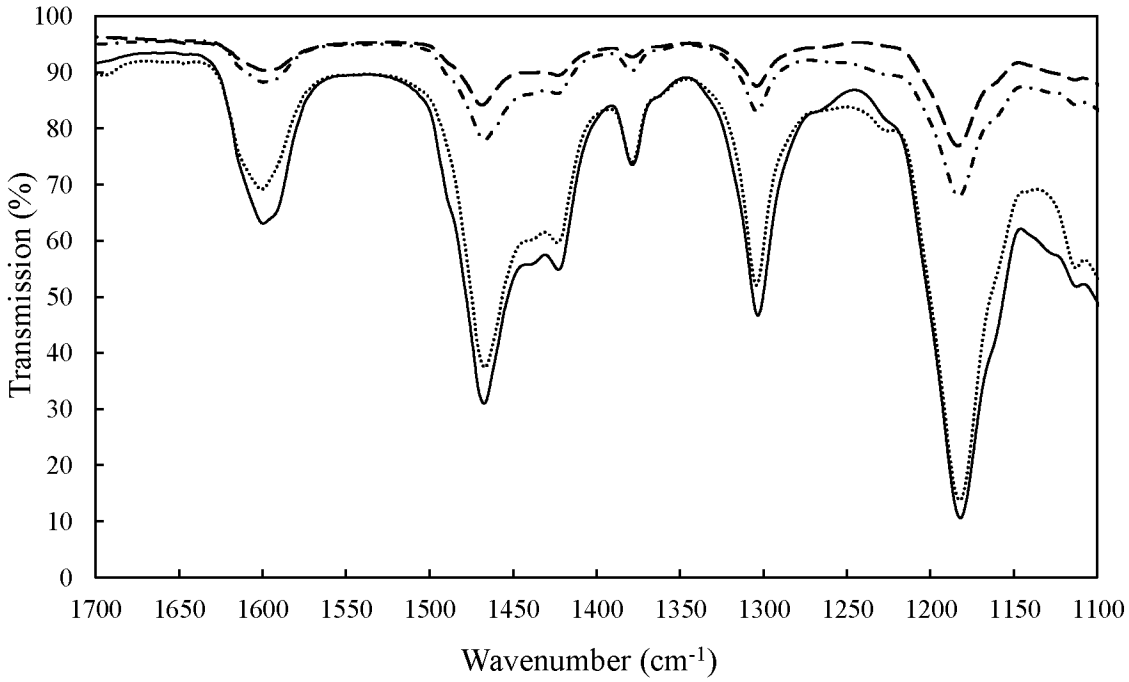


Figure 11

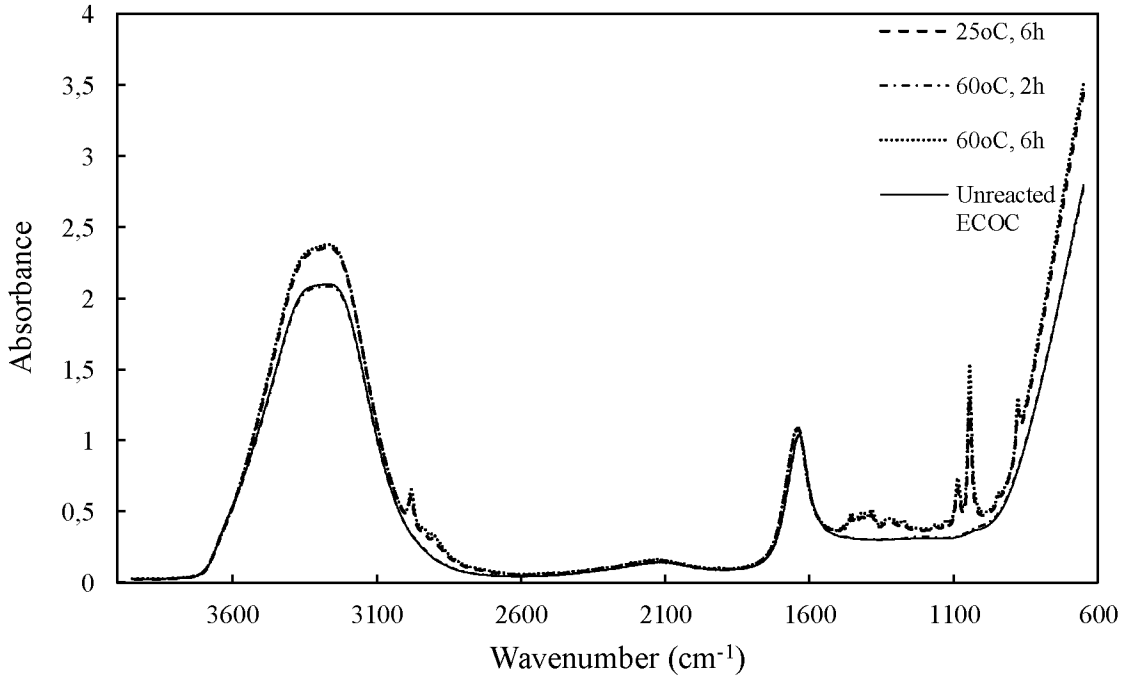


Figure 12

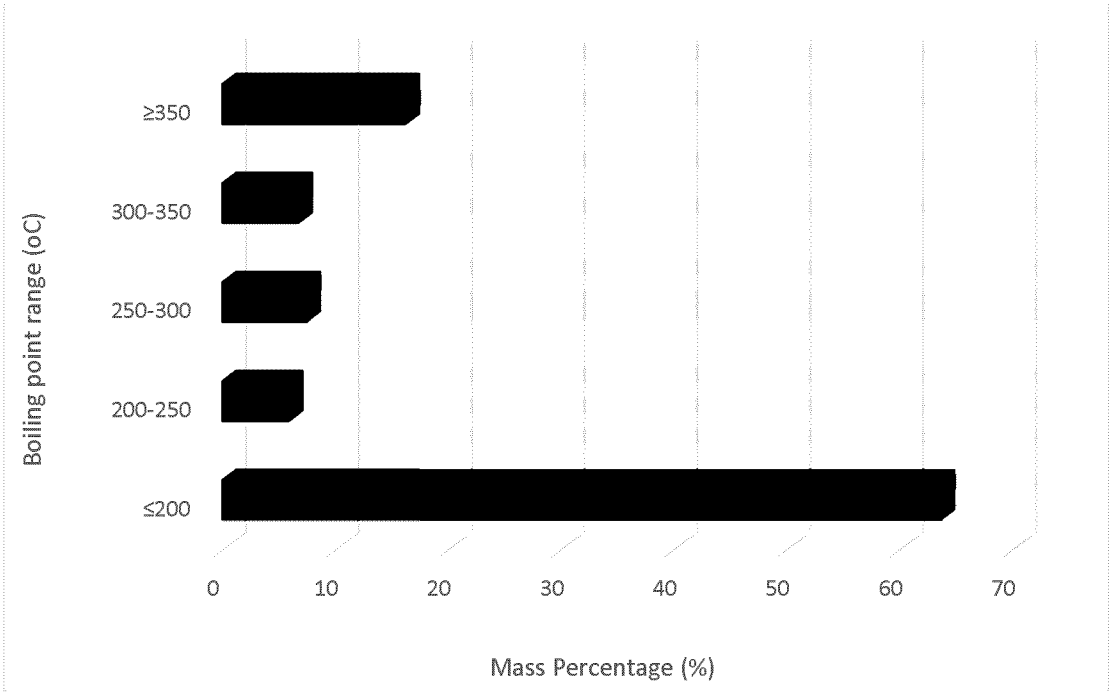


Figure 13

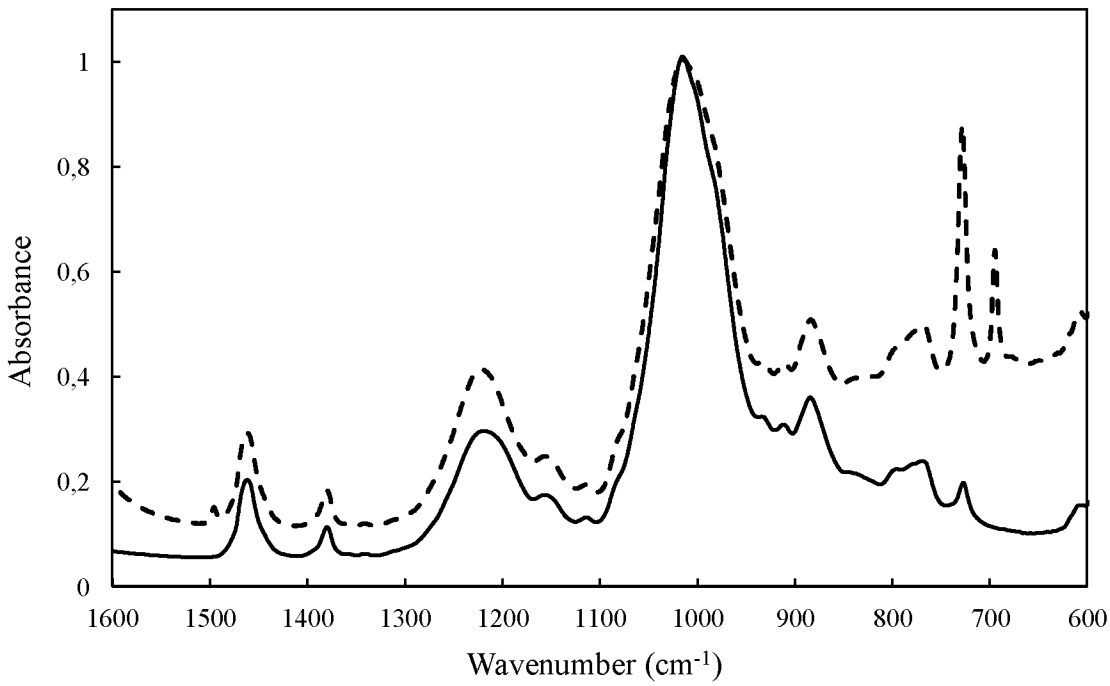


Figure 14

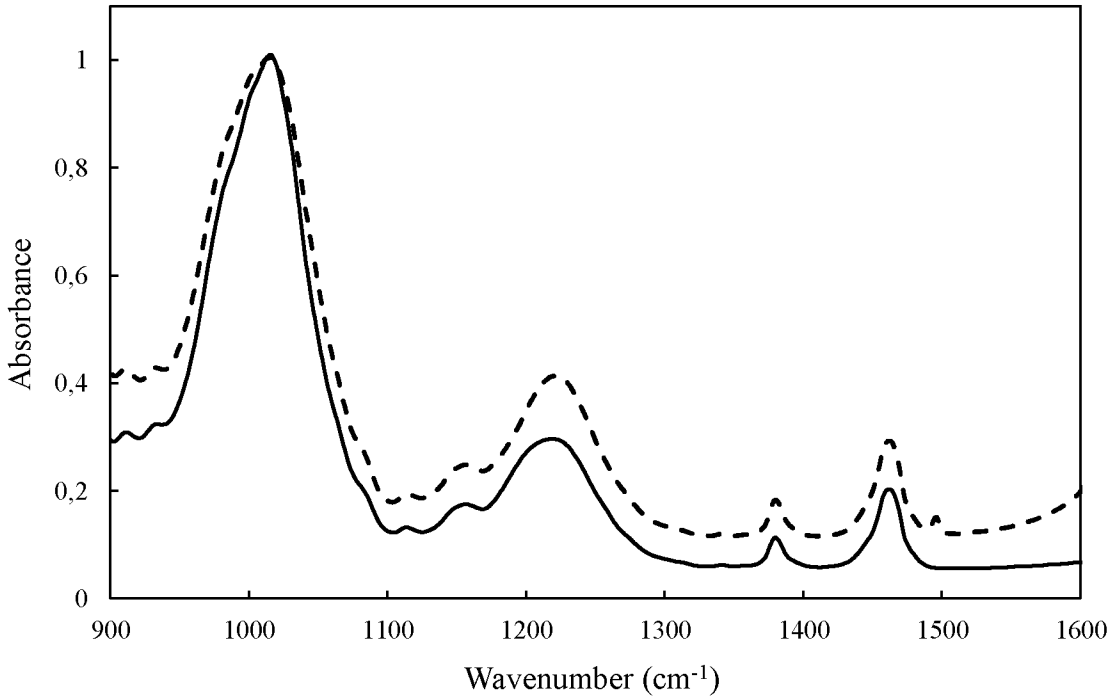


Figure 15

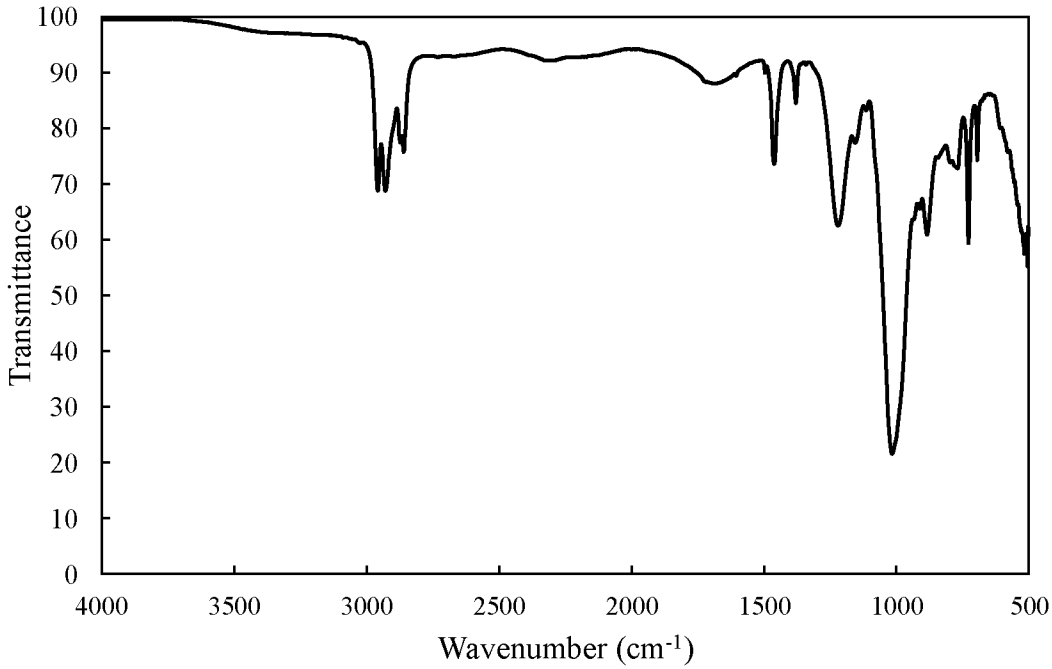
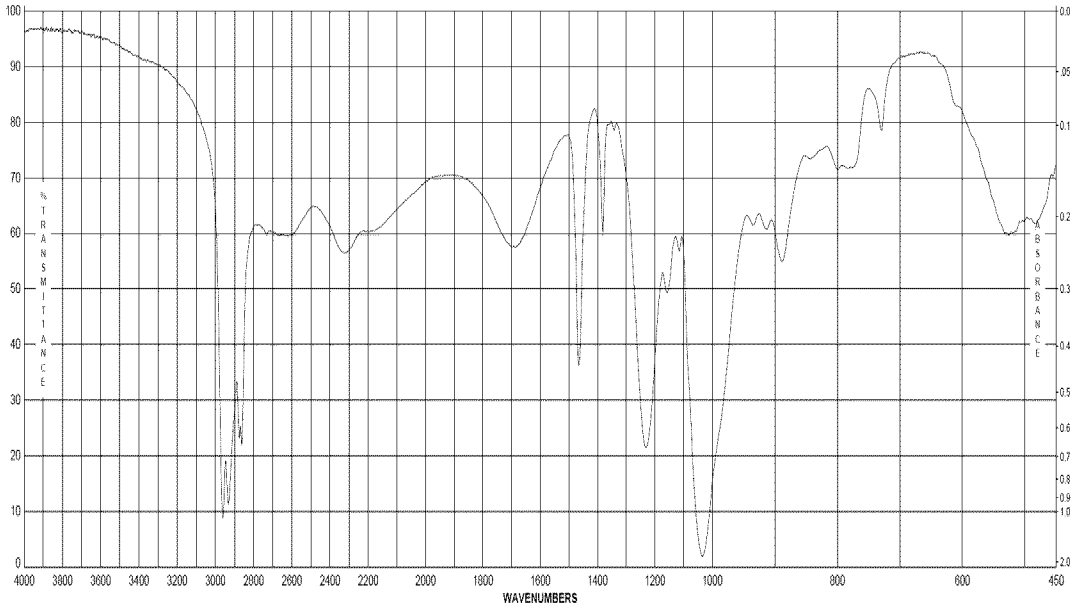


Figure 16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WAVENUMBERS

Figure 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2021/050700

A. CLASSIFICATION OF SUBJECT MATTER
IPC: **C08J 11/04** (2006.01) , ***A62D 3/40*** (2007.01) , ***B01D 53/68*** (2006.01) , ***B09B 3/00*** (2006.01) , ***B29B 17/00*** (2006.01) , ***C07B 63/02*** (2006.01), ***C08J 11/12*** (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: C08J 11/04 (2006.01), A62D 3/40 (2007.01), B01D 53/68 (2006.01), B09B 3/00 (2006.01), B29B 17/00 (2006.01), C07B 63/02 (2006.01), C08J 11/12 (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: Questel Orbit, Scopus, EBSCO
Keywords: dehalogenation, gas emission, phosphoric acid ester, DEHPA, HDEHP, microwave, pyrolysis, plastic, e-waste, weee

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO2021087059 A1 (WU, X. et al.) 06 May 2021 (06-05-2021) (see entire document)	1, 2, 7, 8, 24, 27, 34, 35
X	WO2019141504A1 (LUTHE, G. et al.) 25 July 2019 (25-07-2019) (see entire document)	1, 2, 7, 8, 24, 27, 34, 35
X	JP2002020535A (MORIMOTO, K.) 23 January 2002 (23-01-2002) (see entire document)	1, 2, 7, 8, 34, 35
X	XIAONING YANG, LUSHI SUN, JUN XIANG, SONG HU, SHENG SU, "*Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): A review*". Waste Management, 2013, Vol. 33, pp. 462-473, [available on 27 August 2012 (27-08-2012)]. (see entire document)	1, 2, 7, 8, 34, 35

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"D"	document cited by the applicant in the international application
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 22 July 2021 (22-07-2021)	Date of mailing of the international search report 05 August 2021 (05-08-2021)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Erin Todd (819) 639-9402

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YINGNA CHANG, YINGCHUN PANG, QIDONG DANG, ANUJ KUMAR, GUOXIN ZHANG, "*Converting Polyvinyl Chloride Plastic Wastes to Carbonaceous Materials via Room-Temperature Dehalogenation for High-Performance Supercapacitor*", ACS Applied Energy Materials, 12 September 2018 (12-09-2018), Vol. 1, pp. 5685-5693. (see entire document)	1, 2, 7, 8, 34, 35
X	CN102743963A (BUFANG, Z.) 24 October 2012 (24-10-2012) (see entire document)	29, 32, 34, 35
X	BRYAN C. DRAVIS, KEITH E. LEJEUNE, AMY D. HETRO, ALAN J. RUSSELL, "*Enzymatic Dehalogenation of Gas Phase Substrates with Haloalkane Dehalogenase*", Biotechnology and Bioengineering, 5 August 2000 (05-08-2000), Vol. 69(3), pp. 235-241. (see entire document)	29, 32, 34, 35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2021/050700

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

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

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

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:
See extra sheet.

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

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

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

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

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continuation of Box III.

The claims are directed to a plurality of inventive concepts as follows:

Group A - Claims 1, 2 (in full), 3-23 (in part), 24-28 (in full) and 34-35 (in part) are directed to a process for recycling contaminated solid material containing a pre-treatment involving a dehalogenation agent. Claims 13-28 define a process of pretreating waste with a dehalogenation agent, heating the material, separating the gas phase and purifying it with additional dehalogenation agent; and

Group B - Claims 3-23 (in part), 29-33 (in full) and 34-35 (in part) are directed to a process for purifying a gas emission with a dehalogenation agent. This process is also included in the process of claims 13-23.

The claims must be limited to one inventive concept as set out in PCT Rule 13. There is no common inventive linking feature between independent claims 1 and 24 with independent claim 29. Claims 1 and 24 define a process of dehalogenating **solid** waste prior to pyrolysis. Claim 13 defines the process of claim 1 and then a second step of further dehalogenating a gas emission. Claim 29 defines only the second step of dehalogenating a **gas** emission so claims 1, 24 and 29 are not linked at all except through claim 13 (i.e. claims 1 and 24 could be grouped with claim 13 and claim 13 could be grouped with claim 29). Since the dehalogenation agent is not a new compound (or even defined in the independent claims), there is no common inventive linking features in claims 1 and 29.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2021/050700

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