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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 May 2025 (15.05.2025)

WIPO | PCT

(10) International Publication Number
WO 2025/101481 A1

(51) International Patent Classification:
C08F 10/06 (2006.01) *C10B 53/07* (2006.01)
C08J 11/04 (2006.01)

(21) International Application Number:
PCT/US2024/054510

(22) International Filing Date:
05 November 2024 (05.11.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/597,309 08 November 2023 (08.11.2023) 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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, 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))*

(54) Title: PROCESSES FOR THE CONVERSION OF PLASTIC WASTE TO POLYPROPYLENE

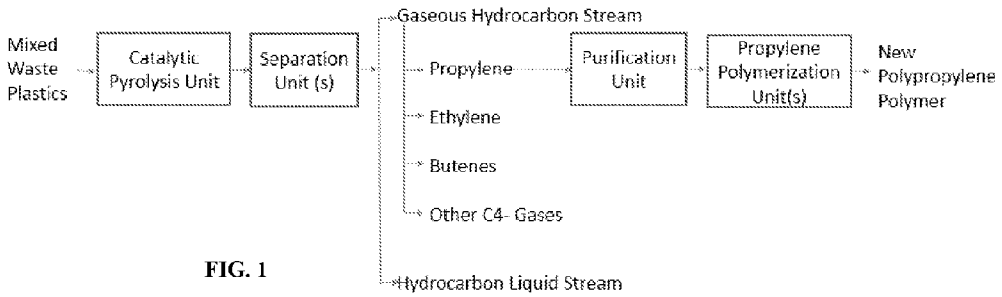

FIG. 1

(57) Abstract: A process of converting plastic waste to polypropylene includes (a) converting a plastic waste to a hydrocarbon liquid stream and a gaseous hydrocarbon stream in a catalytic pyrolysis unit, wherein the gaseous hydrocarbon stream is greater than about 60 wt% of the output, and the gaseous hydrocarbon stream contains greater than about 40 wt% light olefins; (b) introducing the gaseous hydrocarbon stream to one or more separating units to produce a first propylene stream, a first ethylene stream, a first butylene stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons; (c) optionally, feeding the first propylene stream to a purification unit to produce a polymer grade propylene stream; and (d) feeding the first propylene stream and if present, the polymer grade propylene stream, to a polymerization unit to produce polypropylene.

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PROCESSES FOR THE CONVERSION OF PLASTIC WASTE TO POLYPROPYLENE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Application No. 63/597,309 filed on November 8, 2023, the contents of which are incorporated by reference herein in their entirety.

FIELD

[0002] The present technology is generally related to the conversion of plastic waste to polypropylene. Specifically, the technology is related to using unit configurations to directly convert plastic waste to polypropylene and maximize polypropylene yield.

BACKGROUND

[0003] Catalytic pyrolysis, which involves the degradation of the polymeric materials by heating them in the absence of oxygen and in the presence of a catalyst, represents an attractive method for recycling plastic waste. While catalytic pyrolysis has been extensively studied, there remains a need to develop more efficient catalytic pyrolysis methods that maximize of the yield of desirable products, such as light olefins. In particular, propylene is a light olefin in high demand as it is used in many of the world's largest and fastest growing synthetic materials and thermoplastics.

[0004] This disclosure provides processes for the direct conversion of plastic waste to polypropylene with a series of connected process units. The processes described herein increase the net yield of propylene and decrease the required size of the catalytic pyrolysis unit to feed a given size polymerization unit, thereby reducing capital costs, operating costs, and separation and purification costs and also reducing the need to find additional outlets for the non-propylene products.

SUMMARY

[0005] In one aspect is a process of converting plastic waste to polypropylene, the process comprising:

(a) converting a plastic waste to a hydrocarbon liquid stream and a gaseous hydrocarbon stream in a catalytic pyrolysis unit, wherein the gaseous hydrocarbon stream is greater than about 60 wt% of the output, and the gaseous hydrocarbon stream contains greater than about 40 wt% light olefins;

(b) introducing the gaseous hydrocarbon stream to one or more separating units to produce a first propylene stream, a first ethylene stream, a first butylene stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons;

(c) optionally, feeding the first propylene stream to a purification unit to produce a polymer grade propylene stream; and

(d) feeding the first propylene stream and if present, the polymer grade propylene stream, to a polymerization unit to produce polypropylene.

[0006] In some embodiments, the process further comprises:

feeding the first ethylene stream and the first butylene stream to a metathesis unit to produce a second propylene stream, wherein metathesis unit comprises a metathesis catalyst;

combining the first propylene stream and second propylene to produce a combined propylene stream;

optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

[0007] In some embodiments, the process further comprising:

feeding the first ethylene stream and the first butylene stream to one or more separation units prior to feeding to first ethylene stream and the first butylene stream to a metathesis unit.

[0008] In some embodiments, converting a plastic waste also comprises producing a liquid products stream in a catalytic pyrolysis unit.

[0009] In some embodiments, the liquid products stream comprises one or more of paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. In some embodiments, the liquid products stream is recycled by feeding the steam back into the catalytic pyrolysis unit. In some embodiments, the liquid products stream is fed to a secondary cracking unit to produce a third propylene stream.

[0010] In some embodiments, the process further comprises:

combining the third propylene stream with the first propylene stream, the second propylene stream, or any combination thereof to produce a combined propylene stream;

optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

[0011] In some embodiments, the polypropylene is homopolymer polypropylene.

[0012] In some embodiments, the polymerization unit comprises one or more reactors. In some embodiments, additional ethylene or 1-butene is added to the polymer grade propylene stream before step (c). In some embodiments, feeding the polymer grade propylene stream with additional ethylene or 1-butene to a polymerization unit produces copolymer polypropylene. In some embodiments, the copolymer polypropylene is random copolymer polypropylene. In some embodiments, the copolymer polypropylene is impact copolymer polypropylene.

[0013] In some embodiments, the gaseous hydrocarbon stream in step (b) is separated by distillation. In some embodiments, isobutylene is removed from the first butylene stream after step (b).

[0014] In some embodiments, one or more of the first ethylene stream and the first butylene stream are purified to provide chemical or polymer grade ethylene stream, chemical or polymer grade butylene stream, and any combination thereof.

[0015] In some embodiments, the metathesis unit utilizes a catalyst comprising ruthenium or molybdenum.

[0016] In some embodiments, a petroleum-based olefin stream is not added to the hydrocarbon liquid stream after step (a). In some embodiments, a petroleum-based olefin stream is not added to the gaseous hydrocarbon stream after step (a). In some embodiments, a petroleum-based olefin stream is not added to the hydrocarbon liquid stream after step (a), and a petroleum-based olefin stream is not added to the gaseous hydrocarbon stream after step (a). In some embodiments, a petroleum-based olefin stream is not added the first propylene stream or combined propylene stream after step (b). In some embodiments, a petroleum-based olefin stream is not added to the polymer grade propylene stream before step (d).

[0017] Provided in another aspect is a polypropylene produced by a process of any one of the processes described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a schematic depiction of an exemplary embodiment of a process for converting plastic waste to polypropylene as described herein.

[0019] FIG. 2 is a schematic depiction of an exemplary embodiment of a process for converting plastic waste to polypropylene using a metathesis unit as described herein.

[0020] FIG. 3 is a schematic depiction of an exemplary embodiment of a process for converting plastic waste to polypropylene using a secondary cracking unit as described herein.

[0021] FIG. 4 is a schematic depiction of an exemplary embodiment of a process for converting plastic waste to polypropylene using a recycle loop as described herein.

DETAILED DESCRIPTION

[0022] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).

[0023] As used herein, "about" will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, "about" will mean up to plus or minus 10% of the particular term.

[0024] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential.

[0025] Disclosed herein are processes for directly converting plastic waste to polypropylene by using a series of connected process units. Specifically, these processes described herein involve using unit configurations to maximize polypropylene yield from the catalytic pyrolysis of plastic waste. Specifically, the processes described herein combine at least

a catalytic pyrolysis unit and a polymerization unit. The catalytic pyrolysis unit takes the plastic waste and converts it to ethylene, propylene, and butenes, wherein the propylene can be added to the propylene polymerization unit. As described herein, a metathesis unit, a secondary cracking unit, and/or a recycle loop may be used to increase the net yield of propylene.

[0026] As demonstrated in the Examples, the addition of the metathesis unit and/or a secondary cracking unit decreases the required size of the catalytic pyrolysis unit to feed a given size polymerization unit, thereby reducing capital costs and operating costs. Another advantage of the processes described herein is that the conversion of waste plastics to polypropylene is in one location, thus leaving no ambiguity that the polypropylene is 100% recycled content. In contrast, almost every other approach requires a mathematical "mass-balance" approach to estimate recycled content.

[0027] FIG. 1 illustrates an embodiment of the processes disclosed herein for the direct conversion of plastic waste to polypropylene. Examples of suitable plastic waste include, but are not limited, to those comprising non-chlorinated plastics (e.g., polyolefins, polyethylene, polypropylene, polystyrene, copolymers, etc.), chlorinated plastics (e.g., polyvinylchloride (PVC), polyvinylidene chloride (PVDC), etc.), and the like, or mixtures thereof. Other examples of plastic waste include at least one of polyethylene, polypropylene, polystyrene, polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide, polycarbonate, polyurethane, polyester, natural and synthetic rubber, tires, filled polymers, composites, and plastic alloys.

[0028] As shown in FIG. 1, the plastic waste is loaded into or fed into a catalytic pyrolysis unit to produce a hydrocarbon liquid stream and a gaseous hydrocarbon stream. The catalytic pyrolysis unit may be any suitable vessel configured to convert waste plastics into gas phase and liquid phase products (e.g., simultaneously). The vessel may be configured for gas phase, liquid phase, vapor-liquid phase, gas-solid phase, liquid-solid phase, or slurry phase operation. The vessel may contain one or more beds of inert material or pyrolysis catalyst comprising sand, zeolite, alumina, a catalytic cracking catalyst, or combinations thereof. These

beds may be fluidized , rotating, moving, or screw conveyor beds. In some embodiments, motion of the bed may be used to assist in catalyst regeneration over time.

[0029] The hydrocarbon liquid stream may comprise C_6+ hydrocarbons, including paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. Examples of paraffins that may be present in the hydrocarbon liquid stream include, but are not limited to, C_1 to C_{22} n-paraffins and i-paraffins. Examples of olefins that may be present in hydrocarbon liquid stream include, but are not limited to, C_2 to C_{10} olefins and combinations thereof. Examples of naphthenes that may be present in the hydrocarbon liquid stream include, but are not limited to, cyclopentane, cyclohexane, cycloheptane, and cyclooctane. Nonlimiting examples of aromatic hydrocarbons present in the hydrocarbon liquid stream include benzene, toluene, xylenes, ethylbenzene, propylbenzenes, trimethylbenzenes, tetramethylbenzenes, butylbenzenes, dimethylnaphthalene, biphenyl, and the like, or combinations thereof.

[0030] The gaseous hydrocarbon stream may comprise C_2-C_5 hydrocarbons, including propylene, ethylene, butylene, C_1 to C_4 saturated hydrocarbons, and any combination thereof. As shown in the Figure 1, the gaseous hydrocarbon stream is introduced to a separating unit to produce a propylene stream, a ethylene stream, a butylene stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons.

[0031] The gaseous hydrocarbon stream may be greater than about 60 wt% of the output, including greater than about 65 wt%, greater than about 70 wt%, greater than about 75 wt%, greater than about 80 wt%, greater than about 85 wt% of the output, greater than about 90 wt%, greater than about 95 wt%, and greater than about 99 wt%. The gaseous hydrocarbon stream may be from about 60 wt% to about 95 wt% of the output, including from about 60 wt% to about 99 wt% of the output, from about 60 wt% to about 99.9 wt% of the output, and from about 60 wt% to about 99.99 wt% of the output. In some embodiments, the gaseous hydrocarbon stream may be about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, about 80 wt%, about 85

wt%, about 90 wt%, about 95 wt%, about 99 wt%, about 99.9 wt%, or about 99.99 wt% of the output.

[0032] The gaseous hydrocarbon stream may comprise greater than about 40 wt% light olefins (e.g., ethylene, propylene, and butylene), including greater than about 45 wt%, greater than about 50 wt%, greater than about 55 wt%, greater than about 60 wt%, greater than about 65 wt%, and greater than about 70 wt%. The gaseous hydrocarbon stream may comprise from about 40 wt% to about 70 wt% light olefins (e.g., ethylene, propylene, and butylene) Including about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, and about 70 wt%.

[0033] The one or more separating units can be any suitable separating units configured to separate the gaseous hydrocarbon stream into a propylene stream, a ethylene stream, a butylene stream, and a saturated gas stream. For example, the one or more separating units may employ distillation columns, cryogenic distillation columns, extractive distillation columns, selective adsorption units, selective absorption units, and the like, or combinations thereof.

[0034] As shown in FIG. 1, the propylene stream may then be optionally fed to a purification unit to produce a polymer grade or chemical grade propylene stream prior to feeding the propylene polymerization unit(s). The purification unit may comprise any suitable purification unit suitable for converting plastic waste to polypropylene. The polymer grade propylene stream may then be fed polymerization unit to produce polypropylene polymer. The polymerization unit may comprise one or more any suitable polymerization reactors suitable for converting plastic waste to polypropylene and to produce many different types of polypropylene grades.

[0035] Prior to feeding the polypropylene steam to the polymerization unit(s), it is possible to add either additional ethylene or 1-butene to the polypropylene steam, which may be further purified to provide chemical or polymer grade ethylene or 1-butene stream. Feeding the polypropylene steam with additional ethylene or 1-butene to a polymerization unit(s) comprising one or more polymerization reactors produces copolymer polypropylene (e.g., random

copolymer polypropylene and impact copolymer polypropylene). For instance, impact copolymer polypropylene may be produced by producing pure propylene in the first reactor and then propylene and ethylene in the second reactor.

[0036] FIG. 2 is another illustrative embodiment using a metathesis unit. As shown in FIG. 2, the ethylene stream and/or the butylene stream from the separating unit may be feed to a metathesis unit to produce a second propylene stream comprising propylene. In some instances, the ethylene stream and/or the butylene stream may be fed to a purification unit to provide a chemical or polymer grade ethylene and or butylene stream. The use of the metathesis reaction to convert ethylene and butylenes streams to propylene maximizes the propylene yields. The metathesis unit comprises a metathesis reactor comprising a metathesis catalyst. Generally, olefin metathesis refers to a reaction that entails redistribution of olefin fragments by scission and regeneration of carbon-carbon double bonds, a process also known as transalkylidenation. Olefins Conversion Technology (OCT) of Lummus Technology provides an example of olefin metathesis for the conversion of ethylene and butylenes to propylene.

[0037] The metathesis unit may comprise any suitable metathesis reactor, such as a continuous flow reactor, a batch reactor, a fixed bed reactor, a fluidized bed reactor, a catalytic distillation column reactor, and the like, or combinations thereof. The metathesis unit may be operated at conditions suitable for ethylene and butylenes metathesis to propylene, such as temperatures of equal to or greater than about 50° C., alternatively equal to or greater than about 100° C., alternatively equal to or greater than about 150° C., or alternatively equal to or greater than about 200° C.; pressures of from about 1 psi to about 1,500 psi, alternatively from about 10 psi to about 1,000 psi, or alternatively from about 25 psi to about 500 psi; and WHSVs of from about 0.1 hr^{-1} to about 100 hr^{-1}, alternatively from about 1 hr^{-1} to about 50 hr^{-1}, or alternatively from about 5 hr^{-1} to about 25 hr^{-1}.

[0038] Nonlimiting examples of metathesis catalysts suitable for use in the present disclosure include organometallic compounds, Schrock catalysts, molybdenum alkylidenes, tungsten alkylidenes, Grubbs' catalysts, ruthenium carbenoid complexes, ruthenium carbenoid

complexes modified with a chelating isopropoxystyrene ligand, Hoveyda catalysts, diphenylalkylamino based catalysts, and the like, or combinations thereof. Examples of suitable catalysts include those comprising ruthenium or molybdenum.

[0039] As shown in FIG. 2, the propylene stream produced from the metathesis unit (e.g., second propylene stream) may then be combined with propylene stream that is produced from the separation unit (e.g., first propylene stream) to provide a combined propylene stream. The combined propylene stream may optionally, then be fed to a purification unit to produce a polymer grade or chemical grade combined propylene stream. The purification unit may comprise any suitable purification unit suitable for converting plastic waste to polypropylene. The polymer grade combined propylene stream may then be fed polymerization unit to produce polypropylene polymer. The polymerization unit may comprise any suitable polymerization reactor suitable for converting plastic waste to polypropylene.

[0040] Prior to feeding the combined polypropylene steam to the polymerization unit, it is possible to add either additional ethylene or 1-butene to the combined polypropylene steam, which may be further purified to provide chemical or polymer grade ethylene or 1-butene stream. Feeding the polypropylene steam with additional ethylene or 1-butene to a polymerization unit comprising one or more reactors produces copolymer polypropylene (e.g., random copolymer polypropylene and impact copolymer polypropylene).

[0041] FIG. 3 shows another illustrative embodiment using a secondary cracking unit. As shown in FIG. 3, converting a plastic waste also comprises producing a liquid products stream in a catalytic pyrolysis unit. In some embodiments, the liquid products stream comprises one or more of paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. In some embodiments, the liquid products stream may be purified by removing benzene, toluene, xylene, and/or any aromatic compounds before feeding the liquid products stream into a secondary cracking unit. This pre-separation of aromatics, which is efficient from a capital size and selectivity perspective, is preferred but not required. A secondary cracking unit is a chemical conversion process designed to intake light hydrocarbon

liquids having boiling range between 30 °C and 250°C, and produces a mixed stream of gases and liquids of significantly reduced molecular weight, including propylene. The conversion is achieved by contacting the light hydrocarbon liquids with a catalyst, at a temperature between 400°C and 600°C. As shown in FIG. 3, feeding the liquid products stream into a secondary cracking unit produces a propylene stream that may be combined with the first propylene stream. Propylene yields from this process could range from 5 wt% to 30 wt%, and can be adjusted based on unit operating variables and catalyst quality. Several commercial processes serve this need. One specific embodiment of this process is the MAXOFIN™ catalytic olefins technology offered by KBR.

[0042] FIG. 4 shows another illustrative embodiment using a recycle loop unit. As shown in FIG. 4, converting a plastic waste also comprises producing a liquid products stream in a catalytic pyrolysis unit. In some embodiments, the liquid products stream comprises one or more of paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. As shown in FIG. 4, the liquid products stream may be fed back to the catalytic pyrolysis unit.

[0043] While this disclosure discusses the above process in the context of a single catalytic pyrolysis unit; a single separation unit; a single metathesis unit; a single purification unit; and polymerization unit; etc., it should be understood that any suitable configurations for the production of propylene from plastic waste can be used, wherein any given configuration for may comprise 1, 2, or more catalytic pyrolysis units; 1, 2, or more separation units; 1, 2, or more metathesis units; 1, 2, or more purification units; 1, 2, or more metathesis units; etc.

[0044] Provided in one aspect is a process of converting plastic waste to polypropylene. The process includes (a) converting a plastic waste to a hydrocarbon liquid stream and a gaseous hydrocarbon stream in a catalytic pyrolysis unit, wherein the gaseous hydrocarbon stream is greater than about 60 wt% of the output, and the gaseous hydrocarbon stream contains greater than about 40 wt% light olefins; (b) introducing the gaseous hydrocarbon stream to one or more separating units to produce a first propylene stream, a first ethylene stream, a first butylene

stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons; (c) optionally, feeding the first propylene stream to a purification unit to produce a polymer grade propylene stream; and (d)feeding the first propylene stream and if present, the polymer grade propylene stream, to a polymerization unit to produce polypropylene.

[0045] In some embodiments, the process further includes feeding the first ethylene stream and the first butylene stream to a metathesis unit to produce a second propylene stream, wherein metathesis unit comprises a metathesis catalyst; combining the first propylene stream and second propylene to produce a combined propylene stream; and optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

[0046] In some embodiments, the process further includes feeding the first ethylene stream and the first butylene stream to one or more separation units prior to feeding to first ethylene stream and the first butylene stream to a metathesis unit.

[0047] The converting of the plastic waste may also include producing a liquid products stream in a catalytic pyrolysis unit. In some embodiments, liquid products stream includes one or more of paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. In some embodiments, the liquid products stream is recycled by feeding the steam back into the catalytic pyrolysis unit.

[0048] The liquid products stream may be fed to a secondary cracking unit to produce a third propylene stream. In some embodiments, the process includes combining the third propylene stream with the first propylene stream, the second propylene stream, or any combination thereof to produce a combined propylene stream; and optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

[0049] The polypropylene may be a homopolymer of polypropylene.

[0050] In some embodiments, the polymerization unit includes one or more reactors. Additional ethylene or 1-butene is added to the polymer grade propylene stream before the

optional step of feeding the first propylene stream to a purification unit. Feeding the polymer grade propylene stream with additional ethylene or 1-butene to a polymerization unit may produce a copolymer of polypropylene and the ethylene or 1-butene. In some embodiments, the copolymer polypropylene is random copolymer polypropylene. In some embodiments, the copolymer polypropylene is impact copolymer polypropylene.

[0051] In some embodiments, the gaseous hydrocarbon stream is separated by distillation.

[0052] In some embodiments, isobutylene is removed from the first butylene stream after the introducing step. One or more of the first ethylene stream and the first butylene stream may be purified to provide chemical or polymer grade ethylene stream, chemical or polymer grade butylene stream, or any combination of two or more thereof.

[0053] In some embodiments, the metathesis unit utilizes a catalyst comprising ruthenium or molybdenum.

[0054] In some embodiments, a petroleum-based olefin stream is not added to the hydrocarbon liquid stream. In some embodiments, a petroleum-based olefin stream is not added to a gaseous hydrocarbon stream after step (a). In some embodiments, a petroleum-based olefin stream is not added to the hydrocarbon liquid stream and a gaseous hydrocarbon stream after step (a). In some embodiments, a petroleum-based olefin stream is not added the first propylene stream or combined propylene stream after step (b). In some embodiments, a petroleum-based olefin stream is not added to the polymer grade propylene stream before step (d).

[0055] Provided in another aspect is a process of converting plastic waste to polypropylene. The process may include (a) converting a plastic waste to a hydrocarbon liquid stream and a gaseous hydrocarbon stream in a catalytic pyrolysis unit, wherein the gaseous hydrocarbon stream is greater than about 60 wt% of the output, and the gaseous hydrocarbon stream contains greater than about 40 wt% light olefins; (b) introducing the gaseous hydrocarbon stream to a first separating unit to produce a first propylene stream, a first ethylene stream, a first

butylene stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons; (c) feeding the first ethylene stream and the first butylene stream to a metathesis unit to produce a second propylene stream, wherein the metathesis unit comprises a metathesis catalyst; (d) combining the first propylene stream and second propylene to produce a combined propylene stream; (e) optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream; and (f) feeding the polymer grade propylene stream to a polymerization unit to produce polypropylene.

[0056] Converting the plastic waste may include producing a liquid products stream in a catalytic pyrolysis unit. In such embodiments, the liquid products stream may include one or more of paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof. The liquid products stream is fed to a secondary cracking unit to produce a third propylene stream. The process may also include combining the third propylene stream with the first propylene stream, the second propylene stream, or any combination thereof to produce a combined propylene stream; and optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

[0057] Also provided herein is a polypropylene produced by any one of the processes described herein.

[0058] The present invention, thus generally described, will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting of the present invention.

EXAMPLES

[0059] **Example 1**. FIG. 2 illustrates an embodiment of the process for converting plastic waste to polypropylene in accordance with this disclosure, which utilizes a catalytic pyrolysis unit, a olefins metathesis unit and a polymerization unit for the conversion of plastic waste to polypropylene.

[0060] A catalytic pyrolysis unit can convert a mixed waste plastic directly to light olefins and other valuable products. For example, with a ZSM-5 based catalyst, polypropylene can be converted into following compounds as shown in the below table.

	Output of Catalytic Pyrolysis as wt% of Input Plastic
Ethylene	8
Propylene	25
1-Butene	3
Other Butenes (including cis/trans-2-butene)	14
Other Gases	16
Other Liquids	9
Benzene	1
Toluene	9
Xylene	8

These wt% do not add to 100% because between 5 and 10% of the plastic is used to create heat for the endothermic reaction.

[0061] A propylene polymerization reactor is designed to take a propylene feed. For some products, a co-polymerization of propylene and ethylene, or a co-polymerization of propylene and 1-butene can be performed.

[0062] A propylene polymerization reactor of 20KTA would need an 80KTA catalytic pyrolysis unit to match the propylene output and input, while about 75% of the products of the catalytic pyrolysis unit would need to find another outlet. These products (ethylene, butenes, benzene, toluene, xylene) are marketable because they are made with recycled content and could be used to create recycled polymers.

[0063] A metathesis unit may be used to react ethylene and cis/trans-2-butene to form propylene. Thus, if cis/trans-2-butene was approximately 8 wt% of the "other butenes" from the above table, the net amount of propylene created as a wt% of plastic waste input would be 16% + 25% = 40%.

[0064] At 40%, the size of the catalytic pyrolysis unit would need to be 50 KTA to match the propylene input of a 20 KTA polymerization unit. That is the addition of a metathesis unit decreases the required size of the catalytic pyrolysis unit to feed a given size polymerization reactor. This smaller unit for the catalytic pyrolysis unit would save capital cost, operating costs, reduced separation and purification costs, and reduce the need to find additional outlets for the non-propylene products.

[0065] **Example 2**. This example illustrates an embodiment of the process for converting plastic waste to polypropylene in accordance with this disclosure, which utilizes a catalytic pyrolysis unit, a olefins metathesis unit, a polymerization unit, and a secondary cracking unit for the conversion of plastic waste to polypropylene (see FIGS. 2 and 3).

[0066] To further increase propylene yield, a secondary cracking unit, which converts light hydrocarbon liquids, preferably paraffinic in nature, to propylene, may be used. A secondary cracking unit is a chemical conversion process designed to intake light hydrocarbon liquids having boiling range between 30 °C and 250°C, and produces a mixed stream of gases and liquids of significantly reduced molecular weight. The conversion is achieved by contacting the light hydrocarbon liquids with a catalyst, at a temperature between 400°C and 600°C. Propylene yields from this process could range from 5 wt% to 30 wt%, and can be adjusted based on unit operating variables and catalyst quality. Several commercial processes serve this need. One specific embodiment of this process is the MAXOFIN™ catalytic olefins technology offered by KBR. In the reaction scheme shown in FIG. 3, the benzene, toluene, and xylene may be separated from the light hydrocarbon liquid stream before the stream enters into the secondary cracking unit. This pre-separation of aromatics, which is efficient from a capital size and selectivity perspective, is preferred but not required.

[0067] This disclosure describes two methods for increasing propylene yield between a catalytic pyrolysis unit and an olefin polymerization unit. The application of these methods can be done together as they treat different streams, or singly (i.e., only a metathesis unit or only a secondary cracking unit).

[0068] If both a metathesis unit and a secondary cracking unit are employed, this could increase the propylene yield to 45% on the input plastic. At 45%, the size of the catalytic pyrolysis unit would need to be 44 KTA to match the propylene input of a 20 KTA polymerization unit. That is the addition of a metathesis unit decreases the required size of the catalytic pyrolysis unit to feed a given size polymerization reactor. This smaller unit for the catalytic pyrolysis unit would save capital cost, operating costs, reduced separation and purification costs, and reduce the need to find additional outlets for the non-propylene products.

[0069] While certain embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

[0070] The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising," "including," "containing," etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the claimed technology. Additionally, the phrase "consisting essentially of" will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase "consisting of" excludes any element not specified.

[0071] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such

modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, or compositions, which can of course vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0072] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0073] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, *etc.* As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, *etc.* As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0074] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0075] Other embodiments are set forth in the following claims.

WHAT IS CLAIMED IS:

1. A process of converting plastic waste to polypropylene, the process comprising:
   (a) converting a plastic waste to a hydrocarbon liquid stream and a gaseous hydrocarbon stream in a catalytic pyrolysis unit, wherein the gaseous hydrocarbon stream is greater than about 60 wt% of the output, and the gaseous hydrocarbon stream contains greater than about 40 wt% light olefins;
   (b) introducing the gaseous hydrocarbon stream to one or more separating units to produce a first propylene stream, a first ethylene stream, a first butylene stream, and a saturated gas stream, wherein the saturated gas stream comprises C_1 to C_4 saturated hydrocarbons;
   (c) optionally, feeding the first propylene stream to a purification unit to produce a polymer grade propylene stream; and
   (d) feeding the first propylene stream and if present, the polymer grade propylene stream, to a polymerization unit to produce polypropylene.

2. The process of claim 1, further comprising:
   feeding the first ethylene stream and the first butylene stream to a metathesis unit to produce a second propylene stream, wherein metathesis unit comprises a metathesis catalyst;
   combining the first propylene stream and second propylene to produce a combined propylene stream;
   optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

3. The process of claim 2, further comprising:
   feeding the first ethylene stream and the first butylene stream to one or more separation units prior to feeding to first ethylene stream and the first butylene stream to a metathesis unit.

4. The process of any one of claims 1-3, wherein converting the plastic waste also comprises producing a liquid products stream in a catalytic pyrolysis unit.

5. The process of claim 4, wherein the liquid products stream comprises one or more paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, organic chlorides, or combinations thereof.

6. The process of claims 4 or 5, wherein the liquid products stream is recycled by feeding the steam back into the catalytic pyrolysis unit.

7. The process of any one of claims 4-6, wherein the liquid products stream is fed to a secondary cracking unit to produce a third propylene stream.

8. The process of claim 7, further comprising:
   combining the third propylene stream with the first propylene stream, the second propylene stream, or any combination thereof to produce a combined propylene stream; and
   optionally, feeding the combined propylene stream to a purification unit to produce a polymer grade propylene stream.

9. The process of any one of claims 1-8, wherein the polypropylene is a homopolymer of polypropylene.

10. The process of any one of claims 1-9, wherein the polymerization unit comprises one or more reactors.

11. The process of any one of claims 1-10, wherein additional ethylene or 1-butene is added to the polymer grade propylene stream before step (c).

12. The process of claim 11, wherein feeding the polymer grade propylene stream with additional ethylene or 1-butene to a polymerization unit produces copolymer polypropylene.

13. The process of claim 12, wherein the copolymer polypropylene is random copolymer polypropylene.

14. The process of claim 12, wherein the copolymer polypropylene is impact copolymer polypropylene.

15. The process of any one of claims 1-14, wherein the gaseous hydrocarbon stream in step (b) is separated by distillation.

16. The process of any one of claims 1-15, wherein isobutylene is removed from the first butylene stream after step (b).

17. The process of any one of claims 1-16, one or more of the first ethylene stream and the first butylene stream are purified to provide chemical or polymer grade ethylene stream, chemical or polymer grade butylene stream, and any combination thereof.

18. The process of any one of claims 1-17, wherein the metathesis unit utilizes a catalyst comprising ruthenium or molybdenum.

19. The process of any one of claims 1-18, wherein a petroleum-based olefin stream is not added to the hydrocarbon liquid stream after step (a).

20. The process of any one of claims 1-19, wherein a petroleum-based olefin stream is not added to the gaseous hydrocarbon stream after step (a).

21. The process of any one of claims 1-20, wherein a petroleum-based olefin stream is not added the first propylene stream or combined propylene stream after step (b).

22. The process of any one of claims 1-21, wherein a petroleum-based olefin stream is not added to the polymer grade propylene stream before step (d).

23. A polypropylene produced by a process of any one of claims 1-22.

FIG. 1

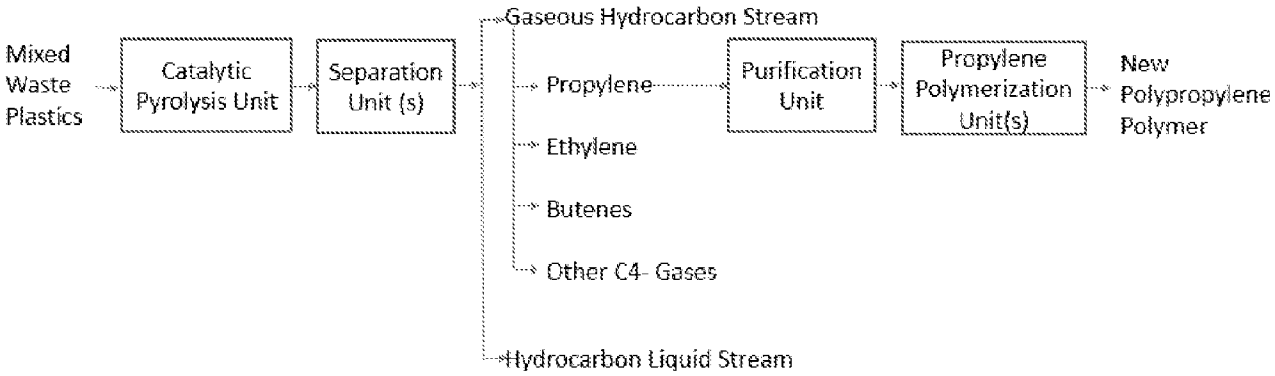

Mixed Waste Plastics
Catalytic Pyrolysis Unit
Separation Unit (s)
Gaseous Hydrocarbon Stream
Propylene
Ethylene
Butenes
Other C4- Gases
Hydrocarbon Liquid Stream
Purification Unit
Propylene Polymerization Unit(s)
New Polypropylene Polymer

FIG. 2

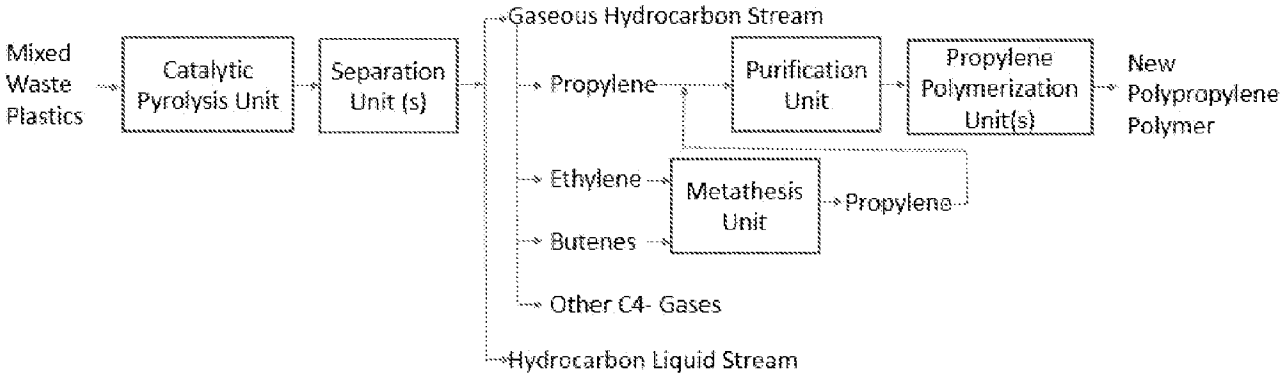

Mixed Waste Plastics
Catalytic Pyrolysis Unit
Separation Unit (s)
Gaseous Hydrocarbon Stream
Propylene
Ethylene
Butenes
Other C4- Gases
Hydrocarbon Liquid Stream
Purification Unit
Propylene Polymerization Unit(s)
New Polypropylene Polymer
Metathesis Unit
Propylene

FIG. 3

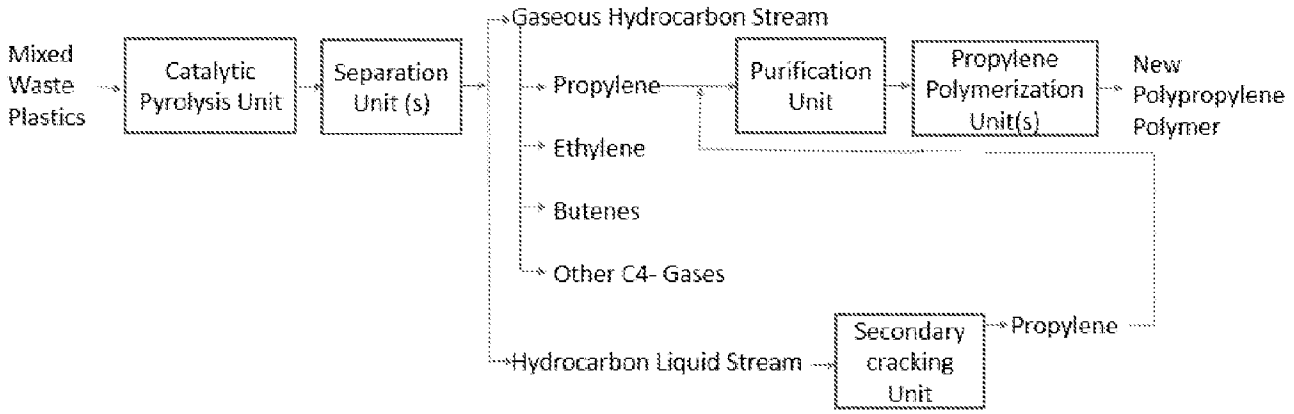
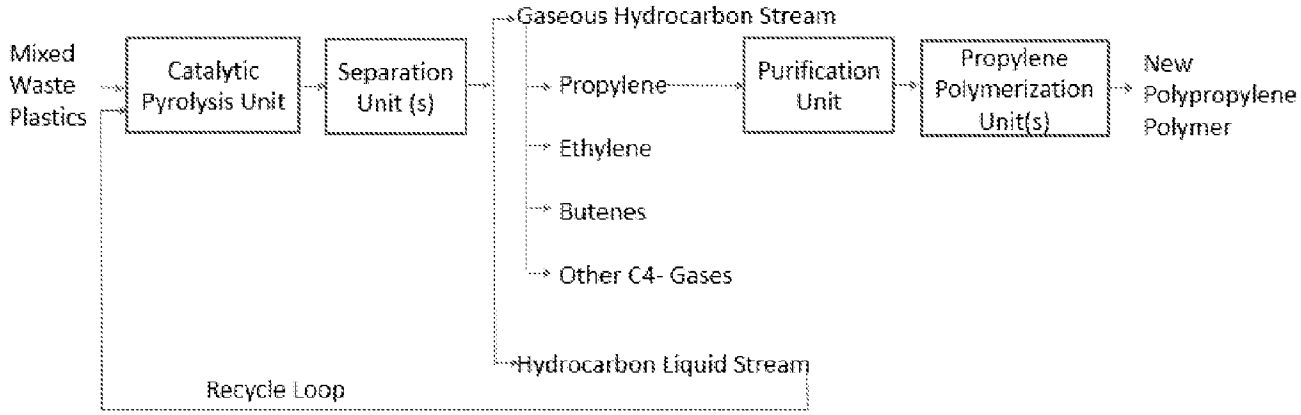

Mixed Waste Plastics
Catalytic Pyrolysis Unit
Separation Unit (s)
Gaseous Hydrocarbon Stream
Propylene
Ethylene
Butenes
Other C4- Gases
Purification Unit
Propylene Polymerization Unit(s)
New Polypropylene Polymer
Hydrocarbon Liquid Stream
Secondary cracking Unit
Propylene

FIG. 4


Mixed Waste Plastics
Catalytic Pyrolysis Unit
Separation Unit (s)
Gaseous Hydrocarbon Stream
Propylene
Ethylene
Butenes
Other C4- Gases
Purification Unit
Propylene Polymerization Unit(s)
New Polypropylene Polymer
Hydrocarbon Liquid Stream
Recycle Loop

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/054510

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08F 10/06*** (2024.01); ***C08J 11/04*** (2024.01); ***C10B 53/07*** (2024.01)

CPC: ***C08F 10/06; C08J 11/04; C10B 53/07***

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 2022/0340820 A1 (CHEVRON PHILLIPS CHEMICAL COMPANY LP) 27 October 2022 (27.10.2022)	
X	entire document	1, 4, 5
Y	entire document	2, 3
	US 10,851,309 B2 (SABIC GLOBAL TECHNOLOGIES B.V.) 01 December 2020 (01.12.2020)	
Y	entire document	2, 3
	WO 2023/059738 A1 (W.R. GRACE & CO.-CONN. et al.) 13 April 2023 (13.04.2023)	
A	entire document	1-5
	US 2022/0073655 A1 (REXTAC LLC) 10 March 2022 (10.03.2022)	
A	entire document	1-5
	WO 2018/055555 A1 (SABIC GLOBAL TECHNOLOGIES B.V.) 29 March 2018 (29.03.2018)	
A	entire document	1-5

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
13 December 2024 (13.12.2024)	**23 January 2025 (23.01.2025)**

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/054510

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

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

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

2. ☐ Claims Nos.:
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. ☑ Claims Nos.: **6-23**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).