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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 May 2024 (23.05.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/108199 A1

(51) International Patent Classification:
C10B 53/07 (2006.01) *C10G 1/10* (2006.01)
C10B 57/02 (2006.01) *C10G 1/00* (2006.01)
C10B 57/06 (2006.01)

(21) International Application Number:
PCT/US2023/080426

(22) International Filing Date:
18 November 2023 (18.11.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
17/990,642 18 November 2022 (18.11.2022) US
63/579,945 31 August 2023 (31.08.2023) US

(71) Applicant: **ANELLOTECH, INC.** [US/US]; 401 North Middletown Road, No. 170A, Pearl River, NY 10965 (US).

(72) Inventors: **CARLSON, Torren**; 401 North Middletown Road, No. 170A, Pearl River, NY 10965 (US). **MLECKZO, Leslaw**; Quittenweg 1, 41452 Dormagen (DE). **BASHAR, Omar, M.**; 210 Plymouth Road, Wilmington, DE 19803 (US). **IGOE, William**; 7 Sunrise Ave., Wilton, ME 04294 (US).

(74) Agent: **ROSENBERG, Frank**; 5737 Kanan Road, No. 190, Agoura Hills, CA 91301 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, 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,

(54) Title: PROCESSES AND SYSTEM FOR CHEMICALLY RECYCLING PLASTIC WASTE INVOLVING CATALYTIC PYROLYSIS

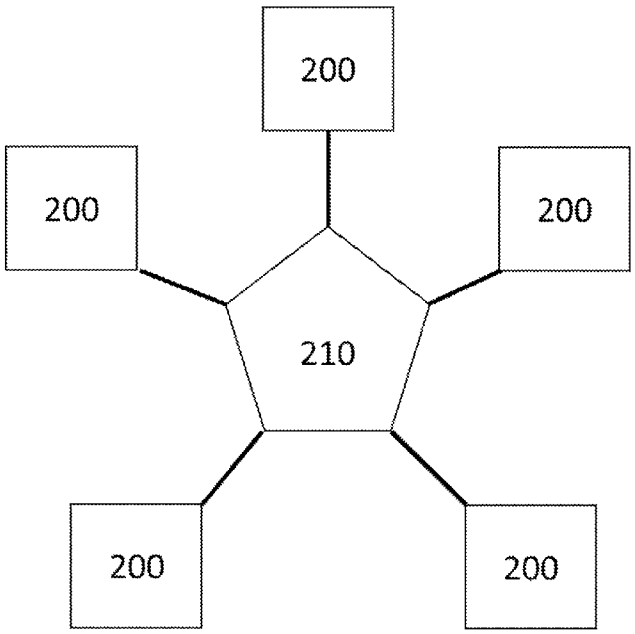


FIG. 3

(57) Abstract: A distributed system for the conversion of waste plastics, polymers, and other waste materials to useful chemical and fuel products such as paraffins, olefins, and aromatics such as BTX in a thermochemical process that includes the pretreatment of the feed mixture before a catalytic pyrolytic process, is described; the pretreatment includes raising the temperature of the waste plastics to at least 100 °C. A two-step process is described that includes a pyrolytic first step and a catalytic fluid bed second step that without separation upgrades the resulting raw pyrolysis products, for the conversion of waste plastics, polymers, and other waste materials to useful chemical and fuel products such as paraffins, olefins, and aromatics such as BTX. In another embodiment, the method or system for upgrading waste plastics to useful products comprising a first pyrolysis reactor and a catalytic fluidized bed reactor that together form one spoke of a ' hub-and-spoke' network for producing refined chemical intermediates, wherein each of the more than one plastics

WO 2024/108199 A1

[Continued on next page]

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))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

upgrading sites (the spokes) produces condensed phase products that are sent to a central processing facility (the hub) for separation and purification into product streams or for catalytic upgrading, separation, and purification into product streams.

PROCESSES FOR CHEMICALLY RECYCLING PLASTIC WASTE

Related Applications:

This application claims the priority benefit of US Patent Application Ser. No. 17/990,642 filed 18 November 2022 and US Provisional Patent Application Ser. No. 63/579,945 filed 31 August 2023.

FIELD OF THE INVENTION

This invention relates to the conversion of waste plastics, polymers, and other waste materials to useful chemical and fuel products such as paraffins, olefins, and aromatics such as BTX (a mixture of benzene, toluene, and xylenes) in a thermochemical process; preferably a two-step process that includes a pyrolytic first step and a second step that upgrades the resulting product mixture.

INTRODUCTION

In 2019, plastics generation in the United States was 55.2 million tons, which was 13 percent of MSW generation. World-wide over 368 million tons of plastics were produced. By some estimates, of the 8.3 billion tons of plastics ever produced, 6.3 billion tons ended up as waste, of which only 9% has been recycled. Plastic recycling recovers scrap or waste plastic and reprocesses the material into useful products. However, since China banned the import of waste plastics in 2018 the recycle rate in the US is estimated to have dropped to only 4.4%.

Plastic recycling is challenging due to the chemical nature of the long chain organic polymers and low economic returns. In addition, waste plastic materials often need sorting into the various plastic resin types, e.g., low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene-terephthalate (PET) for separate recycling treatments. Pyrolytic and catalytic pyrolytic processes are known in which waste plastics are heated to produce products such as liquid oils, gases, and carbon black.

Plas-TCat™ is a catalytic fluid bed process using zeolite catalysts to convert polymer/plastic material, especially waste plastics that otherwise might be sent to a landfill or incinerator, to a mixed product of permanent gases, C2-C4 light olefins, C1-C4 light paraffins,

and C5+ hydrocarbons including benzene, toluene, and xylenes ("BTX"), aromatic and non-aromatic naphtha range molecules, C11+ hydrocarbons, coke and char, and minor byproducts. Plastic mixtures that have relatively high hydrogen to carbon molar ratio, such as polyethylene (PE), polypropylene, polystyrene, and combinations thereof, can be converted to olefins and aromatics.

U.S. Pat. Appl. No. 2016/0289569 from Baird et al describes a process of pyrolyzing biomass to bio-oil, separating and upgrading the pyrolysis oil, deoxygenating the upgraded pyrolysis oil to obtain aromatic and paraffinic products, and further upgrading the paraffinic product by aromatization.

U.S. Pat. No. 10,233,395 to Ward relates to a process for converting mixed waste plastic (MWP) into petrochemicals wherein a MWP stream is fed to a pyrolysis reactor, converting said MWP into separated gaseous stream and liquid streams, and further separately processing the gaseous stream and the liquid stream.

Fukuda et al in U.S. Pat. No. 4,851,601, describe a process for pyrolyzing plastics in a tank reactor with an added solid to minimize materials sticking to the reactor wall, and reacting the vapors in a fixed bed catalytic reactor.

Bartek et al in U.S. Pat. No. 9,040,761 describe a process for pyrolyzing biomass and plastic in a fluidized bed of heat transfer material and reacting the products with a catalyst in a second reactor to produce a bio-oil.

Saito et al in U.S. Pat. No. 4,584,421 describe a process for melting and thermally decomposing plastic scraps with heat and passing the vaporous product through a bed of catalyst particles.

Barbarias et al in "Catalyst Performance in the HDPE Pyrolysis-Reforming Under Reaction-Regeneration Cycle," *Catalysts* **2019**, *9*, 414, and "Waste Plastics Valorization by Fast Pyrolysis and in Line Catalytic Steam Reforming for Hydrogen Production," in M. Olazar *Materials Science*, DOI:10.5772/INTECHOPEN.85048, 9 July **2019**, describe the conversion of waste plastic to syngas by thermal pyrolysis in a conical spouted bed reactor and steam reforming of the volatiles formed (gas and waxes) in a fluid bed of Ni-containing catalyst.

Schenk et al in US Patent Application US20220195310A1 describe a process for preparing BTX by pyrolyzing a plastic mixture at 600-1000 °C and catalytically upgrading the vapors in a fluidized bed at 450-700 °C to a mixture comprising aromatics.

Diebold et al. in U.S. Pat. No. 7,909,899 disclose a process for converting biomass to a gaseous fuel using downdraft gasification in an automated process that can be part of a distributed system with automated central control.

Foody et al. in U.S. Pat. No. 11,289,696, describe a method for producing partially purified biogas at a first processing site and transporting it by vehicle to a second processing site where the methane is processed to a fuel or fuel intermediate along with methane from other processing sites.

Doucet and Chaouki in U.S. Pat. Appl. No. 2016/0200982 disclose a system for performing small scale pyrolysis in a distributed way, collecting the byproducts, and transporting the byproducts to a byproduct processor for further use.

Waste plastics are collected locally at numerous facilities that each handle small amounts of plastics in any one day, either as part of general waste (municipal solid waste) or a separate recycling stream. In either case, most of the material ends up among the 25 million tons of plastics that are sent to one of more than 2,600 landfills in the USA each year. The amount of waste plastic available at any one site is typically on the order of only a few tens of metric tonnes per day.

A chemical plastics recycling plant includes feed handling, cleaning, processing (e.g. pyrolysis and catalytic pyrolysis), recovery, separations, and purifications operations. The cost of the separations and purification facilities often constitute 35-50% of the capital cost of a complete facility. The small size of the individual resources is an economic disadvantage since upgrading processes are not able to take advantage of the economies of scale available to large scale resources.

Plants that have small capacities are more expensive on a per-tonne-of-product basis than larger plants due to the lack of the economy of scale. One way to take advantage of economies of scale for the separations and purifications functions is to network together several plants that produce crude mixtures of liquid products of a similar composition and send the crude mixtures to a refinery or other central processing facility for separation and purification into chemical grade materials.

Another challenge is the very different compositions of the waste materials at different locations due to local conditions and sources of such materials. For example, one site may be located near a source of construction waste that comprises significant quantities of chlorine-

containing plastics such as PVC whereas another site may receive wastes that contain little or no chlorine-containing wastes. Simply combining these wastes for processing would require a process that can accommodate chlorine-containing materials whereas processing of the chlorine-free material could be accomplished with less complex and expensive equipment. In short, different mixtures of waste plastics require different pretreatment schemes to make them acceptable as feeds to pyrolysis upgrading processes.

Yet another challenge is the transport and storage of post-consumer plastics recovered from waste facilities that are often contaminated with food, farm waste, feces, or other harmful wastes. Contaminated plastics may harbor diseases, parasites, and pathogens, and may be the source of noxious odors and irritating vapors. Transport and storage of these contaminated materials pose a health hazard to workers handling them and to people in nearby areas. One goal of this invention is to disclose pretreatment processes for the sanitization, decontamination, and/or sterilization of the plastics before they are transported and stored for upgrading to valuable products.

A need exists for a system for upgrading waste plastic materials wherein the waste plastics may be pretreated at individual sites, each configured to accommodate the particular waste composition, and the pretreated materials from each of multiple sites are catalytically upgraded at either the same sites as the pretreatment, or are collected at a central site for catalytic upgrading, to produce aromatics, olefins, paraffins, or similar valuable products.

SUMMARY

A method of producing olefinic and aromatic hydrocarbons from waste plastics comprising feeding a mixture of plastics to a two-stage process including a first stage in which the plastic mixture is pyrolyzed anaerobically and a second stage in which, without separation, the raw products of the first stage are catalytically reacted to produce olefins and aromatics.

In one aspect, the invention provides a method or system for upgrading waste plastics to useful products comprising a first pyrolysis reactor and catalytic fluidized bed reactor that together form one spoke of a 'hub-and-spoke' network for producing refined chemical intermediates, wherein each of the more than one plastics upgrading sites (the spokes) produces condensed phase products that are sent to a central processing facility (the hub) for separation and purification into product streams or for catalytic upgrading, separation, and purification into

product streams. The chemical intermediates may be selected from the group consisting of benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, naphthalene, and combinations of these. The chemical intermediates can be separated and purified at the central separation and purification facility. In a preferred method or system at least 2, or at least 3, or at least 5, or at least 7, or at least 10, or at least 15, or from 2 to 20, or from 3 to 10, or from 5 to 10 plastics pyrolysis facilities feed a central catalytic upgrading, separation, and purification facility. The method or system is suitable for operation at large scale, for example, the total crude product mixture prepared at the plastics pyrolysis facilities is introduced into a central catalytic upgrading, separation, and purification facility is at least 20, at least 50, at least 100, at least 150, or at least 200 metric tons per day, or from 20 to 500, from 30 to 200, or from 50 to 150 metric tons per day of crude product mixture. The central facility for catalytic upgrading, separation, and purification can be at a refinery.

In another aspect, this invention provides a system and/or method for upgrading waste plastics to useful products, comprising multiple plastics pretreatment facilities, a. wherein each pretreatment facility forms one spoke of a 'hub-and-spoke' network, b. wherein pretreatment at each pretreatment facility includes raising the temperature of the waste plastics to at least 100 °C, c. wherein either the hub comprises a catalytic pyrolysis unit, or each spoke comprises a catalytic pyrolysis unit, and d. at least a portion of the products of each spoke is collected and processed at a central processing facility (the hub) for upgrading, separation, and purification into product streams.

In another aspect, the invention provides a method of converting plastics to olefins, or aromatics, or a mixture of olefins and aromatics, comprising: pretreating a mixture of plastics in a pretreatment facility that is one among several pretreatment facilities; raising the temperature of the plastics mixture to at least 100 °C during the pretreatment process; transferring at least a portion of the products from the pretreatment facility to a fluidized bed catalytic reactor where, in the presence of a catalyst, the mixture is converted to a product mixture; wherein the fluidized bed catalytic reactor is either at the same site as the pretreatment facility or, at a different, central site; recovering at least a portion of the products from the one or more catalytic pyrolysis reactors; and recovering olefins or aromatics or some combination thereof from the catalytic pyrolysis products in a central product upgrading, separation, and purification facility.

In a further aspect, the invention provides a method for producing chemicals or fuels comprising: a. providing waste plastics at a first processing site, said first processing site configured to receive waste plastics; b. at the first processing site, pretreating the waste plastics at a temperature of at least 100 °C and transferring the pretreated waste plastics into one or more mobile carriers; c. transporting the one or more mobile carriers to a second processing site, the second processing site configured to receive pretreated waste plastics from at least one additional plastics source; d. removing the pretreated waste plastics from the one or more mobile carriers transported in step (c); and e. producing chemicals, fuels, or both using plastics from at least the pretreated waste plastics removed in step (d) and plastics from at least one other plastics source.

The inventive method and/or system may be further characterized by one or any combination of the following features: wherein the pretreatment processes or system may include one or more of the following: collecting, separating, sorting, mixing, removing contaminants, thermal treatment, sanitization, decontamination, sterilization, dechlorination, washing, drying, sizing, melting, filtering, pelleting, or combinations thereof; wherein at least one pretreatment step raises the temperature of the plastic mixture to at least 100, 120, 150, 180, 200, or 220 °C; wherein the pretreatment process steps can be conducted in any order; wherein the product of the catalytic pyrolysis comprises one or more of benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, or naphthalene, hydrogen or some combination of these. wherein the thermal treatment reactor comprises one or more reactors; wherein the thermal treatment reactor or pyrolysis reactor is one or more moving bed, 1-screw extruder, twin-screw extruder, multiple-screw extruder, planetary extruder, ultrasonically assisted extruder, auger reactor, rotating kiln reactor, stirred tank reactor, or a stepped grate reactor, or some combination thereof; wherein the pretreatment facility further comprises a shredder, a granulator, a depackaging unit, a dewatering unit, or any combination thereof; wherein the waste plastic collection bins or containers are equipped with RFID tags or barcodes for efficient tracking and management of the waste plastics; wherein the transportation vehicles for waste plastic collection are selected from trucks, trailers, railcars, shipping containers, or any suitable means of transportation; wherein the waste plastics are collected from residential, commercial, industrial, or municipal waste or some combination thereof; wherein the central processing facility (the hub) is located within 1 mile (1.6 km) of a waste plastic collection facility; wherein the system

further comprises a central database or control center that receives and processes real-time data from each pretreatment facility, the catalytic pyrolysis reactor, and other relevant components, wherein the central database or control center regulates and optimizes the operation of the distributed system; wherein the transportation of pretreated waste plastics from each pretreatment facility to the central processing facility or the catalytic pyrolysis reactor is facilitated through an intelligent logistic system, which autonomously schedules and dispatches transportation vehicles or devices based on the real-time capacity and demand of each facility. wherein the central processing facility (the hub) or any of the pretreatment facilities is a portable modular system; wherein material is heated to a temperature between 180 °C and 300 °C in the thermal treatment reactor and the condensed products are passed to a second thermal treatment reactor; wherein a sweep gas such as H_2O, N_2, Air, Ar, CO_2, or other inert gas or some combination thereof, is fed to the thermal treatment reactor and the vapors are exhausted; wherein a vapor stream comprising at least one of HCl, HBr, HI, NH3, CO2, or CH4, is exhausted from the thermal treatment reactor; wherein the thermal treatment reactor comprises an inlet port and an exit port, the temperatures can be from 20 to 225 °C, such as 20 to 100 °C, or 20 to 50 °C, at or near the inlet port, and the range of temperatures at the high-temperature exit port can be from 300 to 700 °C, such as from 325 to 650 °C, from 350 to 600 °C, or from 350 to 575 °C; wherein the residence time of condensed phases in the thermal treatment reactor, or in either reactor when there is more than one thermal treatment reactor, is at least 0.5, or at least 5 10 20, or at least 30, or from 1 to 60, 5 to 30, 10 to 30, or 0.5 to 10 minutes; wherein the thermal treatment reactor comprises one or more 1-screw or twin-screw or multiple screw or planetary or ultrasonically assisted extruders, and a stirred tank reactor; wherein the filtering is accomplished by first heating the plastic mixture to at least 200 °C in a thermal treatment reactor to achieve a molten state and filtered to remove solids; wherein the mixing is accomplished by passing the molten feed mixture through one or more static mixing devices held at a temperature of at least 100, 150, 200, 225, or 250 °C, or from 100 to 350, 150 to 350, 150 to 300, or 200 °C to 250 °C. wherein contaminants are removed by heating the feed mixture anaerobically to a temperature of between 150 °C and 350 °C or between 250 °C and 300 °C in a thermal treatment reactor to at least partially decompose the polymers; wherein the feed is heated to a temperature between 250 and 300 °C in the thermal treatment reactor and the products are passed to a second thermal

treatment reactor; wherein at least one of the thermal treatment reactors comprises a stirred tank reactor; wherein a solid co-reactant material is fed to the thermal treatment reactor; wherein the solid co-reactant comprises one or more materials chosen from among agricultural lime, calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, hydrotalcites, activated carbon, or zeolite, or other solid basic material, or some combination thereof; wherein the solid co-reactant material recovered from the thermal treatment reactor is transferred to a combustion regenerator wherein the carbonaceous materials are reacted with air and at least a portion of the hot solid co-reactant material is returned to the thermal treatment reactor; wherein the products produced in the pretreatment process are transferred, without separating a significant portion of the products, to a catalytic pyrolysis reactor containing a catalyst; wherein the molten products of the pretreatment are fed to a pelleting process and cut into pellets; wherein the feed to the catalytic pyrolysis reactor comprises pellets; feeding a feed mixture comprising plastics to a pretreatment facility; wherein the non-vapor products of the catalytic pyrolysis reactor, or a portion of the gases remaining after removal of desired products, or both, are combusted to provide energy for the pyrolysis or catalytic pyrolysis process; wherein a vapor phase co-reactant comprising H2, CO, or olefins, or some combination of these, or a recycle stream is fed directly to the thermal treatment reactor or the catalytic pyrolysis reactor; wherein a portion of the vapor products from the catalytic pyrolysis process is fed to a condenser where it is cooled to produce condensed materials; wherein a portion of the condensed material separated from the product stream from the thermal treatment or the catalytic pyrolysis reactor is separated into fractions and at least a portion is recycled to the thermal treatment reactor; wherein the condensed material is separated into fractions by distillation and at least a portion of the paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms is recycled to the thermal treatment or catalytic pyrolysis reactor; and wherein the condensed material separated from the product stream from the thermal treatment or the catalytic pyrolysis reactor is separated into fractions by distillation and at least a portion of the fraction boiling above 300 °C or boiling in the range 300 to 800 °C is recycled to the thermal treatment or catalytic pyrolysis reactor.

In a further aspect of this invention a mixture comprising polymers is converted in an anaerobic process in a reactor to produce a pyrolyzed stream that is fed to a fluid bed catalytic pyrolysis process to produce olefins and aromatics.

In another aspect, the invention provides a method of converting plastics to olefins, or aromatics, or a mixture of olefins and aromatics, comprising: feeding a polymer or mixture of polymers to a first pyrolysis reactor; anaerobically pyrolyzing the stream in the first reactor under conditions sufficient to produce a raw product mixture comprising one or more olefins and paraffins; without separation transferring the raw product mixture from the first pyrolysis reactor to a fluidized bed catalytic reactor where, in the presence of a catalyst, the mixture is converted to a product vapor mixture; and recovering olefins or aromatics or some combination thereof from the product vapor mixture.

In a further aspect, the invention provides a method for producing olefins and aromatics comprising: feeding a stream comprising plastics to a first pyrolysis reactor; anaerobically pyrolyzing the stream in the first pyrolysis reactor at a temperature between 250 and 300 °C and holding at that temperature range while vapors are removed; (holding is preferably at least 2 minutes, or at least 5 minutes or at least 10 minutes, and preferably 1 hour or less or 30 minutes or less); and further pyrolyzing at higher temperature in the first pyrolysis reactor to prepare a first product mixture; without separating, passing the first product mixture produced in the first pyrolysis reactor to a second pyrolysis reactor that comprises a fluidized bed reactor fitted with a catalyst; catalytically reacting the product mixture in the fluidized bed reactor to form a catalytic pyrolysis product mixture; and recovering olefins, or aromatics, or some combination thereof from the pyrolysis product mixture. The invention can be further characterized by one or any combination of the following: wherein the first product mixture produced in the first pyrolysis reactor is passed to the second pyrolysis reactor at a temperature above 350 °C without cooling; wherein the first pyrolysis reactor comprises a feed inlet port and an exit port and the temperature in the pyrolysis reactor ranges from a lower temperature near the feed inlet port to a higher temperature at the exit port; wherein the first pyrolysis reactor comprises two or more reactors in series; wherein the catalyst in the fluidized bed reactor comprises a zeolite; wherein the catalyst has a silica to alumina greater than 12, or from 12 to 240, and a CI (constraint index) from 1 to 12 or from 5 to 10; wherein the catalyst comprises ZSM-5; wherein a product vapor mixture from the fluidized bed catalytic reactor comprises at least 20 mass% BTX; wherein a solid co-reactant is fed to the first pyrolysis reactor wherein the solid co-reactant fed to the first pyrolysis reactor comprises agricultural lime, or calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, hydrotalcites, activated carbon, or zeolite, or other solid

basic material, or some combination thereof; wherein the temperature of the fluidized bed reactor is in the range from 300 °C to 800 °C, from 350 °C to 750 °C, from 400 °C to 700 °C, from 450 °C to 650 °C, from 500 °C to 600 °C, or from 525 °C to 575 °C; wherein benzene, toluene, or xylenes are separated or recovered from the catalytic pyrolysis product mixture; wherein at least a portion of the aromatic products in the catalytic pyrolysis product mixture is hydrogenated to produce naphthenes; wherein the catalytic pyrolysis product mixture is subjected to a separation process to produce a stream of gases enriched in CH_4, CO, and H_2; and passing at least a portion of the stream of gases enriched in CH_4, CO, and H_2 to a regenerator where they are combusted; wherein the feedstock comprises a mix of waste plastic chosen from among polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC) or polyvinylidene (PVCD), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), or mixed resins, or some combination thereof; wherein a portion of the ~~vapor products from the~~ catalytic pyrolysis ~~process~~ product mixture is fed to a condenser where it is cooled to produce condensed materials and a portion of the condensed materials is recycled to the first pyrolysis reactor; wherein a portion of the condensed materials is separated into fractions and at least a portion of the condensed materials is recycled to the first pyrolysis reactor or the second pyrolysis reactor; wherein the condensed materials is separated into fractions by distillation and at least a portion comprising paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms is recycled to the first pyrolysis reactor or the second pyrolysis reactor; wherein the step of further pyrolyzing at higher temperature is in the range of 350 to 600 °C; wherein the temperature in the second pyrolysis reactor is maintained at a temperature at least 5 °C higher than the temperature at the exit port.

The invention in any of its aspects may be further characterized by one or any combination of the following features:

feeding a feed mixture comprising plastics to a pyrolysis reactor; wherein the feed mixture comprises plastics chosen from among polyethylene, polypropylene, polyesters, polyethylene terephthalate (PET), acrylonitrile-butadiene-styrene (ABS) copolymers, polyamide, polyurethane, polyethers, polycarbonates, poly(oxides), poly(sulfides), polyarylates, polyetherketones, polyetherimides, polysulfones, polyurethanes, polyvinyl alcohols, and polymers produced by polymerization of monomers, such as, for example, dienes, olefins, styrenes, acrylates, acrylonitrile, methacrylates, methacrylonitrile, diacids and diols, lactones,

diacids and diamines, lactams, vinyl esters, block copolymers thereof, and alloys thereof; thermoset polymers such as, for example, epoxy resins; phenolic resins; melamine resins; alkyd resins; vinyl ester resins; unsaturated polyester resins; crosslinked polyurethanes; polyisocyanurates; crosslinked elastomers, including but not limited to, polyisoprene, polybutadiene, styrene-butadiene, styrene-isoprene, ethylene-propylene-diene monomer polymer; and mixtures thereof, wherein the feedstock comprises a mix of waste plastic chosen from among polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC) or polyvinylidene (PVCD), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), or mixed resins, or some combination thereof;

wherein the feed stream of plastics is first heated to at least 200 °C in a thermal treatment reactor to achieve a molten state and filtered to remove solids; wherein the feed mixture is heated anaerobically to a temperature of between 250 and 300 °C to at least partially decompose the polymers in the pyrolysis reactor;

wherein the thermal treatment or pyrolysis reactor is one or more moving bed, 1-screw extruder, two screw extruder, auger reactor, rotating kiln reactor, or a stepped grate reactor, or some combination thereof; wherein the first pyrolysis reactor comprises and inlet port and an exit port, the temperatures can be from 20 to 225 °C, such as 20 to 100 °C, or 20 to 50 °C, at or near the inlet port, and the range of temperatures at the high temperature exit port can be from 300 to 700 °C, such as from 325 to 650 °C, from 350 to 600 °C, or from 350 to 575 °C;

a two step process comprising a temperature between 250 and 300 °C and holding at that temperature range while vapors are removed (holding is preferably at least 2 minutes, or at least 5 minutes or at least 10 minutes, and preferably 1 hour or less or 30 minutes or less).

wherein the residence time of condensed phases in the first pyrolysis reactor, or in either reactor when there are more than one pyrolysis reactors (prior to the catalytic fluidized bed reactor), is at least 1, or at least 5, or at least 10, or at least 20, or at least 30, or from 1 to 60, or from 5 to 30, or from 10 to 30 minutes;

wherein the pyrolysis reactor comprises two or more reactors in series;

wherein the feed is heated to a temperature between 250 and 300 °C in the first pyrolysis reactor and the products are passed to a second pyrolysis reactor;

wherein a sweep gas such as H2O, N2, Ar, CO2, or some combination thereof, is fed to the thermal treatment reactor and the vapors are exhausted;

wherein the non-vapor products of the catalytic pyrolysis reactor, or a portion of the gases remaining after removal of desired products, or both, are combusted to provide energy for the pyrolysis or catalytic pyrolysis process;

wherein a solid co-reactant material is fed to a thermal treatment reactor;

wherein the solid co-reactant comprises one or more materials chosen from among agricultural lime, calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, hydrotalcites, activated carbon, or zeolite, or other solid basic material, or some combination thereof;

wherein the solid co-reactant material is transferred to a combustion regenerator wherein the carbonaceous materials are reacted with air and at least a portion of the hot solid co-reactant material is returned to the thermal treatment reactor;

wherein the products produced in the pyrolysis reactor are transferred, without separating a significant portion of the products, to a catalytic pyrolysis reactor containing a catalyst;

wherein a vapor phase co-reactant comprising H2, CO, or olefins, or some combination of these, or a recycle stream is fed directly to the pyrolysis reactor or the catalytic pyrolysis reactor;

wherein a portion of the vapor products from the catalytic pyrolysis process is fed to a condenser where it is cooled to produce condensed materials;

wherein a portion of the condensed material separated from the product stream from the pyrolysis or the catalytic pyrolysis reactor is separated into fractions and at least a portion is recycled to the pyrolysis reactor;

wherein the condensed material is separated into fractions by distillation and at least a portion of the paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms is recycled to the pyrolysis or catalytic pyrolysis reactor;

wherein the condensed material separated from the product stream from the pyrolysis or the catalytic pyrolysis reactor the condensed material is separated into fractions by distillation and at least a portion of the fraction boiling above 300 °C or boiling in the range 300 to 800 °C is recycled to the pyrolysis or catalytic pyrolysis reactor.;

wherein the catalytic reactor is a fluidized bed reactor;

wherein the catalytic reaction is conducted in a fluidized bed, circulating bed, bubbling bed, or riser reactor at an operating temperature in the range from 300 °C to 800 °C, from 350 °C

to 750 °C, from 400 °C to 700 °C, from 450 °C to 650 °C, from 500 °C to 600 °C, or from 525 °C to 575 °C;

wherein the pressure is at least 0.1 MPa (1 bar), at least 0.3 MPa (3bar), or at least 0.4 MPa (4 bar), or from 0.1 to 2.0 MPa (1 to 20 bar), from 0.1 to 1.0 MPa (1 to 10 bar), or from 0.3 to 0.8 MPa (3 to 8 bar), preferably from 0.4 to 0.6 MPa (4 to 6 bar);

wherein the fluidization gas for the catalytic pyrolysis can comprise H2, CO, CO2, H2O, C1-C4 paraffins or olefins or both, N2, Ar, He, or a recycle stream, or some combination thereof;

wherein the residence time of the fluidization gas in the catalytic pyrolysis reactor, defined as the volume of the reactor divided by the volumetric flow rate of the fluidization fluid under process conditions of temperature and pressure, can be from 1 second to 480 seconds, or from 1 second to 240 seconds, or from 2 seconds to 60 seconds, or from 3 seconds to 30 seconds, or from 4 seconds to 15 seconds;

wherein the catalyst is a solid catalyst and the step of catalytically pyrolyzing comprises pyrolyzing in the presence of the solid catalyst in a fluidized bed reactor to produce a fluid product stream and used catalyst with coke, and wherein at least 95% the carbon in the feed is converted to coke and volatile products; wherein the catalyst comprises a zeolite; wherein the catalyst is selected from ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, or combinations thereof; wherein the catalyst comprises ZSM-5;

wherein the product vapor mixture from the catalytic conversion comprises at least 20 mass% olefins, or at least 50 mass% olefins, in some embodiments in the range of 20 to 90 mass% olefins;

wherein the catalyst composition comprises a crystalline molecular sieve characterized by an SAR from greater than 12 to 240 and a CI from 5 to 10;

wherein the mass yield of olefins in the product vapor mixture from the catalytic conversion is at least 30%, or at least 40%, or at least 45%, or at least 50%, or at least 55%, or at least 60%, or from 20% to 90%, or from 30% to 70%, or from 45% to 60%, olefins based on the mass in the polymer feed;

wherein the mass yield of BTX in the gaseous product mixture from the catalytic conversion is at least 30%, or at least 40%, or at least 45%, or at least 50%, or at least 55%, or at least 60%, or from 20% to 90%, or from 30% to 70%, or from 45% to 60% BTX based on the mass in the polymer feed;

wherein the vapor products of the catalytic pyrolysis are passed through one or more solids separation devices comprising a cyclone;

wherein catalyst in the catalytic pyrolysis reactor is withdrawn and regenerated by oxidation with air, and returned to the catalytic pyrolysis reactor;

wherein heat from the regeneration of the catalyst provides energy to the step of thermal treatment or pyrolyzing;

wherein at least a portion of the gases in the product mixture are combusted in the regenerator;

wherein the gaseous catalytic pyrolysis product mixture is subjected to a separation process to produce a stream of gases enriched in CH_4, CO, and H_2; and passing at least a portion of the stream of gases enriched in CH_4, CO, and H_2 to the regenerator where they are combusted;

wherein the gaseous catalytic pyrolysis product mixture comprises CH4 and C2-C4 paraffins; wherein 50 to 100 mass% of the CH_4 and C2-C4 paraffins is combusted in the regenerator;

wherein at least 2, or at least 3, or at least 5, or at least 7, or at least 10, or at least 15, or from 2 to 20, or from 3 to 10, or from 5 to 10 plastics upgrading facilities, i.e., pyrolysis and catalytic pyrolysis units, feed a central separation and purification facility;

wherein the total crude product mixture prepared at the at least 2 plastics upgrading facilities that is introduced into a central separation and purification facility is at least 20, or at least 50, or at least 100, or at least 150, or at least 200 metric tons per day, or from 20 to 500, or from 30 to 200, or from 50 to 150 metric tons per day of crude product mixture;

wherein the central facility for separation and purification is at a refinery; and

wherein benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, or naphthalene, or others, or some combination of these prepared from waste plastics at more than one upgrading facility, is separated and purified at a central separation and purification facility.

There are many advantages of chemically recycling plastics by pyrolysis in a thermochemical reactor including: a mixture of any type of plastics is suitable, the plastic particles need not be ground to small size since the long residence time in the pyrolysis reactor or reactors ensures that the plastic pieces are heated to decomposition temperatures, the pyrolysis

can be operated at high temperatures, and undesirable contaminants can be removed in an optional thermal treatment reactor.

Providing, installing, and/or operating a network of remote plastics pretreatment facilities, is advantageous with regard to the collection of the pretreated waste plastics. For example, it allows pretreated waste plastics to be formed into readily handled sizes and shapes, thereby improving the speed of the handling. In addition, it allows the pretreated waste plastics to be transferred and fed directly into a mobile storage container, which improves the collection by allowing the transport of relatively larger batches of pretreated waste plastics to a central processing facility (e.g., in a hub-and-spoke configuration). Moreover, it allows for the waste plastic material to be sanitized to make it safer for transport and storage than non-pretreated materials.

Providing, installing, and/or operating a remote pretreatment system, and collecting the pretreated plastics for transport to a centralized processing facility is advantageous for the centralized processing facility in that it merits providing a larger and/or more efficient processing system. For example, for plastics upgrading, economies of scale indicate that larger plants are favored for producing purified products, higher plant efficiency, and higher profitability. Moreover, centralized processing facilities can be sited adjacent to existing facilities such as refineries or chemical plants where the products of plastics upgrading can be further separated and purified using existing equipment, either along with or in place of petroleum-based materials. Pretreated material that has been sanitized makes the storage and handling of the material safer for workers at the central processing facility, reduces environmental hazards and undesirable contaminants, and reduces the production of noxious odors and irritating vapors.

Another advantage of providing a distributed plastics pretreatment process and a central facility that upgrades the pretreated plastics is that different sources of plastic comprise different mixtures of materials that can be blended or mixed together at a central facility before processing to improve the operability of the central facility by supplying a more uniform feed mixture to the facility. For example, waste plastics from one site may be rich in PVC that contains chlorine and causes corrosion whereas material from a second site may be nearly free of PVC such that a blend of the two sources can be processed in the central facility without damaging equipment whereas the material that is high in PVC cannot.

A further advantage of a distributed pretreatment process is that materials that are sized similarly from multiple pretreatment facilities can be handled more readily and can be mixed together to provide a more uniform feed to the upgrading processes.

Use of a pelleting process in the distributed pretreatment system has the advantage of forming the materials into easily handled sizes and shapes for transport, and metering in further processes. Pelleted materials may also be stored more readily with little concern for degradation by chemical or biological processes, or attack by pests such as insects, bacteria, fungi, or animals.

Advantages of a two-step plastics upgrading process include: simple feeding system for the raw pyrolysis product to the catalytic step, no danger of agglomeration in the fluidized bed causing defluidization or clumping in the bed, no need for good mixing of solid or molten plastic feed with catalyst particles, significantly narrower residence time distribution for pyrolysis gas in the catalytic reactor compared with the feed of solids, thus resulting in fewer heavy products, no carryover of plastic particles into the catalyst regenerator, fewer external impurities transferred into the catalytic reactor and no inorganic particles embedded in the polymer like fillers or additives are transferred into the catalytic reactor when an optional thermal treatment reactor is used (fillers are usually alkaline (basic) and when reacting with the acidic catalyst cause its deactivation), heat is convectively supplied to the plastics without the use of steam that causes deactivation (dealumination) of the catalyst, and a greatly reduced need for additional fluidization gas rendering product recovery simpler and less costly.

Another advantage of the two step plastics upgrading process is that the production of a crude liquid product stream made from recycled plastic by the inventive process can be conducted at a separate location from the product separation and purification system, and this "distributed processing" scheme minimizes the costs of separation and purification for small scale regional plastics upgrading facilities

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates a process for converting mixed plastic materials to valuable products by pyrolyzing the mixed plastics and catalytically reacting the raw product mixture to produce olefins, aromatics, or some combination thereof.

Figure 2 schematically illustrates a process for converting mixed plastic materials to valuable products by pyrolyzing the mixed plastics and catalytically reacting the products to produce olefins, aromatics, or some combination thereof, wherein a thermal treatment reactor is used to remove contaminants before feeding the pyrolysis reactor.

Figure 3 schematically illustrates an embodiment of the invention in which five plastics upgrading units are connected to feed a single product separation and purification facility in a hub and spoke system.

Figure 4 shows a drawing of the reactor used in the Examples.

Figure 5 presents a conceptual embodiment of the process for converting mixed plastic materials to valuable products in a distributed system wherein the pretreatment processes are conducted at a variety of sites and the catalytic pyrolysis and product upgrading, separation, and purification are conducted at a single central site.

Figure 6 presents a conceptual embodiment of the process for converting mixed plastic materials to valuable products in a distributed system wherein the pretreatment processes and catalytic pyrolysis are conducted at a variety of sites and the product upgrading, separation, and purification are conducted at a single central site.

Figure 7 presents one embodiment of a pretreatment process for pretreating waste plastic to make it suitable for catalytic upgrading.

Figure 8 shows a generalized schematic of the flow profiles and mixing behavior in typical static mixers.

GLOSSARY

Aromatics - As used herein, the terms “aromatics” or “aromatic compound” are used to refer to a hydrocarbon compound or compounds comprising one or more aromatic groups such as, for example, single aromatic ring systems (e.g., benzyl, phenyl, etc.) and fused polycyclic aromatic ring systems (e.g., naphthyl, 1,2,3,4-tetrahydronaphthyl, etc.). Examples of aromatic compounds include, but are not limited to, benzene, toluene, indane, indene, 2-ethyl toluene, 3-ethyl toluene, 4-ethyl toluene, trimethyl benzene (e.g., 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, 1,2,3-trimethyl benzene, etc.), ethylbenzene, styrene, cumene, methylbenzene, propylbenzene, xylenes (e.g., p-xylene, m-xylene, o-xylene, etc.), naphthalene, methyl-naphthalene (e.g., 1-methyl naphthalene, anthracene, 9.10-dimethylanthracene, pyrene,

phenanthrene, dimethyl-naphthalene (e.g., 1,5-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,5-dimethylnaphthalene, etc.), ethyl-naphthalene, hydrindene, methyl-hydrindene, and dymethyl-hydrindene. Single- ring and/or higher ring aromatics may also be produced in some embodiments.

Fluid - The term "fluid" refers to a gas, a liquid, a mixture of a gas and a liquid, or a gas or a liquid containing dispersed solids, liquid droplets and/or gaseous bubbles. The terms "gas" and "vapor" have the same meaning and are sometimes used interchangeably. In some embodiments, it may be advantageous to control the residence time of the fluidization fluid in the reactor. The fluidization residence time of the fluidization fluid is defined as the volume of the reactor divided by the volumetric flow rate of the fluidization fluid under process conditions of temperature and pressure.

Fluidized Bed Reactor – The term "fluidized bed reactor" is given its conventional meaning in the art and is used to refer to reactors comprising a vessel that can contain a granular solid material (e.g., silica particles, catalyst particles, etc.), in which a fluid (e.g., a gas or a liquid) is passed through the granular solid material at velocities sufficiently high as to suspend the solid material and cause it to behave as though it were a fluid. Examples of fluidized bed reactors are described in "Fluidization Engineering" by D. Kunii and O. Levenspiel, Butterworth-Heinemann, 1991, incorporated herein by reference. The term "circulating fluidized bed reactor" is also given its conventional meaning in the art and is used to refer to fluidized bed reactors in which the granular solid material is passed out of the reactor, circulated through a line in fluid communication with the reactor, and recycled back into the reactor. Examples of circulating fluidized bed reactors are described in "Fluidization Engineering" by D. Kunii and O. Levenspiel, Butterworth-Heinemann, 1991.

Bubbling fluidized bed reactors and turbulent fluidized bed reactors are also known to those skilled in the art. In bubbling fluidized bed reactors, the fluid stream used to fluidize the granular solid material is operated at a sufficiently low flow rate such that bubbles and voids are observed within the volume of the fluidized bed during operation. In turbulent fluidized bed reactors, the flow rate of the fluidizing stream is higher than that employed in a bubbling fluidized bed reactor, and hence, bubbles and voids are not observed within the volume of the fluidized bed during operation. Examples of bubbling and turbulent fluidized bed reactors are

described in Kirk-Othmer Encyclopedia of Chemical Technology (online), Vol. 11, Hoboken, N.J.: Wiley-Interscience, 2001, pages 791-825, incorporated herein by reference.

Olefins - The terms "olefin" or "olefin compound" (a.k.a. "alkenes") are given their ordinary meaning in the art and are used to refer to any unsaturated hydrocarbon containing one or more pairs of carbon atoms linked by a double bond. Olefins include both cyclic and acyclic (aliphatic) olefins, in which the double bond is located between carbon atoms forming part of a cyclic (closed-ring) or of an open-chain grouping, respectively. In addition, olefins may include any suitable number of double bonds (e.g., monoolefins, diolefins, triolefins, etc.). Examples of olefin compounds include, but are not limited to, ethene, propene, allene (propadiene), 1-butene, 2-butene, isobutene (2 methyl propene), butadiene, and isoprene, among others. Examples of cyclic olefins include cyclopentene, cyclohexane, cycloheptene, among others. Aromatic compounds such as toluene are not considered olefins; however, olefins that include aromatic moieties are considered olefins, for example, benzyl acrylate or styrene.

Catalysts - Catalyst components useful in the context of this invention can be selected from any catalyst known in the art, or as would be understood by those skilled in the art. Catalysts promote and/or affect reactions. Thus, as used herein, catalysts lower the activation energy (increase the rate) of a chemical process, and/or improve the distribution of products or intermediates in a chemical reaction (for example, a shape selective catalyst). Examples of reactions that can be catalyzed include: dehydration, dehydrogenation, isomerization, hydrogen transfer, hydrogenation, polymerization, cyclization, desulfurization, denitrogenation, deoxygenation, aromatization, decarbonylation, decarboxylation, aldol condensation, and combinations thereof. Catalyst components can be considered acidic, neutral, or basic, as would be understood by those skilled in the art.

For catalytic pyrolysis, particularly advantageous catalysts include those containing internal porosity selected according to pore size (e.g., mesoporous and pore sizes typically associated with zeolites), e.g., average pore sizes of less than about 10 nm, less than about 5 nm, less than about 2 nm, less than about 1 nm, less than about 0.5 nm, or smaller. In some embodiments, catalysts with average pore sizes of from about 0.5 nm to about 10 nm may be used. In some embodiments, catalysts with average pore sizes of between about 0.55 nm and about 0.65 nm, or between about 0.59 nm and about 0.63 nm may be used. In some cases,

catalysts with average pore sizes of between about 0.7 nm and about 0.8 nm, or between about 0.72 nm and about 0.78 nm may be used.

In some preferred embodiments of catalytic pyrolysis, the catalyst may be selected from naturally occurring zeolites, synthetic zeolites and combinations thereof. In certain embodiments, the catalyst may be a ZSM-5 zeolite catalyst, as would be understood by those skilled in the art. Optionally, such a catalyst can comprise acidic sites. Other types of zeolite catalysts include: ferrierite, zeolite Y, zeolite beta, mordenite, MCM-22, ZSM-23, ZSM-57, SUZ-4, EU-1, ZSM-11, (S)AlPO-31, SSZ-23, among others. Zeolites and other small pore materials are often characterized by their Constraint Index. The Constraint Index approximates the ratio of the cracking rate constants for normal hexane and 3-methylpentane. The method by which Constraint Index is determined is described more fully in U.S. Pat. No. 4,029,716, incorporated by reference for details of the method.

Constraint Index (CI) values for some typical materials are:

Table 1. Constraint Indices of some common zeolites.

Material	Constraint Index	Test Temp, °C
ZSM-4	0.5	316
ZSM-5	6-8.3	371-316
ZSM-11	5-8.7	371-316
ZSM-12	2.3	316
ZSM-20	0.5	371
ZSM-22	7.3	427
ZSM-23	9.1	427
ZSM-34	50	371
ZSM-35	4.5	454
ZSM-48	3.5	538
ZSM-50	2.1	427
Mordenite	0.5	316
REY	0.4	316
Dealuminized Y	0.5	510
Beta	0.6-2	316-399

The CI may vary within the indicated range of 1 to 12. Likewise, other variables such as crystal size or the presence of possibly occluded contaminants and binders intimately combined with the crystal may affect the CI. It is understood to those skilled in the art that the CI, as utilized herein, while affording a highly useful means for characterizing the molecular sieves of interest is approximate, taking into consideration the manner of its determination, with the possibility, in some instances, of compounding variable extremes. However, the CI will have a value for any given molecular sieve useful herein within the approximate range of 1 to 12.

In other embodiments, non-zeolite catalysts may be used; for example, WOx/ZrO2, aluminum phosphates, etc. In some embodiments, the catalyst may comprise a metal and/or a metal oxide. Suitable metals and/or oxides include, for example, nickel, palladium, platinum, titanium, vanadium, chromium, manganese, iron, cobalt, zinc, copper, gallium, and/or any of their oxides, among others. In some cases promoter elements chosen from among the rare earth elements, i.e., elements 57-71, cerium, zirconium or their oxides for combinations of these may be included to modify activity or structure of the catalyst. In addition, in some cases, properties of the catalysts (e.g., pore structure, type and/or number of acid sites, etc.) may be chosen to selectively produce a desired product.

Catalysts for other processes, such as alkylation of olefins, aromatization (hydrocarbon reforming), hydrogenation, hydrotreating, deoxygenation, denitrogenation, and desulfurization are well-known and can be selected for the olefin conversion or other processes described herein.

Hub-and-spoke – A hub-and-spoke system consists of a centralized processing center (hub) and multiple preliminary processing centers (spokes) that feed at least a portion of the materials they process to the hub for further processing.

Plastics or Polymers - The terms “plastics” and “polymers” are used interchangeably herein. A polymer is a carbon-based (at least 50 mass% C) material chiefly made up of repeating units and having a number average molecular weight of at least 100, typically greater than 1000 or greater than 10,000. Polymers include thermoplastic polymers such as, for example, polyethylene, polypropylene, polyesters, polyethylene terephthalate (PET), acrylonitrile-butadiene-styrene (ABS) copolymers, polyamide, polyurethane, polyethers, polycarbonates, poly(oxides), poly(sulfides), polyarylates, polyetherketones, polyetherimides, polysulfones, polyurethanes, polyvinyl alcohols, and polymers produced by polymerization of monomers, such as, for example, dienes, olefins, styrenes, acrylates, acrylonitrile, methacrylates,

methacrylonitrile, diacids and diols, lactones, diacids and diamines, lactams, vinyl halides, vinyl esters, block copolymers thereof, and alloys thereof, thermoset polymers such as, for example, epoxy resins; phenolic resins; melamine resins; alkyd resins; vinyl ester resins; unsaturated polyester resins; crosslinked polyurethanes; polyisocyanurates; crosslinked elastomers, including but not limited to, polyisoprene, polybutadiene, styrene-butadiene, styrene-isoprene, ethylene-propylene-diene monomer polymer; and blends thereof. Mixtures of polymers separated from municipal solid waste or other waste streams are suitable feeds provided they contain only small fractions of contaminants such as S, N, O, halogens, minerals, metals, or carbon black. Polymers yielding halogenated material upon pyrolysis, for example, polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), and other halogenated polymers, are generally minimized or excluded from the feed materials useful in this invention.

Pretreatment – The term "pretreatment" as used herein comprises any of the processes that are conducted to prepare the waste plastics for use in a catalytic pyrolysis or other upgrading process. Some of the processes that can be part of a pretreatment process include: 1) separating or grading by type of material, which selectively removes some materials that are not desirable and serves to make the feed mixture more homogeneous, 2) washing, which can include solvent or water or aqueous solution treatment to remove dirt, organic material clinging to the plastics, labels, or the like, 3) drying, which is the removal of water or other solvents or volatile materials, 4) sizing, which means cutting or comminuting or reducing the dimensions of larger particles into sizes more amenable to further processing, 5) contaminant removal, which can be a thermal or chemical or both thermal and chemical treatment that results in a reduction of the concentration of elements other than carbon and hydrogen, particularly removal of halides F, Cl, Br, or I, nitrogen, oxygen, sulfur, or metals, or a combination of these elements. Pretreatment processes may comprise any process selected from among: collecting, separating, mixing, contaminant removal, dechlorination, dehalogenation, desulfurization, distilling, oxidizing, hydrotreating, pyrolyzing, washing, sizing, melting, pelleting, filtering, drying, or combinations thereof.

Pyrolysis - The terms "pyrolysis" and "pyrolyzing" are given their conventional meaning in the art and are used to refer to the transformation of a compound, e.g., a solid hydrocarbonaceous material, into one or more other substances, e.g., volatile organic compounds, gases and coke, by heat, preferably without the addition of, or in the absence of, O_2.

Preferably, the volume fraction of O_2 present in a pyrolysis reaction chamber is 0.5% or less. Pyrolysis may take place with or without the use of a catalyst. "Catalytic pyrolysis" refers to pyrolysis performed in the presence of a catalyst and may involve steps as described in more detail below. Example of catalytic pyrolysis processes are outlined, for example, in Huber, G.W. et al, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," Chem. Rev. 106, (2006), pp. 4044-4098.

"Residence time" is defined as the volume of the reactor or device, or specific portion of a device, divided by the exit flow rate of all materials out of the reactor, or device or portion of the reactor or device, including fluidization gas, products, and impurities, measured or calculated at the average temperature of the reactor or device and the exit pressure of the reactor or device or portion thereof.

"Thermal treatment" is used herein as a process for heating a feed mixture to modest temperature at which some contaminants such as HCl, H2S, NH3 are evolved and can be exhausted, and the feed mixture becomes molten so that solids such as minerals, metals, and carbon black can be removed by filtration.

As is standard patent terminology, the term "comprising" means "including" and does not exclude additional components. Any of the inventive aspects described in conjunction with the term "comprising" also include narrower embodiments in which the term "comprising" is replaced by the narrower terms "consisting essentially of" or "consisting of." As used in this specification, the terms "includes" or "including" should not be read as limiting the invention but, rather, listing exemplary components.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 presents a schematic of an inventive process for converting plastic waste to olefins and aromatics. A mixture of plastics 10 is introduced into an optional feed system 100 that prepares the plastic mixture for introduction into the process by, for example, removing undesirable feed materials 102 such as metal, minerals, halogenated materials, and the like, or sizing the material to the desired size range, or both. The steps of removal of undesirable feed materials and sizing can be conducted in any order, i.e. either step can be conducted first and the other step conducted second. The remaining plastic mixture 101 is passed to an optional washing process 110 wherein the plastic mixture may be washed for example by treatment with a

wash solution 112 to remove unwanted materials such as dirt, or labels, or coatings, or the like, to produce washed plastic mixture 111 and used solution 113. The plastic mixture 111 is passed to pyrolysis reactor 120. Optionally a vapor phase co-reactant comprising H2, CO, or olefins, or some combination of these, or a recycle stream can be fed directly to the pyrolysis reactor 120 or the catalytic pyrolysis reactor 140 (not shown). In the pyrolysis reactor 120 the mixture is heated to a temperature to decompose the plastics into a product mixture comprising a combination of vapor, solid and liquid phases. Without separation, at least a portion of the raw pyrolysis product mixture 121 is passed to catalytic reactor 140 while maintaining the temperature of the pyrolysis product mixture at least at the temperature at which it left the pyrolysis reactor 120. The pyrolysis product mixture 121 is passed to a hot catalytic reactor 140 that is charged with an aromatization catalyst effective at converting paraffins, or olefins, or both to aromatics, shown as catalytic product 141. A portion of the catalyst 142 is continuously withdrawn from reactor 140, or can be separated from the product 141, or both, and passed to catalyst regenerator 150. In catalyst regenerator 150 the catalyst is oxidized by treatment with a source of oxygen such as air 151 and the regenerated catalyst 143 is returned to reactor 140 and the combustion product gases 152 are vented or used to provide heat to the pyrolysis reactor or reactors. Catalytic product 141 can be separated into components such as ethylene, propylene, butenes, C1-C5 paraffins, benzene, toluene, xylenes, naphthalene, and other fractions in a separation scheme using conventional separation techniques. A portion of the materials separated from catalytic product stream 141 can be recycled to pyrolysis reactor 120 or catalytic pyrolysis reactor 140, or both.

Figure 2 presents a schematic of another embodiment of the inventive process for converting plastic waste to olefins and aromatics. A mixture of plastics 10 is introduced into an optional feed system 100 that prepares the plastic mixture for introduction into the process by, for example, removing undesirable feed materials 102 such as metal, minerals, halogenated materials, and the like, or sizing the material to the desired size range, or both. The steps of removal of undesirable feed materials and sizing can be conducted in any order, i.e., either step can be conducted first and the other step conducted second. The remaining plastic mixture 101 is passed to an optional washing process 110 wherein the plastic mixture may be washed for example by treatment with a wash solution 112 to remove unwanted materials such as dirt, or labels, or coatings, or the like, to produce washed plastic mixture 111 and used solution 113. The prepared plastic mixture 111 is passed to thermal treatment reactor 115 with optional co-

reactant 122 such as a heat transfer medium or getter or the like, where the mixture is heated to an intermediate temperature to partially decompose the plastics, e.g., decompose PVC or PVDC to release HCl, or decompose another halogenated polymer to release HCl, HBr, or HI, or release vapors such as NH_3, H_2O, or the like. An optional sweep gas 124 such as H_2O, N_2, Ar, CO_2, or some combination thereof is fed to thermal treatment reactor 115 to aid in the removal of vapors produced therein which are exhausted through exit port 125. With or without a sweep gas, the vapor 125 can be treated to capture or neutralize HCl and toxic materials prior to release or transfer to water treatment. The vapor 125 typically comprises at least 60% or at least 80% H_2O, and may contain HCl, halogenated carbon compounds, and other species more volatile than molten polymers. The condensed phases 126 are passed to pyrolysis reactor 120 where they are heated to decompose into a product mixture comprising a combination of solid, liquid, and vapor phases. While maintaining the temperature of the pyrolysis product mixture at least at the temperature at which it left pyrolysis reactor 120, the raw product mixture 121 is passed to a hot catalytic reactor 140 that is charged with an aromatization catalyst effective at converting paraffins, or olefins, or both to aromatics, shown as catalytic product 141. A portion of the catalyst 142 can be continuously withdrawn from reactor 140, or can be separated from the product 141, or both, and passed to catalyst regenerator 150. In catalyst regenerator 150 the catalyst is oxidized by treatment with a source of oxygen such as air 151 and the regenerated catalyst 143 is returned to reactor 140 and the combustion product gases 152 are vented or used to provide heat to the pyrolysis reactor or reactors. Catalytic product 141 can be separated into components such as ethylene, propylene, butenes, C1-C5 paraffins, benzene, toluene, xylenes, naphthalene, and other fractions in a separation scheme using conventional separation techniques. A portion of the materials separated from catalytic product stream 141 can be recycled to pyrolysis reactor 120 or catalytic pyrolysis reactor 140, or both

Combustible gases such as methane, ethane, propane, butanes, CO and H2, optionally, can be recovered from vapor stream 125 or recovered from the gases produced in the catalytic pyrolysis in the fluidized bed reactor. Combustible gases can provide heat for the process. Heat in reactors 115 or 120 may also be provided by pressure/friction and/or other heat sources such as resistive or inductive heating.

When recycled polymeric materials are used, impurities may optionally be removed from the feed composition prior to being fed to the reactor, e.g., by an optional separation step such as

100 in Figure 1 or Figure 2. In some instances, the separation step may include mechanical separation, sink/float separation, air elutriation, or other known separation processes, preferably in an automated mode. In some instances, the particle size of the solid polymer feed composition may be reduced in a size reduction system as part of 100 prior to passing the feed to the thermal treatment reactor or pyrolysis reactor. In some embodiments, the average diameter of the reduced size feed composition exiting the size reduction system may comprise no more than about 50%, not more than about 25%, no more than about 10%, no more than about 5%, no more than about 2% of the mass average diameter of the feed composition fed to the size reduction system. The feed mixture may comprise plastics mixtures in which at least 85% by mass, or at least 90% by mass, or at least 95% by mass of the particles pass through a 0.25 inch (0.6 cm), or 0.5 inch (1.2 cm), or 1.0 inch (2.5 cm), or 1.5 inch (3.7 cm), or 2 inch (5.0 cm), or 4 inch (10.0 cm) screen. Average diameter (size) can be determined by sieving through mesh (screen). Large-particle feed material may be more easily transportable and less difficult to process than small-particle feed material. On the other hand, in some cases it may be advantageous to feed small particles to the reactor. The use of a size reduction system allows for the transport of large-particle feed between the source and the process, while enabling the feed of small particles to the reactor.

The feed materials suitable for use in the invention can comprise all types of polymeric materials including polyethylene (PE), polypropylene (PP), polyacetylene, polybutylene, polyolefins, polyethylene terephthalate (PET), polybutylene terephthalate, polyester, copolyesters, polycarbonate, polyurethanes, polyamides, polystyrene (PS), polyacetal, epoxies, polycyanurates, polyacrylics, polyurea, vinyl esters, polyacrylonitrile, polyamide, polyurethane, polyethers, polycarbonates, poly(oxides), poly(sulfides), polyarylates, polyetherketones, polyetherimides, polysulfones, polyurethanes, polyvinyl alcohol, polyvinylchloride (PVC), polyvinyl dichloride (PVDC), polyvinyl acetate, nylon, copolymers such as ethylene-propylene, acrylonitrile-butadiene-styrene (ABS), nitrile rubber, natural and synthetic rubber, tires, styrene-butadiene, styrene-acrylonitrile, styrene-isoprene, styrene-maleic anhydride, ethylene-vinyl acetate, nylon 12/6/66, filled polymers, polymer composites, plastic alloys, other polymeric materials, and polymers or plastics dissolved in a solvent, whether obtained from polymer or plastic manufacturing processes as waste or discarded materials, post-consumer recycled polymer materials, materials separated from waste streams such as municipal solid waste, and

polymers produced by polymerization of monomers, such as, for example, dienes, olefins, styrenes, acrylates, acrylonitrile, methacrylates, methacrylonitrile, diacids and diols, lactones, diacids and diamines, lactams, vinyl esters, block copolymers thereof, and alloys thereof; thermoset polymers such as, for example, epoxy resins; phenolic resins; melamine resins; alkyd resins; vinyl ester resins; unsaturated polyester resins; crosslinked polyurethanes; polyisocyanurates; crosslinked elastomers, including but not limited to, polyisoprene, polybutadiene, styrene-butadiene, styrene-isoprene, or some combination of these. The invention includes subcombinations of these materials, as desired, or as available from a particular location; the invention can be described as comprising one or any combination of these materials.

In any of the methods, the thermal treatment reactor 115 or pyrolysis reactor 120, or more than one of these, can be a moving bed reactor wherein the feed material is impelled along the length of the reactor by mechanical or gravitational means or both mechanical and gravitational means. Typical examples of reactors suitable for the thermal treatment reactor 115 or pyrolysis reactor 120, include a 1-screw extruder, 2-screw extruder, auger reactor, rotating kiln reactor, or stepped grate reactor. The pyrolysis reactor may have multiple heating zones with successively higher temperatures in later zones. The pyrolysis reactor can be fitted with a gas outlet at an area of the reactor where the temperature of the materials in the reactor is less than 300 °C or between 250 °C and 300 °C to allow for the removal of products produced at low temperatures such as steam, HCl, NH_3, or other materials from the reactor. A separating screen is fitted within the pyrolysis reactor immediately downstream of the gas outlet to at least partially prevent gases evolved at low temperature from passing along with the molten and solid materials into the hotter portions of the reactor. A gas inlet for the introduction of hot inert or recycle gas such as a gas comprising any of CH_4, H_2, CO, CO_2, and C2-C4 paraffins or olefins, or a mixture, can be fitted immediately downstream of the gas vent and optional screen.

Optionally, solid co-reactants 122, such as CaO, MgO, hydrotalcites, activated carbon, or zeolites, or some combination of these, that trap or remove undesirable components can be fed to thermal treatment reactor 115 and separated therefrom by filtration through a screen.

Where an auger reactor is utilized for thermal treatment or pyrolysis, the helical augers that optionally have different pitch dimensions at different portions of the auger in order to adjust the velocity of the condensed phases from the entry to the exit of the reactor. The flight

thickness and shaft diameter may also be of variable dimension along the length of the auger in order to control the flow velocity of the vapor and condensed phases. Augers with paddles, or cuts, or folded flights are also envisioned as within the scope of the invention.

A rotating kiln reactor can be utilized for thermal treatment or pyrolysis. A kiln cylinder can be fitted with lifters, such as helical lifters attached to the cylinder wall or tabular lifters, folded lifters, or segmented lifters extending from the cylinder wall. A rotating kiln reactor as envisioned herein can also be inclined either up or down towards the exit end of the kiln depending on the desired residence time and flow velocity desired for the condensed phases within the kiln, thus taking advantage of gravity to control residence time of the condensed phases. It is also envisioned that the rotation rate of the rotating kiln reactor can be adjusted as desired, for example between 20 revolutions per minute to 0.2 revolution per minute depending on the nature of the feed mixture and the co-reactant added in order to provide thorough mixing and high heat transfer. A rotating kiln reactor as envisioned may be heated externally by the combustion of waste process gases such as CH_4, C2-C4 paraffins, H_2, CO, and the like recycled from the product separation or natural gas or electrically.

In any of the embodiments, the temperature profile within the pyrolysis reactor can range from a lower temperature near the feed entry port to a higher temperature at the exit port or ports. For example, the range of temperatures can be from 20 °C to 225 °C, such as 20 to 100 °C, or 20 to 50 °C, at or near the inlet port, and the range of temperatures at the high-temperature exit port can be from 300 °C to 700 °C, such as from 325 to 650 °C, from 350 to 600 °C, or from 350 to 575 °C.

A solid co-reactant fed to the thermal treatment reactor can optionally be transferred to a combustion regenerator wherein the carbonaceous materials are reacted with air and at least a portion of the hot solid co-reactant material is returned to the thermal treatment reactor. The hot flue gas exiting the solid co-reactant regenerator can be passed to a catalyst heater to heat the catalyst for the catalytic pyrolysis reactor.

After leaving the thermal treatment reactor 115, the raw product preferably does not contact any cool surfaces that could condense products, and the surfaces are preferably maintained at a temperature of at least 300 °C, at least 325, or at least 350 °C or within 25 or 50 °C of the temperature exiting the reactor 115. Preferably, in any of the embodiments, the temperature of the mixture is maintained at a temperature at least 2 °C, or at least 3 °C, or at least

5 °C, or at least 10 °C higher than the temperature of the mixture at the exit end of the thermal treatment reactor.

In any of the inventive aspects, the catalytic reactor 140 can be a fluidized bed reactor; wherein the catalyst is a solid catalyst and the step of catalytically pyrolyzing comprises pyrolyzing in the presence of the solid catalyst in a fluidized bed reactor to produce a fluid product stream 141 and used catalyst with coke 142; and wherein at least a portion of the used catalyst with coke is transferred to a regenerator 150 where the coke is reacted with oxygen or air to form hot regenerated catalyst, and returning at least a portion of the hot regenerated catalyst 143 to the fluidized bed reactor, wherein heat from the hot regenerated catalyst provides energy to the step of catalytic pyrolyzing. In any of the methods the vapors exiting the catalytic pyrolysis reactor can be passed through an optional solids separation device such as a cyclone or screen to remove entrained solids. These entrained solids can be passed to the catalyst regenerator, or at least a portion can be returned to the catalytic pyrolysis reactor, or discarded, or some combination of these.

In any of the methods, the step of catalytically pyrolyzing may comprise pyrolysis in the presence of a fluid bed catalyst. The catalytic pyrolysis reactor may comprise a fluidized bed, circulating bed, bubbling bed, or riser reactor operating at a temperature in the range from 300 °C to 800 °C, from 350 °C to 750 °C, from 400 °C to 700 °C, from 450 °C to 650 °C, from 500 °C to 600 °C. or from 525 °C to 575 °C. The residence time of the vapors in the catalytic pyrolysis can be from 1 second to 480 seconds, from 1 second to 240 seconds, from 2 seconds to 60 seconds, from 3 seconds to 30 seconds, or from 4 seconds to 15 seconds. The pressure of the catalytic pyrolysis reactor can be at least 0.1 MPa (1 bar), at least 0.3 MPa (3bar), or at least 0.4 MPa (4 bar), or from 0.1 to 2.0 MPa (1 to 20 bar), from 0.1 to 1.0 MPa (1 to 10 bar), or from 0.3 to 0.8 MPa (3 to 8 bar), preferably from 0.4 to 0.6 MPa (4 to 6 bar); pressures are absolute pressures.

Design and conditions of the fluidized bed catalytic reactor can be those conventionally known. A fluidization gas may be needed at start-up; during steady-state operation, fluidization gas may comprise a portion of vapor separated from stream 126 that, optionally, can be piped into the bottom of the fast catalytic pyrolysis fluidized bed reactor. Recycle gas from the process may be used as fluidizing gas. The fluidization gas can comprise H_2, CO, CO_2, H_2O, C1-C4 paraffins or olefins or both, N_2, Ar, He, or a recycle stream, or some combination thereof.

For catalytic pyrolysis, useful catalysts include those containing internal porosity selected according to pore size (e.g., mesoporous and pore sizes typically associated with zeolites), e.g., average pore sizes of less than 10 nm, less than 5 nm, less than 2 nm, less than 1 nm, less than 0.5 nm, or smaller. In some embodiments, catalysts with average pore sizes of from 0.5 to 10 nm may be used. In some embodiments, catalysts with average pore sizes of between 0.5 and 0.65 nm, or between 0.59 and 0.63 nm may be used. In some cases, catalysts with average pore sizes of between 0.7 and 0.8 nm, or between 0.72 and 0.78 nm may be used.

The catalyst composition particularly advantageous in the catalytic pyrolysis fluidized bed reactor of the present invention comprises a crystalline molecular sieve characterized by an SAR (silica to alumina, SiO_2:Al_2O_3 mass ratio) greater than 12, or from 12 to 240, and a CI (constraint index) from 1 to 12. Non-limiting examples of these crystalline molecular sieves are those having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, or combinations thereof. As an embodiment, the catalyst composition comprises a crystalline molecular sieve characterized by an SAR from greater than 12 to 240 and a CI from 5 to 10, such as, for example, molecular sieves having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23 or combinations thereof. The method by which CI is determined is described more fully in U.S. Patent No. 4,029,716, incorporated herein by reference for details of the method.

The molecular sieve for use herein or the catalyst composition comprising same may be thermally treated at high temperatures. This thermal treatment is typically performed by heating at a temperature of at least 370 °C for at least 1 minute and generally not longer than 20 hours (typically in an oxygen containing atmosphere, preferably air). While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be performed at a temperature up to about 925 °C. The thermally treated product is particularly useful in the present process.

For the catalyst compositions useful in this invention, the suitable molecular sieve may be employed in combination with a support or binder material such as, for example, a porous inorganic oxide support or a clay binder. Non-limiting examples of such binder materials include alumina, zirconia, silica, magnesia, thoria, titania, boria, and combinations thereof, generally in the form of dried inorganic oxide gels and gelatinous precipitates. Suitable clay materials include, by way of example, bentonite, kieselguhr, and combinations thereof. The relative proportion of suitable crystalline molecular sieve of the total catalyst composition may vary

widely with the molecular sieve content ranging from 30 to 90 percent by weight and more usually in the range of 40 to 70 percent by weight of the composition. The catalyst composition may be in the form of an extrudate, beads or fluidizable microspheres.

The molecular sieve for use herein or the catalyst composition comprising it may have original cations replaced, in accordance with techniques well known in the art, at least in part, by ion exchange with hydrogen, or hydrogen precursor cations, or non-noble metal ions of Group VIII of the Periodic Table, i.e. nickel, iron or cobalt, or zinc, or gallium, or combinations thereof.

A portion of the vapor products from the catalytic pyrolysis process can be fed to a condenser where it is cooled to produce condensed materials. A portion of the condensed materials can be separated into fractions and at least a portion of the condensed material is recycled to the pyrolysis reactor or the catalytic pyrolysis reactor. The condensed material can be separated into fractions by distillation and at least a portion of the fraction boiling above 300 °C or boiling in the range 300 to 800 °C is recycled to the pyrolysis or catalytic pyrolysis reactor. The condensed material can be separated into fractions by distillation and at least a portion of the paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms recycled to the pyrolysis or catalytic pyrolysis reactor.

In processes in which catalyst from the catalytic pyrolysis is regenerated, heat is generated by the oxidation of coke, char, and other materials in a catalyst regenerator for use in the process, or for conversion to electricity for export. An oxidizing agent can be fed to the regenerator via a stream shown as 151 in Figure 1. The oxidizing agent may originate from any source including, for example, a tank of oxygen, atmospheric air, steam, among others. In the regenerator, the catalyst is re-activated by reacting the catalyst with the oxidizing agent and heat is generated. A solid mixture comprising deactivated catalyst may comprise residual carbon and/or coke as well as coke or char from the process, which may be removed via reaction with the oxidizing agent in the regenerator. In some embodiments a portion of the gaseous products from the catalytic pyrolysis process is fed to the catalyst regenerator to be combusted with the solid materials. The gaseous products may be first separated into an olefin rich stream and an olefin poor stream and at least a portion of the olefin poor stream may be fed to the catalyst regenerator. The regenerator in Figure 1 comprises a vent stream 152 which may include regeneration reaction products, residual oxidizing agent, etc.

In some embodiments of the process at least a portion of the solid materials 123 that are removed from thermal treatment reactor 115 may be recycled to the feed of thermal treatment reactor 115 as a portion of the optional co-reactant 122. In some embodiments of the process, the optional co-reactant 122 may comprise solid materials that react with sulfur or nitrogen compounds to trap the sulfur or nitrogen species in the solid phase. The solid materials in the optional co-reactant 122 can comprise one or more materials chosen from among agricultural lime, calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, or hydrotalcites, activated carbon, or zeolite, or some combination thereof.

Waste plastics are collected locally at numerous facilities that each handle small amounts of plastics in any one day, either as part of general waste (municipal solid waste) or a separate recycling stream. In either case, most of the material ends up among the 25 million tons of plastics that are sent to one of more than 2,600 landfills in the USA each year. The amount of waste plastic available at any one site is typically on the order of only a few tens of metric tonnes per day.

A chemical plastics recycling plant includes feed handling, cleaning, processing (e.g. pyrolysis and catalytic pyrolysis), recovery, separations, and purifications operations. The cost of the separations and purification facilities often constitute 35-50% of the capital cost of a complete facility.

Plants that have small capacities are more expensive on a per-tonne-of-product basis than larger plants due to the lack of the economy of scale. One way to take advantage of economies of scale for the separations and purifications functions is to network together several plants that produce crude mixtures of liquid products of a similar composition, and send the crude mixtures to a refinery or other central processing facility for separation and purification into chemical grade materials.

Several commercial plastics upgrading processes produce liquid products that are not ready for separation and purification due to the presence of long chain hydrocarbons and olefins that must be further upgraded by hydroprocessing such as in a hydrocracker, or hydrotreater, or steam cracker or some combination of these. Hydroprocessing requires a source of hydrogen, whereas the products of the present process require little or no hydrogen for upgrading and can be separated and purified without hydroprocessing. In addition, heating the feeds for hydroprocessing requires energy addition that cannot be fully recovered, which is avoided with

the current invention. Hydroprocessing is exothermic, so considerable heat is released in the process, which can cause problems with heat removal if the level of olefins is too high for the heat removal capabilities of the system.

A benefit of the invention of a two-step process for upgrading plastics by pyrolysis followed by catalytic pyrolysis is the ability to produce a liquid product that is suitable for combining with conventional refinery streams such as the product of a steam cracker or hydrocracker, and which can be more readily stored and transported compared to gaseous products, for separation and purification at a larger facility. This means that a crude liquid product stream made from recycled plastic by the inventive process can be produced in a separate location from the product purification system, and this "distributed processing" scheme may be advantageous as separation and purification costs can be minimized for small scale regional facilities.

Figure 3 shows an embodiment of the invention in which five plastics upgrading units 200 are connected to feed a single product separation and purification facility 210 in a hub and spoke system.

In some embodiments a system for upgrading waste plastics comprises the first pyrolysis reactor and catalytic fluidized bed reactor that together form one spoke of a 'hub-and-spoke' network for producing refined chemical intermediates such as benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, naphthalene, or others. or some combination of these, where each of the more than one plastics upgrading sites (the spokes) produces condensed phase products that are sent to a central processing facility (the hub) for separation and purification into product streams. In some embodiments of the system the number of plastics upgrading facilities that can be in a network feeding a single central separation and purification facility can be at least 2, at least 3, at least 5, at least 7, at least 10, or at least 15, or from 2 to 20, from 3 to 10, or from 5 to 10 plastics upgrading facilities. The total crude product mixture prepared at the plastics upgrading facilities that is introduced into a central separation and purification facility can be at least 20, at least 50, at least 100, at least 150, or at least 200 metric tons per day, or from 20 to 500, from 30 to 200, or from 50 to 150 metric tons per day of crude product mixture.

In some embodiments a system for upgrading plastics comprising the first pyrolysis reactor as one 'spoke' in a 'hub and spoke' network for producing refined chemical

intermediates such as benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, naphthalene, or others. or some combination of these, where each of the more than one plastics upgrading sites (the spokes) produces condensed phase products that are sent to a central processing facility (the hub) that includes a central fluidized bed catalytic process plant (Plas-TCat™) and separation and purification into product streams. In some embodiments of the system the number of plastics pyrolysis facilities that can be in a network feeding a single central catalytic upgrading, separation, and purification facility can be at least 2, at least 3, at least 5, at least 7, at least 10, or at least 15, or from 2 to 20, from 3 to 10, or from 5 to 10 plastics pyrolysis facilities. The total crude product mixture prepared at the plastics pyrolysis facilities that is introduced into a central catalytic upgrading, separation, and purification facility can be at least 20, at least 50, at least 100, at least 150, or at least 200 metric tons per day, or from 20 to 500, from 30 to 200, or from 50 to 150 metric tons per day of crude product mixture.

Figure 5 presents a schematic of an inventive process for converting plastic waste to olefins and aromatics and other valuable products using a distributed feed pretreatment system in which the plastics are pretreated and catalytically pyrolyzed at multiple sites and the products are processed further at a central site. In the Figure, there are 3 sites at which the waste plastic is collected, pretreated, and catalytically pyrolyzed to produce valuable products. In some embodiments there are 2 or more, or as many as 15 sites that conduct pretreatment and catalytic pyrolysis and from which catalytic pyrolysis products are transferred to a central site where any combination of upgrading, separations, and/or purifications are conducted to produce products. The site where the combined products are further processed can be at, or adjacent to, a refinery or chemical plant, or be a dedicated processing site, and the materials may be co-processed with materials from other sources including renewable sources or fossil sources or both. Figure 6 presents an alternative of the inventive process for converting plastic waste to olefins and aromatics and other valuable products using a distributed feed pretreatment system in which the plastics are pretreated at multiple sites and the treated materials are processed further at a central site.

The configurations of Figure 5 and Figure 6 may be combined such that material that has been pretreated and catalytically pyrolyzed at a distributed site, e.g., site 1, site 2, or site 3 of Figure 5, may be combined with the product of the catalytic pyrolysis in site 4 of Figure 6 for

product upgrading, separation, and purification in a central facility. The feed to the central product upgrading, separation, and purification may thus be a combination of materials pretreated and catalytically pyrolyzed in a distributed system as in Figure 5 combined with material pretreated in a distributed system of Figure 6 and catalytically pyrolyzed in the central catalytic pyrolysis facility for product upgrading, separation, and purification.

Figure 7 presents one example of a pretreatment process for pretreating waste plastic to make it suitable for catalytic upgrading. A mixture of plastics is introduced into an optional preliminary sorting system 20 that removes undesirable materials and rejects them in stream 22 and passes the useful materials 21 to a washing process 30. The undesirable materials 22 may include items such as metal, concrete, dirt, wood, mineral matter, glass, or other material that is not readily processed along with waste plastics. In the washing step 30, a solvent, water, or aqueous solution 13 is admixed with the solid waste plastic, optionally agitated, and optionally heated, and the washed solids 31 are separated from the waste wash solution 32 and passed to a drying unit 40. At least a portion of the waste wash solution may be recycled to the washing unit 30. In the dryer 40 moisture and volatile solvents 42 are removed by exposure to a flowing gas stream, optionally heated. The dried material 41 is passed to a sizing unit 50. In the sizing unit, the plastics are shredded by any of a range of cutting devices and large particles that do not pass through a sizing screen 52 are discarded or recycled to the preliminary sorting system 20, and the sized materials 51 are passed to an optional chemical pretreatment unit 60. In the chemical pretreatment unit, the material is heated to melt at least a portion of the plastic and drive off volatile off-gas products 63 such as HCl, HBr, HI, NH_3, CO_2, or other volatile decomposition products to produce a stream 61 of pretreated material that can be cooled and chopped to an appropriate size for use in catalytic pyrolysis, or kept hot and fed directly to the catalytic pyrolysis process. As part of the chemical pretreatment unit 60, the molten mixture may be passed through a screen to remove solids or fragments of material 62 that do not melt under the conditions of the process. The chemical pretreatment unit 60 may comprise one or more static mixers in which the molten mixture may be passed through a static mixing device to increase the homogeneity of the mixture.

The various units of the pretreatment process, i.e., 20, 30, 40, 50, and 60, can be re-arranged to suit the needs of the particular waste plastic mixture, the catalytic pyrolysis process, or other processes, or existing infrastructure, and may comprise any combination of these

elements, or others as needed. In some cases not all of these units will be needed and some can be omitted. In the schematic of Figure 7 a preliminary sorting unit 20 prepares the plastic mixture for further pretreatment by, for example, removing undesirable feed materials 22 such as metal, minerals, halogenated materials, concrete, dirt, wood, glass, and the like. The sorting is often done manually or by any of a number of automated processes that include items such as screens and pickers that are well known in the art.

The washing step 30 comprises introducing a solvent to the mixture under conditions of pressure and temperature, and optionally with a flow velocity, to loosen and remove adherent materials such as dirt, labels, food, organic waste, biomass, feces, dust, or other materials that contain contaminants or interfere with the further pretreatment or processing steps. The solvent 13 can comprise water, aqueous solutions, acidic solutions, basic solutions, organic solvents, or mixed solvents, or some combination thereof that allows the removal of undesirable components. The washing may be conducted at ambient temperature or the solvent may be heated to temperatures between 15 °C and 100 °C. In some embodiments, the washing may include treatment with superheated water or steam or other vapor at temperatures of at least 100 °C. The washing can be a single step or may be repeated, and the different washings may use different solvents or process conditions. Any of the waste solvent(s) 32 is separated and may be discarded or treated for reuse in the washing process. The washing step may include a rinse step in which the material is treated with water or another solvent to remove the washing solution.

The washed material can be dried in a dryer. The drying step is typically operated at temperatures from 20 °C to 150 °C and can be enhanced by a flow of gas, such as air or N2 or other inert gas mixture. The dried plastic materials contain no more than 20, 10, 5, 2, or 1 % by mass moisture.

The washed and dried plastic material can be sized to the desired particle size in sizing step 50. In the sizing unit the plastics are sized by any of a range of cutting devices and large particles that do not pass through a sizing screen 52 can be discarded or recycled to the sorting system. The particles can be sized to be less than 25 cm (10 inches), 15 cm (6 inches) 10 cm (4 inches, 5 cm (2 inches), 2.5 cm (1 inch), 1.5 cm (0.6 inches), or less than 0.75 cm (0.3 inches) or from 0.2 to 25, 0.75 to 10, or from 1.5 to 5 cm in their longest dimension or to pass through a screen of 5 cm (2 inches), 2.5 cm (1 inch), 1.25 cm (0.5 inches), or 0.635 cm (0.25 inches).

An optional sorting step may be conducted after the sizing step 50. An optional sorting step may comprise any of a variety of sorting processes such as automated sorting using optical, near IR, UV, visible, or other, recognition to identify components for removal, and automated removal, sink/float separation, air elutriation, froth flotation, etc. as are well known in the art can be used to remove unwanted materials.

The plastic feed mixture may be mixed to achieve a more homogeneous mixture by passing the molten mixture through one or more static mixing devices. Static mixing devices divide the stream, divert the stream, or both, to induce mixing of the materials. Typical static mixers comprise packing within a pipe that is shaped to divide and divert the passing molten stream or non-linear sections of pipe that induce mixing. Typical static mixers are shown in Figure 8 and can be obtained commercially from numerous vendors. The static mixing device can be operated at any temperature at which the plastic mixture is molten, such as at least 80, 100, 150, 200, 225, or 250 °C, or from 80 to 350, 150 to 350, 150 to 300, or 200 to 250 °C. Particularly in processes depicted in Figure 6 wherein the pretreatment is conducted in more than one facility in a distributed network and the upgrading processes are conducted in a central facility, the pretreatment process may include an additional pelleting or other particle shaping process step to produce waste plastic particles into cylindrical or near spherical shapes that are readily handled. A pelleting process may involve feeding plastic waste materials such as stream 61 in Figure 7 to an extruder where they are heated to form a molten mixture that is passed through an orifice. The resulting extrudate may be cooled and chopped or sliced into the desired size for transport and handling and feed to the pyrolytic upgrading process, such as stream 111. An alternative pelleting process may involve stamping pellets from the solidified mixed plastic.

When recycled polymeric materials are used, impurities may optionally be removed from the feed composition prior to being fed to the reactor, e.g., by an optional separation step such as 100 in Figure 7. In some instances, the separation step may include mechanical separation, sink/float separation, air elutriation, or other known separation processes, preferably in an automated mode. In some instances, the particle size of the solid polymer feed composition may be reduced in a size reduction system as part of 100 prior to passing the feed to the thermal treatment reactor or pyrolysis reactor. In some embodiments, the average diameter of the reduced size feed composition exiting the size reduction system may comprise no more than about 50%, not more than about 25%, no more than about 10%, no more than about 5%, no more

than about 2% of the mass average diameter of the feed composition fed to the size reduction system. The feed mixture may comprise plastics mixtures in which at least 85% by mass, or at least 90% by mass, or at least 95% by mass of the particles pass through a 0.25 inch (0.6 cm), or 0.5 inch (1.2 cm), or 1.0 inch (2.5 cm), or 1.5 inch (3.7 cm), or 2 inch (5.0 cm), or 4 inch (10.0 cm) screen. Average diameter (size) can be determined by sieving through mesh (screen). Large-particle feed material may be more easily transportable and less difficult to process than small-particle feed material. On the other hand, in some cases it may be advantageous to feed small particles to the reactor. The use of a size reduction system allows for the transport of large-particle feed between the source and the process, while enabling the feed of small particles to the reactor.

EXAMPLES 1 through 10

A drop-tube reactor for two-step chemical conversion of plastics without separation between the pyrolysis and catalytic pyrolysis steps comprises a quartz reactor tube (ACE Glass) containing a quartz frit (40 – 90 μm) fused into the center of the tube. FIGURE 4 shows the configuration of the drop-tube reactor. A sample cell (10 mm OD, 8 mm ID, 25 mm length, quartz, made by TGP) is used to contain the feedstock using two pieces of quartz wool (TGP). As illustrated in FIGURE 4, the sample cell was placed in a reactor cap (borosilicate, ACE Glass) and was held by a stopper (1/4 inch (6 mm) aluminum rod, McMaster). The reactor cap and the quartz reactor were then assembled and installed onto the fixed-bed reactor system. The bottom of the reactor was connected to a condenser (borosilicate) filled with perforated stainless steel packing (ACE Glass) immersed in an ice-water bath (0°C). A heating mantle was applied between the reactor bottom and the condenser top to prevent any condensation before the condenser. During the reaction, the heating mantle was set at 210°C.

In the reactor, a small sample of ZSM-5 catalyst (1.5 g) was placed on top of the quartz frit. Feedstock (100 mg for each run) was sealed in a sample cell with the quartz wool. The catalyst/feedstock weight ratio was about 15. Prior to dropping the contents of the sample cell into the reactor, the catalyst was calcined at 550°C under 100 mL/min air flow for 20 min (ramping rate = 12°C/min). After calcination, the reactor was cooled to reaction temperature (500°C). During the cool-down, the condenser was filled with 10 mL of solvent (ethyl acetate for plastics conversion, and acetone for biomass conversion) and held for 10 min for temperature

lineout. The reactor system was then purged with helium flow at 75 mL/min for 20 min to remove air and to purge the gas collection lines. The sample cell containing the feed material was dropped into the reactor by pulling out the stopper rod to initiate the reaction.

A hold period of 10 min allowed the reaction to complete. Gas products, consisting mostly of permanent gases and $C_1 - C_3$ olefins and paraffins were collected in a gas bag. Liquid products (mostly C_{4+}) were collected in the condenser. After reaction the temperature was increased to 650°C without gas flow. Solid products, including coke and char remaining in the reactor, were then burned at 650°C for 10 min under 50 mL/min air flow. The gas products during burning were collected in a second gas bag. An additional 3 mL of solvent was added to the condenser to extract any products remaining on the top of the condenser. All of the liquid in the condenser was then transferred to a 20 mL sample vial. A weighed amount of internal standard (dioxane, typically 3000 – 5000 mg, Sigma-Aldrich) was added to the sample vial. The condenser was washed with acetone and was dried in a drying oven. It is noted that a small amount of liquid was retained in the condenser due to holdup on the packing. Therefore, the weight of the condenser with and without liquid products was measured to obtain the total amount of liquid products. Liquid samples were analyzed by a GC-FID (gas chromatograph with flame ionization detector from Shimadzu 2010Plus) for hydrocarbons and oxygenates. Gas bag samples were analyzed using an Agilent GC 7890B gas chromatograph.

The results of the experiments for various feeds are presented in TABLE 2. The balances of the products unaccounted for in TABLE 2 comprise water, inert solids, and minor components not readily recovered for combustion.

Examples 1 through 10 show that the two-step pyrolysis followed by catalytic pyrolysis without an intervening separation step produces high yields of olefins and aromatics from plastics. The yield of olefins is at least 2% in all cases, and the yield of BTX is at least 10.08% in all cases. Examples 1, 2, 3, 4, and 9 show that for polymers that do not contain fillers (tires) or heteroatoms (PET, nylon), the yield of BTX is at least 32.88%, the yield of olefins is at least 5.58%, and the yield of coke and char is less than 5%, and often less than 2% of the mass of the feed. The yield of olefins for two-step pyrolysis/catalysis for polyolefins (Examples 1, 2, 3, and 4) is at least 10.43%, and the yield for linear, non-branched polyolefins (Examples 1, 2, and 3) is at least 17.25%. The yield of aromatics for two-step pyrolysis/catalysis for polyolefins (Examples 1, 2, 3, and 4) is at least 32.88%, and the yield for linear, non-branched polyolefins (Examples 1, 2, and 3) is at least 45.6%.

TABLE 2. Products of catalytic pyrolysis of various materials with ZSM-5 catalyst in drop tube experiments. All values are weight percent.

Ex	Feed	BTX	Other C5+ Liquid	Coke and Char	Olefins	Paraffins	H2	CO	CO2	Ash	Total
1	Polyethylene (PE)	52.8	3.5	0.9	18.1	16.4	2.6	0.3	0.3	0	94.8
2	Polypropylene (PP)	45.6	4.0	0.7	21.5	16.5	2.4	0	0.2	0	90.8
3	High Density Polyethylene (HDPE)	53.05	3.47	1.05	17.25	18.53	2.7	0	0.21	0	96.3
4	Isoprene	32.88	10.03	1.29	10.43	5.89	1.29	0	0.28	0	62.1
5	Tire Sidewall	14.94	3.13	21.62	8.25	2.08	0.9	0.56	0.95	7.0	59.4
6	Tire Tread	13.9	2.99	20.37	7.53	2.12	0.94	0.25	0.8	7.0	55.9
7	PET	23.73	3.92	17.76	4.98	1.16	0.38	7.65	34.13	0	93.7
8	PET Clothing	23.06	4.12	16.96	2.17	1.3	0.38	7.37	31.67	0	87.0
9	Polystyrene (PS)	38.51	36.29	4.13	5.58	1.49	0.48	0	0.33	0	86.8
10	Nylon	10.08	6.2	10.0	16.57	1.23	1.2	3.72	4.19	0	53.2

What is claimed:

1. A system or method for upgrading waste plastics to useful products comprising multiple plastics pretreatment facilities,

a. wherein each pretreatment facility forms one spoke of a 'hub-and-spoke' network,

b. wherein pretreatment at each pretreatment facility includes raising the temperature of the waste plastics to at least 100 °C,

c. wherein either

i. the hub comprises a catalytic pyrolysis unit, or

ii. each spoke comprises a catalytic pyrolysis unit, and

at least a portion of the products of each spoke is collected and processed at a central processing facility (the hub) for upgrading, separation, and purification into product streams.

2. The system or method of claim 1 wherein the pretreatment comprises one or more of the following: collecting, separating, sorting, mixing, removing contaminants, thermal treatment, sanitization, decontamination, sterilization, dechlorination, washing, drying, sizing, melting, filtering, pelleting, or combinations thereof, conducted in any order.

3. The system or method of claim 1 wherein the product of the catalytic pyrolysis comprises one or more of benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, or naphthalene, hydrogen, or some combination of these.

4. The system or method of claim 2 wherein the pretreatment comprises a thermal treatment comprising two or more thermal treatment reactors.

5. The system or method of claim 2 wherein the pretreatment facility further comprises a shredder, a granulator, a depackaging unit, a dewatering unit, or any combination thereof.

6. The system or method of claim 4 wherein each thermal treatment reactor comprises one or more moving bed, 1-screw extruder, twin-screw extruder, multiple-screw extruder, planetary extruder,

ultrasonically assisted extruder, auger reactor, rotating kiln reactor, stirred tank reactor, or stepped grate reactor, or some combination thereof.

7. The system or method of claim 4 wherein material is heated to a temperature between 180 °C and 300 °C in a first thermal treatment reactor and the condensed products are passed to a second thermal treatment reactor.

8. The system or method of claim 1 wherein a sweep gas is fed to the thermal treatment reactor and a vapor stream comprising at least one of HCl, HBr, HI, NH_3, CO_2, N_2, H_2O, Air, Ar, or CH_4, is exhausted.

9. The system or method of any of the above claims wherein one of the thermal treatment reactors comprises an inlet port and an exit port, the temperatures can be from 20 to 225 °C, such as 20 to 100 °C, or 20 to 50 °C, at or near the inlet port, and the range of temperatures at the high-temperature exit port can be from 300 to 700 °C, such as from 325 to 650 °C, from 350 to 600 °C, or from 350 to 575 °C.

10. The system or method of claim 4 wherein the residence time of condensed phases in the thermal treatment reactor or reactors is at least 0.5, 5, 10, 20, or at least 30, or from 1 to 60, 5 to 30, 10 to 30, or 0.5 to 10 minutes.

11. The system or method of claim 4 wherein the thermal treatment reactors comprises one or more 1-screw or 2-screw extruders, and a stirred tank reactor.

12. The system or method of any of the above claims wherein the filtering is accomplished by first heating the plastic mixture to at least 200 °C in a thermal treatment reactor to achieve a molten state and filtered to remove solids.

13. The system or method of claim 2 wherein the pretreatment comprises passing molten plastic through a static mixer.

14. The system or method of any of the above claims wherein contaminants are removed by heating the feed mixture anaerobically to a temperature of between 150 °C and 350 °C or between 250 °C and 300 °C in a thermal treatment reactor to at least partially decompose the polymers.

15. The system or method of claim 4 wherein the feed is heated to a temperature between 250 and 300 °C in a first thermal treatment reactor and the products from the first thermal reactor are passed to a second thermal treatment reactor.

16. The system or method of any of the above claims wherein a solid co-reactant material is fed to the thermal treatment reactor.

17. The system or method of claim 16 wherein the solid co-reactant comprises one or more materials chosen from among agricultural lime, calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, hydrotalcites, activated carbon, or zeolite, or other solid basic material, or some combination thereof.

18. The system or method of claim 16 wherein the solid co-reactant material is recovered from the thermal treatment reactor and is transferred to a combustion regenerator wherein the carbonaceous materials are reacted with air and at least a portion of the hot solid co-reactant material is returned to the thermal treatment reactor.

19. The system or method of any of the above claims wherein the products produced in the pretreatment process are transferred, without separating a significant portion of the products, to a catalytic pyrolysis reactor containing a catalyst.

20. The system or method of any of the above claims wherein the molten products of the pretreatment are fed to a pelleting process and cut into pellets.

21. The system or method of claim 1 wherein the feed to the catalytic pyrolysis reactor comprises pellets.

22. The system or method of claim 2 wherein a preliminary sorting unit prepares the plastic mixture for further pretreatment by, for example, removing undesirable feed materials comprising metal, minerals, halogenated materials, concrete, dirt, wood, glass, or a combination thereof.

23. The system or method of claim 2 wherein the washing includes treatment with superheated water or steam or other vapor at temperatures of at least 100 °C.

24. The system or method of claim 2 wherein washing is accomplished by mixing water, aqueous solutions, acidic solutions, basic solutions, organic solvents, or mixed solvents, or some combination thereof with the solid waste plastic, and the washed solids are separated from the waste wash solution.

25. The system or method of claim 24 wherein the washing is repeated and the second washing uses a different solvents.

26. The system or method of claims 23, 24, or 25 wherein the washing comprises a rinse step in which the material is treated with water or another solvent to remove the washing solution.

27. The system or method of claim 2 wherein the plastics are dried by removing moisture and volatile solvents from the plastic by exposure to a flowing gas stream, optionally heated at temperatures from 20 °C to 150 °C.

28. The system or method of claim 2 wherein the plastics are sized by a cutting device and large particles that do not pass through a sizing screen are discarded or recycled to the preliminary sorting system.

29. The system or method of claim 28 wherein plastic particles are sized to be less than 25 cm (10 inches), 15 cm (6 inches) 10 cm (4 inches, 5 cm (2 inches), 2.5 cm (1 inch), 1.5 cm (0.6 inches), or less than 0.75 cm (0.3 inches) or from 0.2 to 25, 0.75 to 10, or from 1.5 to 5 cm in their longest dimension or to pass through a screen of 5 cm (2 inches), 2.5 cm (1 inch), 1.25 cm (0.5 inches), or 0.635 cm (0.25 inches).

30. The system or method of claim 1 wherein the pretreatment comprises sorting of sized materials that is accomplished using optical, near IR, UV, visible, or other recognition to identify components for removal, and automated removal, sink/float separation, air elutriation, or froth flotation is used to remove unwanted materials.

31. The system or method of claim 2 wherein the pretreatment process comprises a pelleting or other particle shaping process step to produce waste plastic particles in cylindrical or spherical shapes.

32. The system or method of claim 31 wherein the pelleting process comprises feeding plastic waste materials to an extruder where they are heated to form a molten mixture that is passed through an orifice, cooled, and chopped or sliced into the desired size for transport to the catalytic pyrolytic upgrading facility.

33. The system or method of claim 32 wherein the particle shaping process comprises stamping pellets from a solidified plastic mixture.

34. The system or method of any of the above claims wherein the waste plastics comprise plastics chosen from among polyethylene, polypropylene, polyesters, polyethylene terephthalate (PET), acrylonitrile-butadiene-styrene (ABS) copolymers, polyamide, polyurethane, polyethers, polycarbonates, poly(oxides), poly(sulfides), polyarylates, polyetherketones, polyetherimides, polysulfones, polyurethanes, polyvinyl alcohols, and polymers produced by polymerization of monomers, such as, for example, dienes, olefins, styrenes, acrylates, acrylonitrile, methacrylates, methacrylonitrile, diacids and diols, lactones, diacids and diamines, lactams, vinyl esters, block copolymers thereof, and alloys thereof; thermoset polymers such as, for example, epoxy resins; phenolic resins; melamine resins; alkyd resins; vinyl ester resins; unsaturated polyester resins; crosslinked polyurethanes; polyisocyanurates; crosslinked elastomers, including but not limited to, polyisoprene, polybutadiene, styrene-butadiene, styrene-isoprene, ethylene-propylene-diene monomer polymer; and mixtures thereof.

35. The system or method of any of the above claims wherein the waste plastics comprise a mix of waste plastic chosen from among polyethylene terephthalate (PET), high density polyethylene (HDPE),

polyvinyl chloride (PVC) or polyvinylidene (PVCD), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), or mixed resins, or some combination thereof.

36. The system or method of any of the above claims wherein the catalytic reactor is a fluidized bed, circulating bed, bubbling bed, or riser reactor, comprising a catalyst and operating at a temperature in the range from 300 °C to 800 °C, from 350 °C to 750 °C, from 400 °C to 700 °C, from 450 °C to 650 °C, from 500 °C to 600 °C, or from 525 °C to 575 °C.

37. The system or method of claim 1 wherein the pressure is at least 0.1 MPa (1 bar), at least 0.3 MPa (3bar), or at least 0.4 MPa (4 bar), or from 0.1 to 2.0 MPa (1 to 20 bar), from 0.1 to 1.0 MPa (1 to 10 bar), or from 0.3 to 0.8 MPa (3 to 8 bar), preferably from 0.4 to 0.6 MPa (4 to 6 bar) in the catalytic pyrolysis reactor.

38. The system or method of claim 36 wherein the fluidization gas for the catalytic pyrolysis comprises H_2, CO, CO_2, H_2O, C1-C4 paraffins or olefins or both, N_2, Ar, He, other inert gas, or a recycle stream, or some combination thereof.

39. The system or method of claim 36 wherein the residence time of the fluidization gas in the catalytic pyrolysis reactor, defined as the volume of the reactor divided by the volumetric flow rate of the fluidization fluid under process conditions of temperature and pressure, can be from 1 second to 480 seconds, or from 1 second to 240 seconds, or from 2 seconds to 60 seconds, or from 3 seconds to 30 seconds, or from 4 seconds to 15 seconds.

40. The system or method of claim 36 wherein the catalyst comprises a zeolite.

41. The system or method of claim 36 wherein the catalyst may be selected from naturally occurring zeolites, synthetic zeolites, or combinations thereof, or from among ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, or combinations thereof.

42. The system or method of claim 3 wherein the product vapor mixture from the catalytic conversion comprises at least 20 mass% olefins, or at least 50 mass% olefins, or in the range of 20 to 90 mass% olefins.

43. The system or method of claim 3 wherein the mass yield of BTX in the gaseous product mixture from the catalytic conversion is at least 10%, 20%, 30%, 40%, 50%, or at least 60%, or from 10% to 90%, or from 20% to 70%, or from 30% to 60% BTX based on the mass in the polymer feed.

44. The system or method of claim 3 wherein the vapor products of the catalytic pyrolysis are passed through one or more solids separation devices comprising a cyclone.

45. The system or method of claim 3 wherein catalyst in the catalytic pyrolysis reactor is withdrawn and regenerated by oxidation with air and returned to the catalytic pyrolysis reactor.

46. The system or method of claim 45 wherein heat from the regeneration of the catalyst provides energy to the step of thermal treatment or catalytic pyrolyzing.

47. The system or method of claim 45 wherein at least a portion of the gases in the product mixture are combusted in the regenerator.

48. The system or method of claim 45 wherein the gaseous catalytic pyrolysis product mixture is subjected to a separation process to produce a stream of gases enriched in CH_4, CO, and H_2; and passing at least a portion of the stream of gases enriched in CH_4, CO, and H_2 to the regenerator where they are combusted.

49. The system or method of claim 3 wherein the non-vapor products of the catalytic pyrolysis reactor, or a portion of the gases remaining after removal of desired products, or both, are combusted to provide energy for the pyrolysis or catalytic pyrolysis process.

50. The system or method of claim 3 wherein a portion of the vapor products from the catalytic pyrolysis process is fed to a condenser where it is cooled to produce condensed materials.

51. The system or method of claim 50 wherein the condensed material is separated into fractions by distillation and at least a portion of the paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms, or the fraction boiling above 300 °C or boiling in the range 300 °C to 800 °C, is recycled to the thermal treatment or catalytic pyrolysis reactor.

52. The system or method of any of the above claims wherein at least 2, or at least 3, or at least 5, or at least 7, or at least 10, or at least 15, or from 2 to 20, or from 3 to 10, or from 5 to 10 plastics pretreatment facilities, feed a single catalytic pyrolysis, and product separation and purification facility.

53. The system or method of any of the above claims wherein at least 2, or at least 3, or at least 5, or at least 7, or at least 10, or at least 15, or from 2 to 20, or from 3 to 10, or from 5 to 10 pretreatment and catalytic pyrolysis units, feed a single separation and purification facility.

54. The system or method of any of the above claims wherein the total pretreated product mixture prepared at the at least 2 plastics pretreatment facilities that is introduced into a central catalytic upgrading, separation, and purification facility is at least 20, or at least 50, or at least 100, or at least 150, or at least 200 metric tons per day, or from 20 to 500, or from 30 to 200, or from 50 to 150 metric tons per day of pretreated product mixture.

55. The system or method of any of the above claims wherein the total crude product mixture prepared at the at least 2 plastics pretreatment and catalytic upgrading facilities that is introduced into a central separation and purification facility is at least 20, or at least 50, or at least 100, or at least 150, or at least 200 metric tons per day, or from 20 to 500, or from 30 to 200, or from 50 to 150 metric tons per day of crude product mixture.

56. The system or method of any of the above claims wherein the central facility for separation and purification is at a refinery or chemical production facility.

57. The system or method of any of the above claims wherein benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins,

ethylene, propylene, or naphthalene, or others, or some combination of these prepared from waste plastics pretreated at more than one facility, is separated and purified at a central separation and purification facility.

58. A distributed system for the conversion of waste plastics, polymers, and other waste materials to useful chemical and fuel products such as paraffins, olefins, and aromatics such as BTX in a thermochemical process that includes the pretreatment of the feed mixture at a temperature of at least 100 °C before a catalytic pyrolytic process.

59. A method for producing chemicals, fuels, or both comprising:

a. providing waste plastics at a first processing site, said first processing site configured to receive waste plastics;

b. at the first processing site, pretreating the waste plastics at a temperature of at least 100 °C and transferring the pretreated waste plastics into one or more mobile carriers;

c. transporting the one or mobile carriers to a second processing site, the second processing site configured to receive pretreated waste plastics from at least one additional plastics source;

d. removing the pretreated waste plastics from the one or more mobile carriers transported in step (c); and

e. producing chemicals, fuels, or both using plastics from at least the pretreated waste plastics removed in step (d) and plastics from at least one other plastics source.

60. The method of claim 59 wherein the feed mixture at the first processing site comprises plastics chosen from among polyethylene, polypropylene, polyesters, polyethylene terephthalate (PET), acrylonitrile-butadiene-styrene (ABS) copolymers, polyamide, polyurethane, polyethers, polycarbonates, poly(oxides), poly(sulfides), polyarylates, polyetherketones, polyetherimides, polysulfones, polyurethanes, polyvinyl alcohols, and polymers produced by polymerization of monomers, such as, for example, dienes, olefins, styrenes, acrylates, acrylonitrile, methacrylates, methacrylonitrile, diacids and diols, lactones, diacids and diamines, lactams, vinyl esters, block copolymers thereof, and alloys thereof; thermoset polymers such as, for example, epoxy resins; phenolic resins; melamine resins; alkyd resins; vinyl ester resins; unsaturated polyester resins; crosslinked polyurethanes; polyisocyanurates; crosslinked elastomers, including but not limited to, polyisoprene,

polybutadiene, styrene-butadiene, styrene-isoprene, ethylene-propylene-diene monomer polymer; and mixtures thereof.

61. The method of claim 59 wherein the feedstock comprises a mix of waste plastic chosen from among polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC) or polyvinylidene (PVCD), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), or mixed resins, or some combination thereof.

62. The method of claim 59 wherein the pretreating processes may include one or more of the following: collecting, separating, sorting, mixing, removing contaminants, thermal treatment, dechlorination, washing, drying, sizing, melting, filtering, pelleting, or combinations thereof.

63. The method of claim 59 wherein the pretreatment process steps can be conducted in any order.

64. The method of claim 59 wherein the plastic mixture is filtered by first heating the plastic mixture to at least 80 °C in a thermal treatment reactor to achieve a molten state and filtered to remove solids.

65. The method of claim 59 wherein the residence time of condensed phases in the thermal treatment reactor, or in either reactor when there is more than one thermal treatment reactor, is at least 1, or at least 5, or at least 10, or at least 20, or at least 30, or from 1 to 60, or from 5 to 30, or from 10 to 30 minutes.

66. The method of claim 59 wherein benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, or naphthalene, or others, or some combination of these prepared from waste plastics pretreated at more than one facility, is separated and purified at a central separation and purification facility.

67. A method of producing benzene, toluene, xylenes, p-xylene, m-xylene, o-xylene, BTX (a mixture of benzene, toluene, and xylenes), C6-C20 paraffins and olefins, ethylene, propylene, naphthalene, hydrogen, or others, or some combination of these prepared from waste plastics using any of The system or methods of claims 1 through 66.

68. The system or method of claim 1, wherein the central processing facility (the hub) further comprises a catalytic upgrading unit that converts the products collected from each spoke into higher-value chemicals, fuels, or both.

69. The system or method of claim 1, wherein the central processing facility (the hub) further comprises a purification unit that separates and purifies the upgraded products into individual chemical and fuel streams.

70. The system or method of claim 1, wherein the waste plastics are collected from residential, commercial, industrial, or municipal wastes, or some combination thereof.

71. The system or method of claim 1, wherein the central processing facility (the hub) is integrated with an existing petrochemical or refinery complex.

72. The system or method of claim 1, wherein the central processing facility (the hub) is located within 1 mile of a waste plastic collection facility.

73. The system or method of claim 1, wherein the central processing facility (the hub) utilizes renewable energy including solar, wind, nuclear, renewable diesel, renewable gasoline, renewable jet fuel, renewable natural gas, renewable synthesis gas, or some combination thereof, to power the pretreatment, catalytic pyrolysis, or upgrading processes.

74. The system or method of claim 1, wherein the central processing facility (the hub) further comprises a carbon capture and utilization system to sequester carbon dioxide emissions and optionally uses the captured carbon in the production of chemical products.

75. The system or method of claim 1, wherein the central processing facility (the hub) further comprises a cogeneration system that produces both electricity and heat from the waste plastics conversion process.

76. The system or method of claim 1, wherein the central processing facility (the hub) or any of the pretreatment facilities is a portable modular system.

77. The system or method of claim 1 wherein comprising a central database or control center that receives and processes real-time data from each pretreatment facility, the catalytic pyrolysis reactor, and other relevant components, wherein the central database or control center regulates and optimizes the operation of the distributed system.

78. The system or method of claim 1 wherein the transportation of pretreated waste plastics from each pretreatment facility to the central processing facility or to the catalytic pyrolysis reactor is facilitated through an intelligent logistic system, which autonomously schedules and dispatches transportation vehicles or devices based on the real-time capacity and demand of each facility.

79. The system or method of any of the above claims wherein the hub comprises a catalytic pyrolysis unit.

80. The system or method of any of claims 1-78 wherein each spoke comprises a catalytic pyrolysis unit.

81. A process for producing olefins and aromatics comprising;

feeding a stream comprising plastics to a first pyrolysis reactor;

anaerobically pyrolyzing the stream in the first pyrolysis reactor at a temperature above 350 °C to prepare a first product mixture;

without separating a portion of the first product mixture, passing the first product mixture produced in the first pyrolysis reactor to a second catalytic pyrolysis reactor that comprises a fluidized bed fitted with a catalyst;

catalytically reacting the first product mixture in the fluidized bed reactor to form a catalytic pyrolysis product mixture; and

recovering olefins, or aromatics, or some combination thereof from the product mixture.

82. The process of claim 81 wherein the first product stream produced in the first pyrolysis reactor is passed to the second reactor at a temperature above 350 °C without cooling.

83. The process of any of the preceding claims wherein the first pyrolysis reactor is a moving bed, one-screw extruder, two screw extruder, auger reactor, rotating kiln reactor, or a stepped grate reactor.

84. The process of any of the preceding claims wherein the first pyrolysis reactor comprises a feed inlet port and an exit port and the temperature in the pyrolysis reactor ranges from a lower temperature near the feed entry port to a higher temperature at the exit port.

85. The process of the preceding claim wherein the temperatures in the first pyrolysis reactor can be from 20 °C to 225 °C, such as 20 to 100 °C, or 20 to 50 °C, at or near the inlet port, and the range of temperatures at the exit port can be from 300 °C to 700 °C, such as from 325 to 650 °C, from 350 to 600 °C, or from 350 °C to 575 °C.

86. The process of any of the preceding claims wherein the feed stream is treated in a thermal treatment reactor, such as at a temperature between 250 and 300 °C, and the condensed phases are passed to the first pyrolysis reactor.

87. The process of any of the preceding claims wherein the first pyrolysis reactor comprises two or more reactors in series.

88. The process of any of the preceding claims wherein an inert gas is fed to the thermal treatment reactor and the vapors are exhausted.

89. The process of any of the preceding claims wherein the residence time of condensed phases in the thermal treatment or first pyrolysis reactor or reactors is at least 1, at least 5, at least 10, at least 20, or at least 30, or from 1 to 60, from 5 to 30, or from 10 to 30 minutes.

90. The process of any of the preceding claims wherein a solid co-reactant material is fed to the thermal treatment reactor.

91. The process of claim 90 wherein the solid co-reactant material is transferred to a combustion regenerator wherein the carbonaceous materials are reacted with air and at least a portion of the hot solid co-reactant material is returned to the thermal treatment reactor.

92. The process of claim 91 wherein the hot flue gas exiting the solid co-reactant material regenerator is passed to a catalyst heater to heat the catalyst for the catalytic pyrolysis reactor.

93. The process of any of the preceding claims wherein the catalyst in the fluidized bed reactor comprises a zeolite.

94. The process of claim 93 wherein the catalyst has a SAR (silica to alumina, SiO_2:Al_2O_3 mass ratio) greater than 12, or from 12 to 240, and a CI (constraint index) from 1 to 12 or from 5 to 10.

95. The process of claim 93 wherein the zeolite catalyst is chosen from among ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, or combinations thereof.

96. The process of claim 93 wherein the catalyst comprises ZSM-5.

97. The process of any of the preceding claims wherein the catalyst in the fluidized bed comprises binder materials chosen from among alumina, zirconia, silica, magnesia, thoria, titania, boria, or combinations thereof.

98. The process of any of the preceding claims wherein the catalyst in the fluidized bed comprises a catalytic molecular sieve and wherein the catalytic molecular sieve comprises from 30 to 90 percent by weight or 40 to 70 percent by weight of the composition of the catalyst particles.

99. The process of any of the preceding claims wherein the catalyst in the fluidized bed is in the form of fluidizable microspheres.

100. The process of any of the preceding claims wherein the hot product stream from the thermal treatment reactor is filtered to remove solids before being fed to the first pyrolysis reactor.

101. The process of any of the preceding claims wherein non-vapor products of the thermal treatment reactor, or a portion of the gases remaining after removal of desired products, or both, are combusted to provide energy for the catalytic reaction in the fluidized bed.

102. The process of any of the preceding claims wherein the product vapor mixture from the fluidized bed catalytic reactor comprises at least 20 mass% BTX, in some embodiments in the range of 20 to 90 mass% BTX.

103. The process of claim 10 wherein the solid co-reactant fed to the thermal treatment reactor comprises agricultural lime, or calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, limestone, hydrotalcites, activated carbon, or zeolite, or other solid basic material, or some combination thereof.

104. The process of any of the preceding claims wherein the catalytic pyrolysis product is passed through one or more solids separation devices.

105. The process of claim 104 wherein the solids separation device or devices comprise one or more cyclones.

106. The process of any of the preceding claims wherein catalyst in the fluidized bed catalytic pyrolysis reactor is withdrawn and regenerated by oxidation with air, and returned to the catalytic pyrolysis reactor.

107. The process of claim 106 wherein heat recovered from the catalyst regenerator is used to heat the feed materials, the first pyrolysis reactor or the catalytic pyrolysis in the fluidized bed reactor, or some combination thereof.

108. The process of any of the preceding claims wherein the temperature of the fluidized bed catalytic reactor is in the range from 300 °C to 800 °C, from 350 °C to 750 °C, from 400 °C to 700 °C, from 450 °C to 650 °C, from 500 °C to 600 °C, or from 525 °C to 575 °C.

109. The process of any of the preceding claims wherein the residence time of the fluidization gas in the catalytic pyrolysis reactor is from 1 second to 480 seconds, or from 1 second to 240 seconds, or from 2 seconds to 60 seconds, or from 3 seconds to 30 seconds, or from 4 seconds to 15 seconds.

110. The process of any of the preceding claims wherein the product mixture from the fluidized bed catalytic reactor comprises at least 20 mass% olefins, in some embodiments in the range of 20 to 90 mass% olefins.

111. The process of any of the preceding claims wherein the product mixture from the fluidized bed catalytic reactor comprises at least 30%, at least 40%, at least 45%, at least 50%, at least 55%, or at least 60%, or from 20% to 90%, from 30% to 70%, or from 45% to 60%, olefins based on the mass in the polymer feed.

112. The process of any of the preceding claims wherein the mass yield of BTX in the product vapor mixture from the catalytic conversion is at least 30%, at least 40%, at least 45%, at least 50%, at least 55%, or at least 60%, or from 20% to 90%, from 30% to 70%, or from 45% to 60%, BTX based on the mass in the polymer feed.

113. The process of any of the preceding claims wherein benzene, toluene, or xylenes are separated or recovered from the catalytic pyrolysis product mixture.

114. The process of any of the preceding claims wherein at least a portion of the aromatic products in the catalytic pyrolysis product mixture is hydrogenated to produce naphthenes.

115. The process of any of the preceding claims wherein ethylene, propylene, or butenes are separated from the catalytic pyrolysis product mixture.

116. The process of any of the preceding claims wherein the product vapor mixture is subjected to a separation process to produce a stream of gases enriched in CH_4, CO, and H_2; and passing at least a portion of the stream of gases enriched in CH_4, CO, and H_2 to the regenerator where they are combusted.

117. The process of any of the preceding claims wherein the catalytic pyrolysis product mixture comprises CH_4 and C2-C4 paraffins; and wherein 50 to 100 mass% of the CH_4 and C2-C4 paraffins is combusted in the regenerator.

118. The process of any of the preceding claims wherein the thermal treatment is conducted by heating the feed to a temperature between 250 and 300 °C, held at that temperature while vapors are removed, and then the condensed phases are further pyrolyzed at higher temperature in the first pyrolysis reactor.

119. The process of any of the preceding claims wherein the feedstock comprises a mix of waste plastic chosen from among polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC) or polyvinylidene (PVCD), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), or mixed resins, or some combination thereof.

120. The process of any of the preceding claims wherein the pressure in the fluidized bed reactor is at least 0.1 MPa, at least 0.3 MPa, or at least 0.4 MPa, or from 0.1 to 2.0 MPa (1 to 20 bar), from 0.1 to 1.0 MPa, or from 0.3 to 0.8 MPa, preferably from 0.4 to 0.6 MPa.

121. The process of claim 1 of any of the preceding claims wherein a portion of the vapor products from the catalytic pyrolysis process are fed to a condenser where it is cooled to produce condensed materials and a portion of the condensed materials is recycled to the pyrolysis reactor.

122. The process of claim 121 wherein a portion of the condensed materials is separated into fractions and at least a portion of the condensed material is recycled to the pyrolysis reactor or the catalytic pyrolysis reactor.

123. The process of claim 121 wherein the condensed material is separated into fractions by distillation and at least a portion of the paraffins, olefins, or aromatics or their combination that contain more than 7 carbon atoms is recycled to the pyrolysis or catalytic pyrolysis reactor.

124. The process of claim 121 wherein the condensed material is separated into fractions by distillation and at least a portion of the fraction boiling above 300 °C or boiling in the range 300 to 800 °C is recycled to the pyrolysis or catalytic pyrolysis reactor.

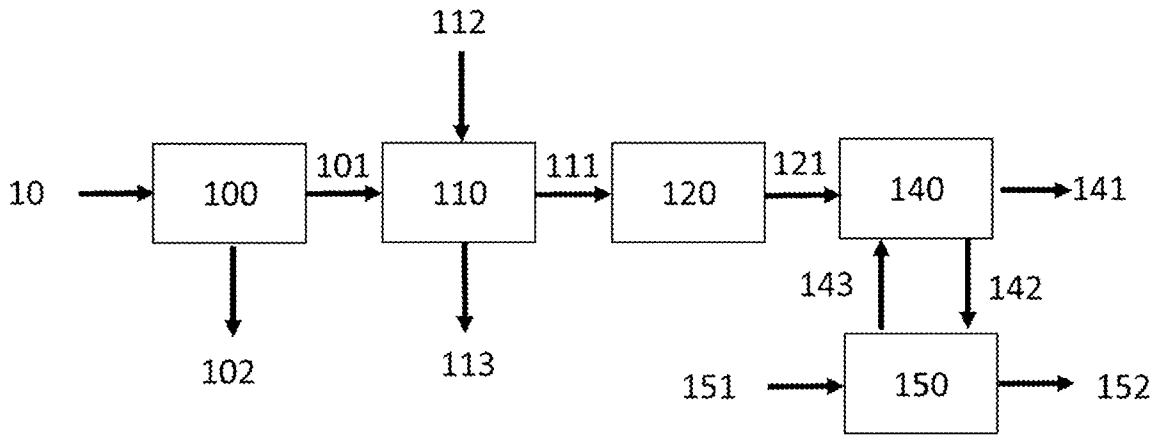

112
10
100
101
110
111
120
121
140
141
143
142
102
113
151
150
152

FIG. 1

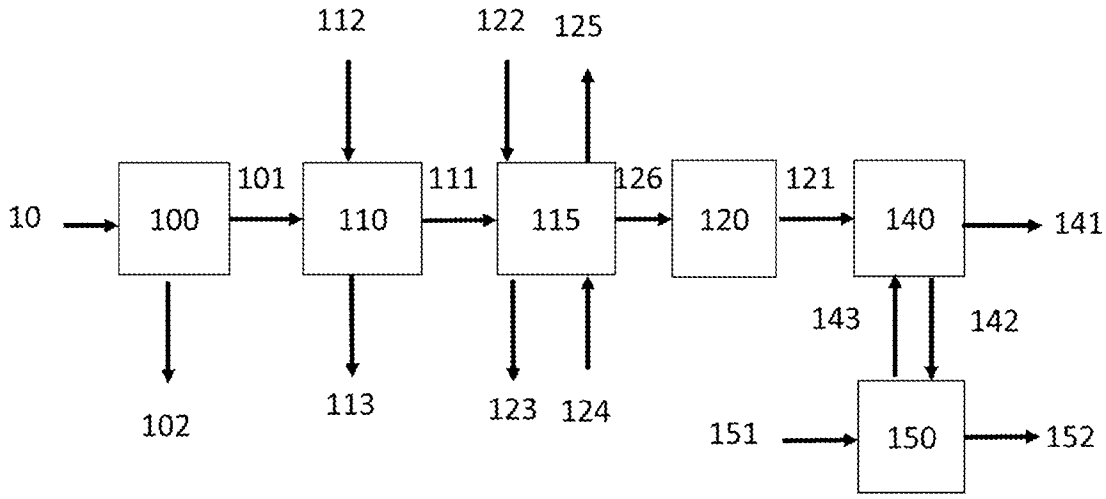

112
122
125
10
100
101
110
111
115
126
120
121
140
141
143
142
102
113
123
124
151
150
152

FIG. 2

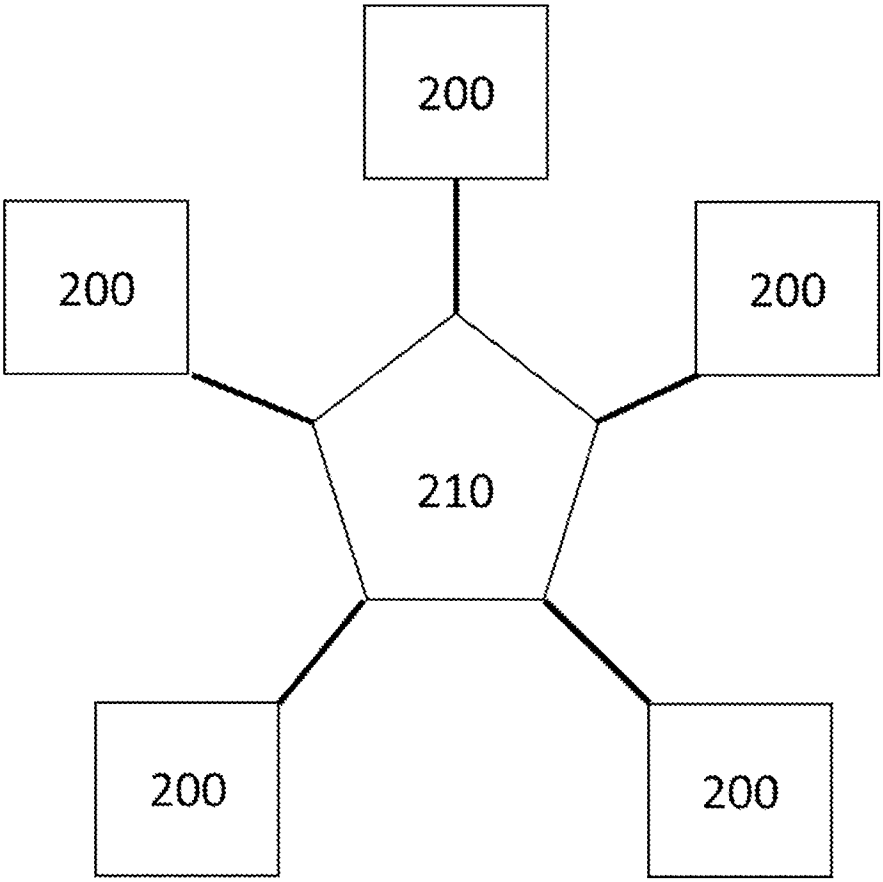


FIG. 3

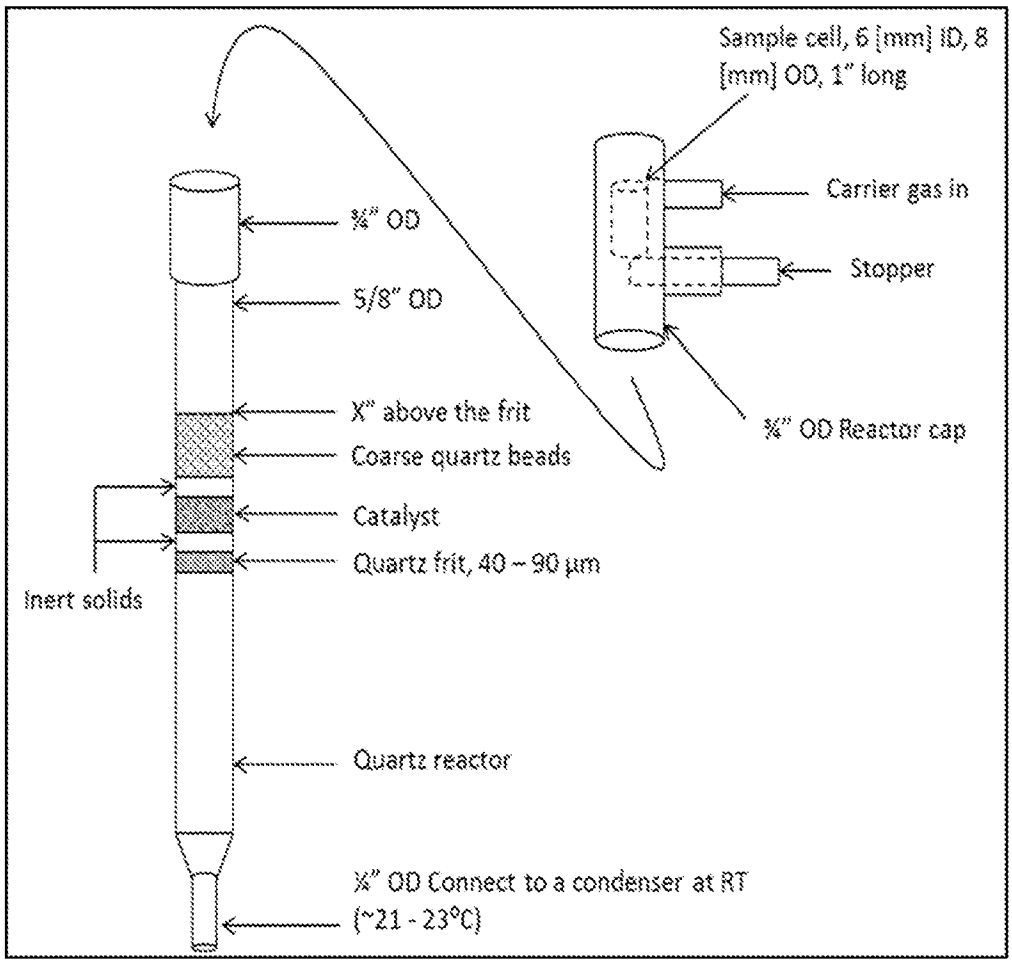

Sample cell, 6 [mm] ID, 8 [mm] OD, 1" long
Carrier gas in
Stopper
¾" OD Reactor cap
¾" OD
5/8" OD
X" above the frit
Coarse quartz beads
Catalyst
Quartz frit, 40 ~ 90 µm
Inert solids
Quartz reactor
¼" OD Connect to a condenser at RT (~21 - 23°C)

FIG. 4

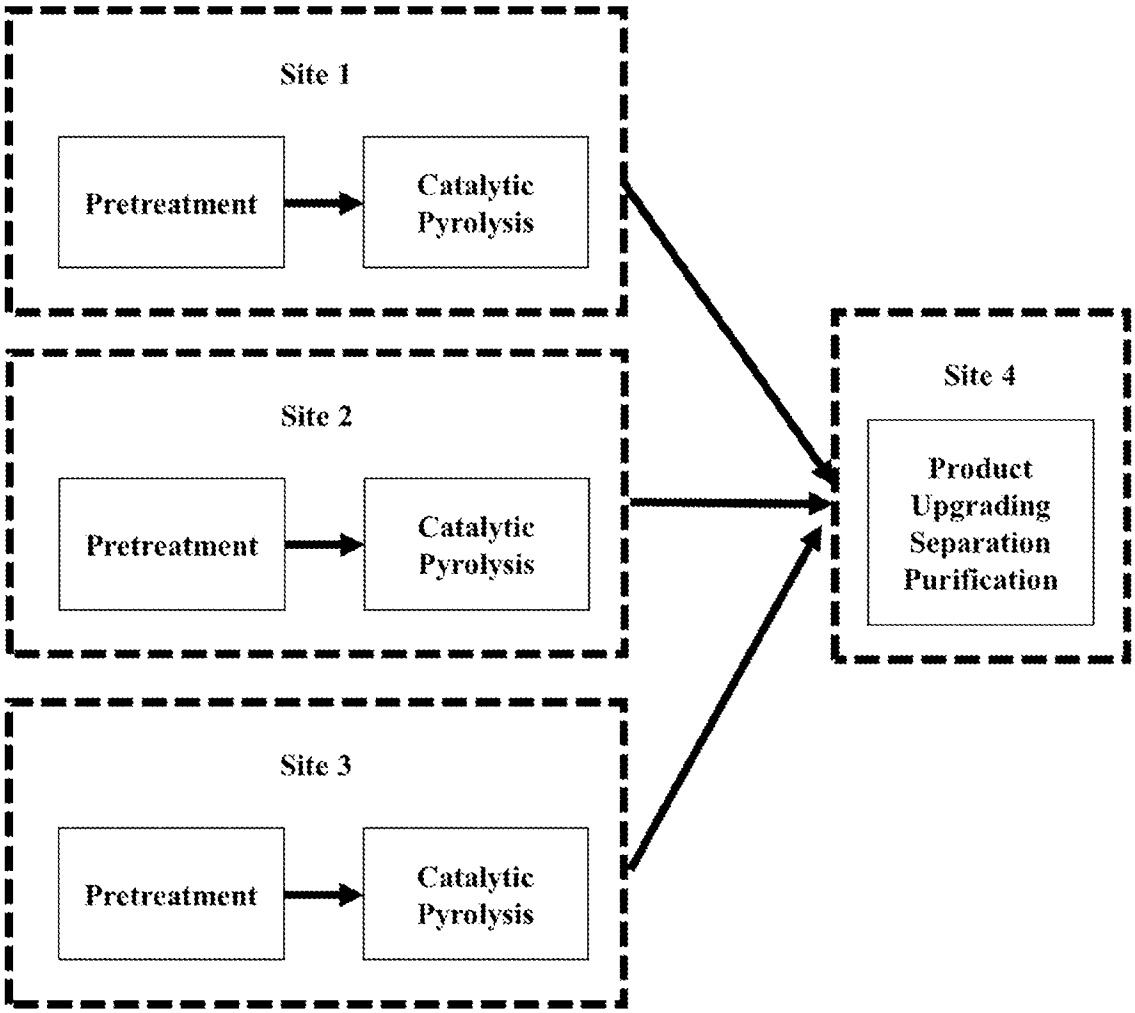

Site 1
Pretreatment
Catalytic Pyrolysis
Site 2
Pretreatment
Catalytic Pyrolysis
Site 3
Pretreatment
Catalytic Pyrolysis
Site 4
Product Upgrading Separation Purification

FIG. 5

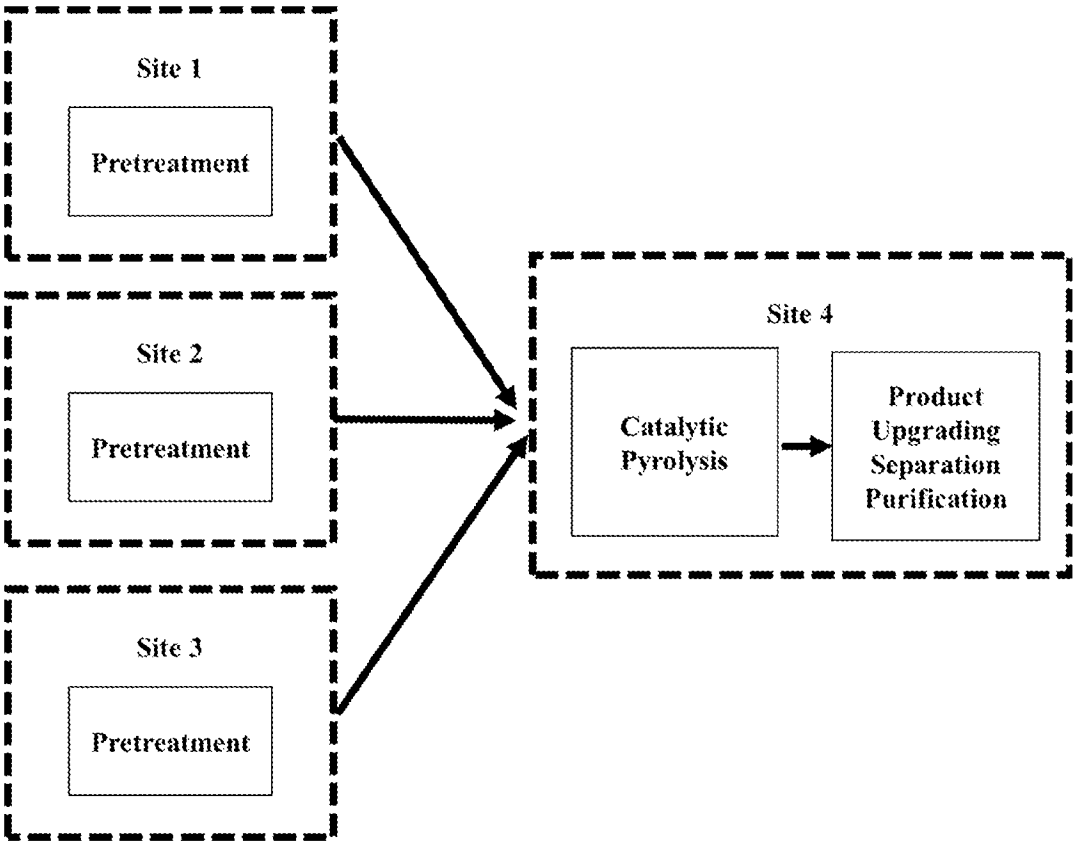

Site 1
Pretreatment
Site 2
Pretreatment
Site 3
Pretreatment
Site 4
Catalytic Pyrolysis
Product Upgrading Separation Purification

FIG. 6

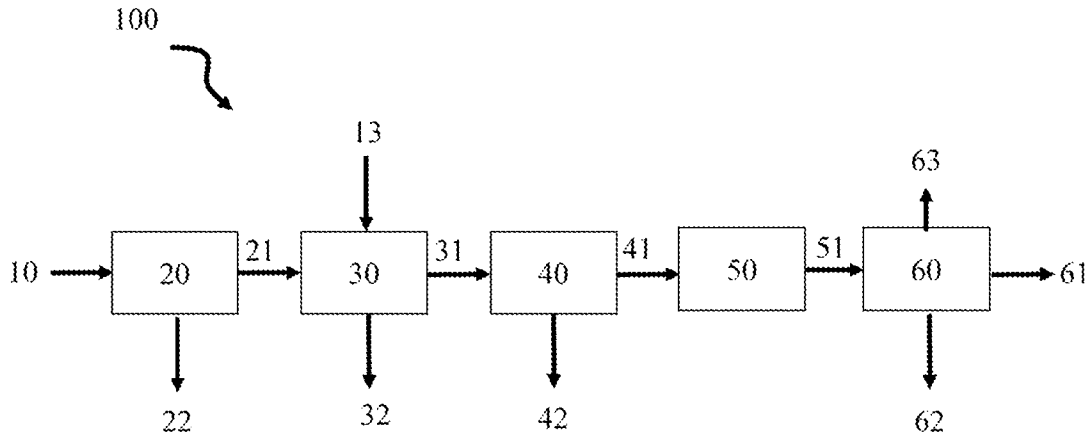

100
13
63
10
20
21
30
31
40
41
50
51
60
61
22
32
42
62

FIG. 7

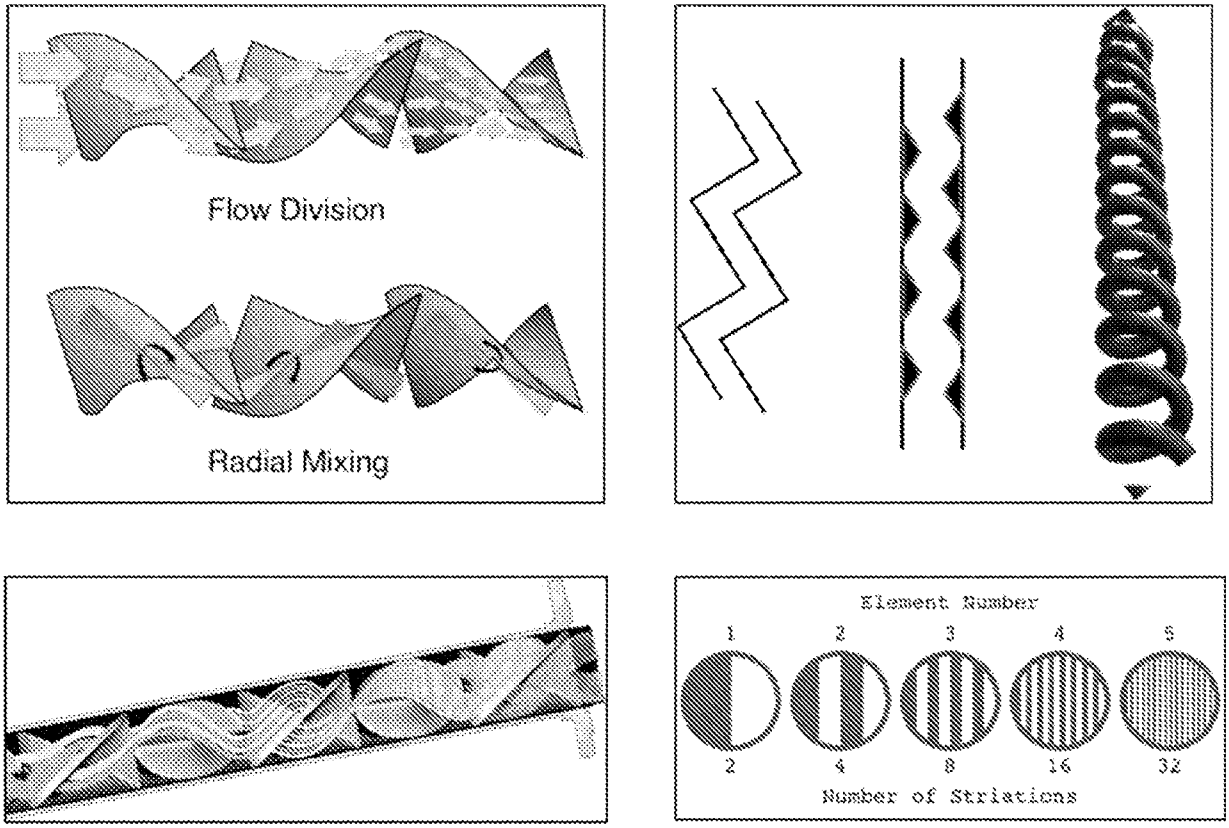

Flow Division
Radial Mixing
Element Number
1
2
3
4
5
2
4
8
16
32
Number of Striations

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/080426

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10B53/07 C10B57/02 C10B57/06 C10G1/10 C10G1/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10B C10G C08J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BUTLER E. ET AL: "Waste Polyolefins to Liquid Fuels via Pyrolysis: Review of Commercial State-of-the-Art and Recent Laboratory Research", WASTE AND BIOMASS VALORIZATION, [Online] vol. 2, no. 3, 1 August 2011 (2011-08-01), pages 227-255, XP055895343, NL ISSN: 1877-2641, DOI: 10.1007/s12649-011-9067-5 Retrieved from the Internet: URL:https://link.springer.com/content/pdf/10.1007/s12649-011-9067-5.pdf> [retrieved on 2024-02-24]	1-58, 67-80, 83-124
Y	figures 5,6,8 PTL Platforms for Liquid Fuel Production table 4	1-58, 67-80, 83-124

-/--

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 March 2024	07/05/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zuurdeeg, Boudewijn

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2003 335710 A (TOSHIBA PLANT KENSETSU CO LTD) 28 November 2003 (2003-11-28) paragraphs [0011], [0012], [0013], [0014], [0015], [0022], [0026] - [0033] figures 1-3 claims 1-4	1-58, 67-80, 83-124
Y	DEWANGGA PRAMUDIA BAGUS ET AL: "Styrene Recovery from the Pyrolysis of Polystyrene Waste Using Bentonite and Natural Zeolite Catalyst", KEY ENGINEERING MATERIALS, TRANS TECH PUBLICATIONS, [Online] vol. 849, 24 June 2020 (2020-06-24), pages 84-89, XP093136557, CH ISSN: 1662-9795, DOI: 10.4028/www.scientific.net/KEM.849.84 Retrieved from the Internet: URL:https://www.scientific.net/KEM.849.84.pdf> [retrieved on 2024-02-29] abstract Experimental Methods tables 1,2 figures 2-4 Conclusions	1-58, 67-80, 83-124
A	JP 2004 002519 A (TOSHIBA PLANT KENSETSU CO LTD; CHUO KAGAKU KK) 8 January 2004 (2004-01-08) figures 1-3 claims 1-5	1-58, 67-80, 83-124
Y	US 2020/362248 A1 (CARTOLANO ANTHONY [US] ET AL) 19 November 2020 (2020-11-19) figures 1-6 paragraphs [0012] - [0026], [0059] examples 1-22 claims 1-55	1-58, 67-80, 83-124
X,P	WO 2023/215421 A1 (ANELLOTECH INC [US]) 9 November 2023 (2023-11-09) page 38, line 1 - page 39, line 2	1-58, 67-80, 83-124

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2023/080426

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.:
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 additional 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 an 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 claims 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 claims Nos.:

1-58, 68-79(completely); 67, 80, 83-124(partially)

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-58, 68-79(completely); 67, 80, 83-124(partially)

A system or method for upgrading waste plastics to useful products comprising multiple plastics pretreatment facilities

---

2. claims: 59-66(completely); 67, 80, 83-124(partially)

A method for producing chemicals, fuels, or both

---

3. claims: 81, 82(completely); 83-124(partially)

A process for producing olefins and aromatics

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/080426

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2003335710 A	28-11-2003	NONE	
JP 2004002519 A	08-01-2004	NONE	
US 2020362248 A1	19-11-2020	EP 3969544 A1	23-03-2022
		JP 2022533116 A	21-07-2022
		US 2020362248 A1	19-11-2020
		WO 2020231488 A1	19-11-2020
WO 2023215421 A1	09-11-2023	US 2023357106 A1	09-11-2023
		WO 2023215421 A1	09-11-2023