

ENHANCED CIRCULARITY AT ENHANCED ETHYLENE YIELD

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/518,382, filed on 09 August 2023, the disclosure of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] A process for upcycling plastic into the building blocks for polyolefins, polyesters, polystyrenes, polyamides, and polyaramids.

BACKGROUND

[0001] World plastics production continues to grow exponentially, slightly ahead of global gross domestic product. According to Plastics Europe Market Research Group, the world plastics production was 335 million tons in 2016, 348 million tons in 2017, 359 million tons in 2018, and 367 million tons in 2020. According to McKinsey & Company, the global plastics-waste volume is estimated to be 460 million tons per year by 2030 if the current trajectory continues.

[0002] Plastic waste has become an increasingly important environmental issue. Since the current policies leave few options for upcycling polyethylene and polypropylene waste plastics into value-added chemical products, only a less than a percent of polyethylene and polypropylene is upcycled via chemical upcycling. Some six percent of plastics (nearly exclusively polyethylene terephthalate or PET) is upcycled mechanically through cleaning and extrusion back into nurdles. Mechanical upcycling is more cost effective than chemical upcycling (which involves breaking a polymer back into its building blocks), but results in a lower-quality plastics through shortening the primary fibers and because the composition of mechanically upcycled plastic is too complex to enable stabilizers to be as effective as the more homogenous original fibers. Some four percent is “recycled into energy” i.e., incinerated with heat captured in steam to power electricity generation. The majority, more than 80%, is simply discarded, not necessarily on a landfill.

[0003] In preparation of regulatory changes to further a more circular (instead of linear) economy, the petrochemical industry is deploying several chemical upcycling processes

of plastics. These chemical upcycling processes are intended to expand the feedstocks that can be upcycled. Current mechanical upcycle processes limit feedstocks to polyethylene terephthalate (PET, code #1 plastic) and to high-density polyethylene (HDPE, code #2 plastic). Chemical recycle expands the feedstock slate to all polyolefins, and can include some polystyrene, polyamides, and polyaramids.

[0004] Chemical recycle consists of 1) sorting post-consumer municipal or post-industrial waste to minimize metals, biogenic material, inorganic solids, and halogenated plastics, coatings and additives, 2) melting of sorted plastics, 3) pyrolysis of the liquid harvested from the melt, 4) hydroporcessing to remove contaminants and yield a hydrocarbon stream, and optionally hydrocracking to assure products are compatible with an existing steam cracker, 5) renewed, more severe pyrolysis in a steam cracker into petrochemical building blocks. The liquid feedstock and pyrolysis conditions set the end boiling point of the feed to the hydroprocessing facility.

[0005] If one has an existing steam cracker, it can be revamped (furnaces added) to expand the feed boiling range, but it is significantly more cost-effective to reduce the end boiling point of the feed to the steam cracker. However, end boiling point reduction of pyrolysis oils using traditional hydrocracking processes degrade the feed quality in that they convert a pyrolysis oil rich in n-paraffins into a stream rich in undesirable i-paraffins.

[0006] Mixed feed stream crackers can crack feedstocks efficiently with an end boiling point as high as 700°F. Such steam crackers have been commercialized. However, the majority of existing, commercial liquid steam crackers are referred to as “naphtha crackers” because they are limited to feedstocks in the naphtha boiling range (32-193°C). Naphtha crackers predate the arrival of cost-effective ethane (harvested from tight natural gas in the USA) in the USA, so that they are and in the Middle East.

[0007] Previously, both UOP and ExxonMobil have practiced n-paraffin pressure swing adsorption processes (e.g., Molex™, IsoSiv™, Maxen™, and Ensorb™) to concentrate the n-paraffins from highly paraffin oils in the naphtha (or even diesel) range to enable subsequent steam cracking. The added costs for concentrating n-alkanes boiling higher than naphtha, however, are quite high because the desorption of n-paraffins requires excess energy when n-paraffins become much longer than n-heptane. Revamping a steam cracker to enable higher boiling feed components is also quite expensive.

[0008] For over a century, hydrocracking and catalytic cracking have been used to reduce the boiling point and to increase the H/C ratio of crude oils and coal-derived

liquids in refineries. Inherently, these catalytic processes also increased the iso-paraffin content of the lighter fractions. This was desirable when the intended use of the cracking products was an internal combustion engine. However, crude oil is now increasingly used for chemical manufacture, and high iso-paraffin content has become an undesirable side effect of acid-catalyzed (hydro)cracking.

[0009] Nobel Laureate George Olah established that acid catalysts do not crack n-paraffins directly into n-paraffins. Instead acids first catalyze the conversion of n-paraffins into iso-paraffins, and only then do they crack the iso-paraffins. Consequently, a product slate with a high iso-paraffin content is generally considered the signature of acid-catalyzed cracking. By contrast, a product slate with a high n-paraffin content is the signature of thermal or metal-catalyzed cracking.

[0010] Globally upcycling of plastic waste has gained great interest to save resources and the environment. Mechanical recycling of plastic waste is rather limited due to different types, properties, additives, and contaminants in the collected plastics. Usually, the recycled plastics are of degraded quality. Chemical recycling to the starting material or value-added chemicals has emerged as a more desirous route.

[0011] However, in order to achieve chemical recycling of single use plastics in an industrially significant quantity to reduce its environmental impact, more robust processes are needed. The improved processes should establish “circular economy” for the waste plastics where the spent waste plastics are upcycled effectively back as starting materials for the polymers or value-added chemicals or fuels.

SUMMARY

[0012] Provided is a process for converting waste plastic into upcycle as starting materials for polymers or value added chemicals. The process comprises selecting waste plastics containing, for example, polyethylene and/or polypropylene. These waste plastics are then passed through a pyrolysis reactor to thermally crack at least a portion of the plastic waste and produce a pyrolyzed effluent. The pyrolyzed effluent is separated into offgas and a pyrolysis oil.

[0013] The pyrolysis oil is then sent to hydroprocessing, which process is run in the presence of an LTA type zeolite, which zeolite has an acid site concentration of at least around 2.7 mol/l or greater. In one embodiment, the acid site concentration is in the range of from 2.6 mol/l to 3.0 mol/l; and in another embodiment in the range of from 2.6 mol/l to 2.8 mol/l. This acid site concentration has been found important. A chosen boiling

range of n-paraffins is then collected from the hydroprocessing reactor. The range generally comprises C₂-C₆ n-paraffins. Any isoparaffins or naphthenics can then be separately subjected to destructive cracking, if desired. The collected C₂-C₆ n-paraffins can then be passed to processing for preparation of value-added chemicals and polymers. In one embodiment, the n-paraffins can be passed to a naphtha steam cracker with good results including improved ethylene production.

[0014] Among other factors the present process is stable and efficient in recycling waste plastics using pyrolysis by passing the pyrolysis oil through hydroconversion using an LTA zeolite. The naphtha products from the hydroconversion can then be used to prepare value-added chemicals, including providing lower alkene production, especially ethylene, when using a naphtha steam cracker. It has been surprisingly found that the LTA zeolite used, with an acid site concentration of about 2.7 mol/l, can reduce n-paraffins, including long n-paraffins in high yield to the desired naphtha range of C₂-C₆ n-paraffins continuously, for months on end, without losing its catalytic activity. The reaction is stable and does not exhibit any issues even with feeds having extremely long n-paraffins. By providing a suitable feedstock for a naphtha steam cracker, the preparation of ethylene and other lower olefins as chemical building blocks can be efficiently realized in good yield as part of a circular economy in waste plastic recycle.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWING

[0015] FIG. 1 depicts the plastic type classification for waste plastics recycling.

[0016] FIG. 2 depicts a process for pyrolysis of post-consumer waste plastics.

[0017] FIG. 3 depicts a process for post-consumer waste upcycling.

[0018] FIGS. 4 and 5 depict processes for cleansing pyrolysis oil through hydrogenation through an olefin saturation reactor followed by a hydrodehalogenation reactor recycling the hydrogenated product

[0019] FIG. 6 depicts the composition of a C₁₂⁺ feed.

[0020] FIG. 7 graphically depicts the results achieved from hydronormalizing a largely n-C₁₂⁺ feed.

[0021] FIG. 8 graphically depicts a steam cracker production.

DETAILED DESCRIPTION

[0022] Definitions:

[0023] Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethylene and propylene. Steam cracker units are facilities in which feedstocks such as ethane, propane, butane, liquefied petroleum gas (LPG), and naphtha are thermally cracked or pyrolyzed in the presence of steam by a short residence time in a furnace at high temperature to produce lighter hydrocarbons. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil. The feed composition, the hydrocarbon-to-steam ratio, the cracking temperature and furnace residence time determine the product composition. Light hydrocarbon feeds such as ethane, LPGs, or light naphtha yield mostly lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphtha or even heavier oil fractions) feeds yield some of these same products, but also aromatic pyrolysis oils.

[0024] Olefins such as ethylene, propylene and butylene are the raw materials of polyolefins. Polyolefins are one of the key building blocks of the global economy. Illustrating its critical roll to economic growth, steam cracking capacity tends to grow slightly ahead of global gross domestic product (GDP). Ethylene capacity in 2021 was 150,000 kiloton/annum (kta) and is growing at 6000-8000 kta of ethylene, produced in ever larger facilities. A current state-of-the-art cracker can produce 2000 kta of ethylene. At such large volumes feedstocks that make incrementally more ethylene have large financial benefits.

[0025] A “naphtha” steam cracker is generally limited to feedstocks in the naphtha boiling range of 32-193°C (C₄-C₁₀). The majority of commercial steam crackers are “naphtha: steam crackers.

[0026] Hydroconversion and hydroconverting: A catalytic process which operates at pressures greater than atmospheric in the presence of hydrogen and which converts normal paraffins into lighter normal paraffins with a minimum of isomerization and without excessive formation of methane and ethane. This can also be referred to as hydro-normalization. Hydrotreating and hydrocracking are distinctly different catalytic processes but which also operate at pressures greater than atmospheric in the presence of hydrogen. Hydrocracking converts normal paraffins into lighter products comprising

significant amounts of iso-paraffins. Hydrotreating does not convert significant quantities of the feedstock to lighter products but does remove impurities such as sulfur- and nitrogen-containing compounds. Also in comparative contrast, thermal cracking converts normal paraffins into lighter products with a minimum of branching, but this process does not use a catalyst, typically operates at much higher temperatures, forms more methane, and makes a mixture of olefins and normal paraffins.

[0027] A LTA (Linde Type A) zeolite is a zeolite that has voids greater than 0.50 in diameter, and apertures characterized by a longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. Such LTA zeolites are described in the Atlas of Zeolite Structure Types, Fourth Revised Edition 1996.

[0028] An “aperture” in a zeolite is the narrowest passage through which an absorbing or desorbing molecule needs to pass to get into the zeolite’s interior. The diameter of the aperture, d_{app} (nm), is defined as the average of the shortest, d_{short} (nm), and the longest, d_{long} (nm) axis provided in the IZA (International Zeolite Association) Zeolite Atlas (<http://www.iza-structure.org/databases/>). Both normal- and iso-paraffins with a methyl group can pass through apertures with a $d_{long} \geq 0.50$ nm, but only normal-paraffins can pass through apertures with $d_{long} < 0.50$ nm provided $d_{short} > 0.30$ nm.

[0029] Apertures provide access to “voids”, the wider parts in the zeolite topology. The diameter of the void, d_{void} (nm), is characterized by the maximum diameter of a sphere that one can inflate inside such a void as per the IZA Zeolite Atlas (<http://www.iza-structure.org/databases/>). This characterizes, e.g., a fairly spherical LTA-type void (or cage) as one with a diameter of 1.1 nm, and an elongated AFX-type void as one with a spherical diameter of 0.78 nm. Voids are defined as cages if $d_{void}/d_{app} \geq 1.4$ nm/nm. These apertures help define a LTA zeolite.

[0030] In the present process, provided is a method to recycle waste plastics such as polyethylene and/or polypropylene back to useful chemicals or polymers such as virgin polyethylene to establish a circular economy. A substantial portion of plastics such as polyethylene and polypropylene polymers are used in single use plastics and get discarded after its use. The single use plastic waste has become an increasingly important environmental issue. At the moment, there appear to be few options for recycling polyethylene and polypropylene waste plastics to value-added chemicals and fuel products. Currently, only a small amount of polyethylene/polypropylene is recycled via

chemical recycling, where recycled and cleaned polymer pellets are pyrolyzed in a pyrolysis unit to make fuels (naphtha, diesel), steam cracker feed or slack wax.

[0031] The present process comprises the steps of (1) sorting waste plastics to minimize metals, biogenic material, inorganic solids and organic halogens; (2) melting the sorted waste, (3) pyrolysis of the sorted plastics; (4) hydronormalizing the pyrolysis oil created; and (5) forwarding the n-paraffin product stream, e.g., C₂-C₆ stream, collected for further processing, e.g., in a naphtha steam cracker.

[0032] The preferred starting material for the present process is sorted waste plastics containing predominantly polyethylene and polypropylene (plastics recycle classification types 2, 4, and 5). The pre-sorted waste plastics are washed and shredded or pelleted to feed to a melting unit which feeds a pyrolysis unit for thermal cracking. FIG. 1 depicts the plastic type classification for waste plastics recycling. Classification types 2, 4, and 5 are high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP), respectively. Any combination of the polyethylene and polypropylene waste plastics can be used. For the present process, at least some polyethylene and/or polypropylene waste plastic is preferred.

[0033] Proper sorting of waste plastics is very important in order to minimize contaminants such as Cl, Br, F, lignocellulose, textile, glass, sand, stones, mercury, metals, N and S. Plastics waste containing polyethylene terephthalate (PET, plastics recycle classification type 1), polyvinyl chloride (PVC, plastics recycle classification type 3) and other polymers (plastics recycle classification type 7) can be present (e.g., PVC fibers are frequently mixed into PE and PP fibers to provide a shine), but their presence is preferably minimized. For example, these latter waste plastics are preferably sorted out to less than 5%, preferably less than 1% and most preferably less than 0.1%. A moderate amount of polystyrene (plastics recycle classification type 6) is more tolerable. Waste polystyrene, however, is preferably sorted out to less than 30%, preferably less than 20% and most preferably less than 5%. The present process can accommodate, however, any combination of waste plastics.

[0034] Washing of waste plastics removes metal contaminants such as sodium, calcium, magnesium, aluminum, and non-metal contaminants coming from other waste sources. Non-metal contaminants include contaminants coming from the Periodic Table Group IV, such as silica, contaminants from Group V, such as phosphorus and nitrogen compounds, contaminants from Group VI, such as sulfur compounds, and halide contaminants from Group VII, such as fluoride, chloride, and iodide. The residual metals,

non-metal contaminants, and halides is preferably removed to less than 50 ppm, preferentially less than 30 ppm and most preferentially to less than 5 ppm.

[0035] If the washing does not remove the metals, non-metal contaminants, and halide impurities adequately, then a separate guard bed can be used to remove the metals and non-metal contaminants.

[0036] The pyrolyzing is carried out by contacting a plastic material feedstock in a pyrolysis zone at pyrolysis conditions, where at least a portion of the feed(s) is cracked, thus forming a pyrolysis zone effluent comprising primarily olefins and paraffins. Pyrolysis conditions include a temperature of from about 400°C to about 700°C, preferably from about 450°C to about 650°C. Conventional pyrolysis technology teaches operating conditions of above-atmospheric pressures. See e.g., U.S. Pat. No. 4,642,401. Additionally, it has been discovered that by adjusting the pressure downward, the yield of a desired product can be controlled. See, e.g., U.S. Pat. No. 6,150,577. Accordingly, in some embodiments where such control is desired, the pyrolysis pressure is sub-atmospheric.

[0037] FIG. 2 shows a diagram of pyrolysis of waste plastics fuel or wax that is generally operated in the industry today. As noted above, generally, polyethylene and polypropylene wastes are sorted together 1. The cleaned polyethylene/polypropylene waste 2 is converted in a pyrolysis unit 3 to offgas 4 and pyrolysis oil (liquid product). The offgas 4 from the pyrolysis unit is used as fuel to operate the pyrolysis unit. A distillation unit in the pyrolysis unit separates the pyrolysis oil to produce naphtha and diesel 5 products which are sold to fuel markets. The heavy pyrolysis oil fraction 6 is recycled back to the pyrolysis unit 3 to maximize the fuel yield. Char 7 is removed from the pyrolysis unit 3. The heavy fraction 6 is rich in long chain, linear hydrocarbons, and is very waxy (i.e., forms paraffinic wax upon cooling to ambient temperature). Wax can be separated from the heavy fraction 6 and sold to the wax markets. The pyrolysis oil fraction 8 can then be forwarded/transported to a hydroconversion reactor.

[0038] The present process converts pyrolyzed polyethylene and/or polypropylene waste plastic in large quantities by integrating the waste polymer pyrolysis product streams into an oil refinery operation. The resulting processes produce the feedstocks for the polymers (naphtha or C₃-C₄ or C₃ only for ethylene cracker), high quality gasoline and diesel fuel.

[0039] Generally, the present process provides a circular economy for polyethylene plants. Polyethylene is produced via polymerization of pure ethylene. Clean ethylene can

be made using a steam cracker. Either naphtha or a C₃ or C₄ stream can be fed to the steam cracker. The ethylene is then polymerized to create polyethylene.

[0040] The pyrolysis unit can be located near the waste plastics collection site, which site could be away from the hydronormalizing reactor and naphtha steam cracker. If the pyrolysis unit is located away from the reactors, then pyrolysis oil (naphtha/diesel and heavies) can be transferred to the reactors by truck, barge, rail car or pipeline. It is preferred, however, that the pyrolysis unit is within the waste plastics collection site or within the reactor system. The reactors can also be part of a refinery.

[0041] FIG. 3 shows a present integrated process, integrating pyrolysis with recycle for effective polyethylene production. In FIG. 3, mixed waste plastics are sorted together 21. The cleaned waste plastic 22 is converted in a pyrolysis unit 23 to offgas 24 and a pyrolysis oil (liquid product) and optionally wax (solid product at ambient temperature). The offgas 24 from the pyrolysis unit can be used as fuel to operate the pyrolysis unit 23. The pyrolysis oil is separated, generally at an on-site distillation unit in the pyrolysis unit 23, into a naphtha/diesel fraction 25, and a heavy fraction 26. Char 27 is removed from the pyrolysis unit 23 after completion of the pyrolysis step.

[0042] The next step of the present process involves the hydronormalization of the eventual feedstock to the naphtha steam cracker by hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins. The process step comprises hydroconverting the pyrolysis oil feedstock, comprising the naphtha fraction 25 and the heavy fraction 26, under hydrocracking conditions, in the presence of a LTA zeolite catalyst, where the zeolite has voids greater than 0.50 in diameter, accessible through apertures characterized by a longest diameter of less than 0.50 nm and a shortest diameter of more than 0.30 nm. The present LTA zeolite also exhibits an acid site concentration of about 2.7 mol/l or greater. The present zeolite can be, and is preferably, loaded with 0.1 to 0.5 wt. % Pd. The zeolite can be cooled with any hydrogenation function metal. The feedstock is passed to the hydroconversion reactor 28.

[0043] It is the zeolite base into which the metal is loaded that is critical to the present processes. For it has been found that the present LTA zeolite catalyst in accordance herewith can provide the high conversion and minimal formation of iso-paraffins. It has been found that the key features of the catalyst zeolite include access to a pore system through apertures of a size less than 0.45 nm, and with the pore system containing voids greater than 0.50 nm in diameter. In another embodiment, the zeolite has voids greater than 0.50 nm in diameter, which are accessible through apertures characterized by a

longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. The LTA-type zeolite has such a zeolite framework. The present LTA zeolite must also exhibit an acid site concentration of at least about 2.7 mol/l. In one embodiment, the acid site concentration is in the range of 2.6 mol/l to 3.0 mol/l, and in another embodiment in the range of 2.6 mol/l to 2.8 mol/l.

[0044] Zeolite A (Linde Type A, framework code LTA) is one of the most used zeolites in separations, adsorption, and ion exchange. This structure contains large spherical cages (diameter ~ 1.4 Å) that are connected in three dimensions by small 8-membered ring (8MR) apertures with a diameter of 4.1 Å. LTA is normally synthesized in hydroxide media in the presence of sodium with Si/Al ~ 1 . By changing the cation, the limiting diameter of the 8MR apertures can be tuned, creating the highly used series of adsorbents 3A (potassium form, 2.9 Å diameter), 4A (sodium form, 3.8 Å diameter) and 5A (calcium form, 4.4 Å diameter) that are used to selectively remove species such as water, NH_3 , SO_2 , CO_2 , H_2S , C_2H_4 , C_2H_6 , C_3H_6 and other n-paraffins from gases and liquids. While LTA is used in vast quantities for the aforementioned applications, the low framework Si/Al ratio and subsequent poor hydrothermal stability limits its use under more demanding process conditions that are commonly found in catalytic applications. Yet surprisingly, the present process is found to be stable and efficient using an LTA zeolite with the requisite acid site concentration.

[0045] The stability of LTA zeolites with 0.4 nm wide constrictions in hydrocracking n-alkanes longer than n-hexane (n-C₆) is stunning. The discovered stability of LTA zeolites with 0.4 nm wide constrictions that hydrocrack n-heptane (n-C₇) and longer n-alkanes out of feed stocks in the vacuum gasoil boiling range for at least three months is not intuitive. It is not intuitive because n-C₇ and longer n-alkanes inherently hydrocrack into branched alkanes. This would imply that the primary branched alkene and alkane products would have further isomerized into n-alkenes so as to egress through 0.4 nm wide constrictors. Particularly for i-butenes (that are allegedly primary cracking products it is not clear what mechanism would be involved to let them egress.

[0046] The discovered hydroprocessing stability of LTA zeolites with an acid concentration as high as 2.7 mol/l is another surprise. Previously it has been shown that the stability is inversely proportional to acid concentration, and the longheld belief is that stable operation requires an acid concentration of at most 1.8 mol/l. At acid concentrations higher than 1.8 mol/l, catalysts are supposed to coke up or crumble.

Lowering the acid site concentration with sodium and calcium cations, however, results in unstable operation.

[0047] The rock-stable operation of LTA-type zeolite (for 3 months, 6 months, 2 years or longer before needing to be replaced) with an acid concentration as high as 2.7 mol/l (well above the historically suggested 1.8 mol/l threshold) in the hydro-normalization of n-alkanes as long as n-C₂₂ remains (well above the historically suggested n-C₆ threshold) remains a bit of a mystery and surprise. Yet this is what has been discovered.

[0048] The LTA catalyst useful in the present processes can typically contain a catalytically active hydrogenation metal. The presence of a catalytically active hydrogenation metal leads to product improvement, especially IV and stability. Typical catalytically active hydrogenation metals include chromium, molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and palladium. The metals platinum and palladium are especially preferred, with platinum most especially preferred. If platinum and/or palladium is used, the total amount of active hydrogenation metal is typically in the range of 0.1 wt. % to 5 wt. % of the total catalyst, usually from 0.1 wt. % to 2 wt. %.

[0049] The zeolite is loaded with a hydrogenation function metal or a mixture of such metals. Such metals are known in the art and have been discussed generally earlier. The preferred metal is typically either a noble metal, such as Pd, Pt, and Au, or a base metal, such as Ni, Mo and W. A mixture of the metals and their sulfides can be used. The loading of the zeolite with the metals can be accomplished by techniques known in the art, such as impregnation or ion exchange. The hydrogenation function metal is loaded on such a selected zeolite to create the catalyst. The created catalyst can then be used in the hydroconversion process.

[0050] In an embodiment, the feedstock's aromatics and organic nitrogen and sulfur content is reduced. This can be achieved by hydrotreating the feedstock prior to the hydroconversion. Contacting the feedstock with a hydrotreating catalyst may serve to effectively hydrogenate aromatics in the feedstock and to remove N- and S- containing compounds from the feed.

[0051] The conditions under which the hydroconversion step of the present process in reactor 28, i.e., the hydronormalization reaction, is carried out will generally include a temperature within a range from about 390° F to about 800° F (199° C to 427° C). In an embodiment, the temperature is in the range from about 550° F to about 700° F (288° C to 371° C). In a further embodiment, the temperature may be in the range from about

590° F to about 675° F (310° C to 357° C). The pressure may be in the range from about 50 to about 5000 psig, and typically in the range from about 100 to about 2000 psig.

[0052] The products recovered from the hydroconversion, which is normal paraffin rich, can include some clean LPG 30 and clean naphtha 31. Some offgas may also be a product 32. The products can then be passed to a steam cracker 40. Using the present LTA zeolite catalyst provides a C₂-C₆ product in very high yields, which product can be easily collected from the hydronormalization process.

[0053] The next step is a steam cracking step in a naphtha steam cracker. The steam cracking process is known in the art. Steam cracking a hydrocarbon feedstock produces olefin streams containing olefins such as ethylene, propylene, and butenes. The present hydroconversion process provides an excellent feedstock for a steam cracker, allowing for maximum ethylene production.

[0054] In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG, or ethane is diluted with steam and briefly heated in a furnace in the absence of oxygen. Typically, the reaction temperature is very high, at around 850°C. The reaction occurs rapidly: the residence time is on the order of milliseconds. Flow rates approach the speed of sound. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

[0055] The products produced in the reaction depend on the composition of the feed, the hydrocarbon-to-steam ratio, and on the cracking temperature and furnace residence time. Light hydrocarbon feeds such as ethane, LPGs, or light naphtha give mainly lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these same products, but also those rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil.

[0056] FIG. 3 shows the offgas 32, the naphtha 31 and LPG 30 recovered from the hydroconversion reactor 28. The LPG 30 and naphtha 31 can be sent via 35 to the steam cracker 40. Ethylene 36 from the steam cracker can be recovered and used as a chemical or passed to ethylene polymerization 41 to make polyethylene and polyethylene products 42.

[0057] FIGS. 4 and 5 show different processes for cleansing pyrolysis oil through hydrogenation in an olefin saturation reactor followed by a hydrodehalogenation reactor with recycling of the hydrogenated product.

[0058] The following examples are provided in order to further illustrate the present process. However, the examples are not meant to be limiting.

Example 1

[0059] Example of LTA zeolite based noble metal catalyst.

[0060] A catalyst was made by extruding 50 wt. % LTA zeolite with 50- wt-% alumina (Pural TH80 from Sasol). The KAQ-type extrudates were loaded with 0.5 wt. % Pd. The LTA zeolite used had an acid site concentration of about 2.7 mol/l.

Example 2

[0061] Hydronormalize the Feedstock

[0062] A process to selectively hydronormalize the long n-paraffins in a feedstock into particularly C₂-C₆ n-paraffins has been discovered. The process thereby provides a tailored feedstock for a naphtha steam cracker, which selectively pyrolyzes the C₂-C₆ n-paraffins to monetize these hydronormalized products.

[0063] Hydronormalization is accomplished through hydroprocessing a feedstock on a hydroprocessing catalyst as described in Example 1, comprising a LTA zeolite with an optimum acid site concentration around 2.7 mol/l. Key features of the hydronormalization process are that the catalyst selectively converts longer normal paraffins in the feed into C₂-C₆ n-paraffins. In the present example, the feed has an initial boiling point of 390°F, thus the shortest n-paraffin in feed is n-dodecane (or n-C₁₂ with a 421°F boiling point, whereas n-undecane or n-C₁₁ exhibits a 385°F boiling point).

[0064] See FIG. 6 which shows a feed exclusively containing n-C₁₂^{plus} with negligible n-C₁₂^{minus}. The products at 81% n-C₁₂^{plus} conversion are nearly exclusively C₂-C₅ n-paraffins. See FIG. 7.

[0065] Contrary to the expectations of the art, the present LTA zeolites have been surprisingly found to not exhibit a dramatic preference for processing n-paraffins up to the length that could easily fit inside a single LTA cage, which would limit the length of readily hydrocracked n-paraffins to that of n-tricosane or n-C₂₃ (716°F boiling point). Longer n-paraffins (n-triacontane or n-C₃₀, 840°F boiling point and longer) are still successfully processed. In addition to a remarkable selectivity for hydrocracking selectively n-C₁₂ and longer n-alkanes, the catalyst also makes some minimal i-paraffins.

Example 3

[0066] Example of steam cracker feed properties.

[0067] A hydrotreated vacuum gasoil is hydroprocessed into an improved steam cracker feed as described in Table 1 below at 1550 psia H₂, 1.6 LHSV, 5100 scf/b H₂. A steam cracker feed produced at 60% n-C₁₂⁺ conversion in the present hydro-normalization step is characterized in Table 1 as follows:

TABLE 1

	Feed	Hydroprocessed
API (°)	35.4	not measured
S (ppm-wt)	5.3	<0.3
N (ppm-wt)	<0.3	<0.3
Composition	Wt%	Wt%
Methane	0.00	0.03
Ethane	0.00	0.04
Propane	0.00	1
i-Butane	0.00	0.2
n-Butane	0.00	1.29
C4-	0.00	2.56
C5-180°F	0.00	2.2
180-350°F	0.00	0.59
350-500°F	7.2	9.58
500°F+	92.8	86.13
C5+	100.0	98.5
WLP Dist, by Wt%		
0.5/5%	392/478	95/445
10/30%	519/606	495/598

50%	666/	660/
70/90%	719/799	716/796
95/99.5%	842/955	840/956

[0068] The distribution between n- and iso-paraffins as determined by GC x GC is as shown in FIG. 8.

[0069] When switching from a feed without hydronormalization to one with hydronormalization, a dramatically lower feed rate (ton/hr) is needed to reach the same desirable ethylene (C₂H₄) yield. At this feed rate, the hydronormalized feed exhibits a shift toward desirable olefins (C₂H₄, C₃H₆, C₄H₈) and aromatics (benzene, toluene, xylenes or BTD) at the cost of heavier products (particularly pyrolysis fuel oil or PFO) (see Table 2 below). This amounts to a dramatic increase in carbon and energy efficiency of the steam cracking process while providing enhanced circularity at maximum yield.

TABLE 2

	Original Feed		Hydroprocessed	
	High Sev	Low Sev	High Sev	Low Sev
Feed, T/h	324.1	392.7	307.7	379.1
H₂	2.4	2.2	2.4	2.1
CH₄	37.2	34.2	37.1	33.6
C₂H₄	100	100	100	100
C₃H₆	46.1	62.2	41.9	61.3
C₄H₆	18.2	21.9	17.8	21.7
C₄H₈	11.4	24	9.8	23.8
C₄H₁₀	0.4	0.6	0.4	0.6
C₅-400F PGO	61.4	77.2	58.1	76.3
400F+ PFO	47	70.4	40.4	59.8
Selectivity, w/w				
C₂H₄	30.86	25.46	32.5	26.38
C₂H₄+C₃H₆	45.07	41.3	46.12	42.53

C2H4+C3H6+C4H8	50.69	46.87	51.9	48.27
BTX	12.08	7.44	12.6	7.45

[0070] As used in this disclosure the word “comprises” or “comprising” is intended as an open-ended transition meaning the inclusion of the named elements, but not necessarily excluding other unnamed elements. The phrase “consists essentially of” or “consisting essentially of” is intended to mean the exclusion of other elements of any essential significance to the composition. The phrase “consisting of” or “consists of” is intended as a transition meaning the exclusion of all but the recited elements with the exception of only minor traces of impurities.

[0071] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible in light of these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the combination of features of the invention cited herein and those of the cited prior art references which complement the features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article, and such combinations are considered within the scope of this invention.

[0072] All of the publications cited in this disclosure are incorporated by reference herein in their entireties for all purposes.

What is claimed is:

1. A continuous process for converting sorted or selected post-consumer or post-industrial plastic waste into recycle for plastic production comprising:
 - (a) selecting waste plastics for maximum polyolefin and minimum organic halogen, organic nitrogen, silicon, phosphate, arsenate, metals and their oxides, lignocellulose, glyceride, and inorganic solids content;
 - (b) melting the waste plastics from (a) and passing them through a pyrolysis reactor to thermally crack at least a portion of the polyolefin waste and produce a pyrolyzed effluent;
 - (c) separating the pyrolyzed effluent into off-gas, char or pitch, partially converted solids, and a pyrolysis oil;
 - (d) passing the pyrolysis oil from (c) to a hydroconversion reactor comprising a hydroconversion catalyst based on a LTA-type zeolite having an acid site concentration in the range of 2.6 mol/l to 3.0 mol/l;
 - (e) recovering cleansed (hydrogenated, hydrodehalogenated, hydrodeoxygenated, (hydro-)demetallized) hydrocarbons from the hydroconversion reactor; and
 - (f) passing the cleansed hydrocarbons from (e) to a steam cracker for olefin and aromatics production.
2. The process of claim 1, wherein the olefins in the pyrolysis oil are hydrogenated in a separate zone before the pyrolysis oil is hydroprocessed further.
3. The process of claim 2, wherein fresh pyrolysis oil is blended with pyrolysis oil that has already been hydrotreated before entering the olefin hydrogenation zone.
4. The process of claim 1, wherein at least some contaminants are removed from the recovered pyrolysis oil of step (c) before the oil is passed to the hydroconversion reactor in (d).
5. The process of claim 1, wherein the waste plastics selected in (a) are from plastics classification group 2, 4, and/or 5.

6. The process of claim 1, wherein the waste plastics passed from (a) contain less than 50 ppm halides.
7. The process of claim 1, wherein the waste plastics contain less than 5 wt. % polyethylene terephthalate and polyvinyl chloride.
8. The process of claim 1, wherein the LTA zeolite has an acid site concentration in the range of from 2.6 mol/l to 2.8 mol/l.
9. The process of claim 1, wherein the LTA zeolite has an acid site concentration of about 2.7 mol/l.