

CIRCULAR ECONOMY FOR PLASTIC WASTE TO POLYETHYLENE VIA REFINERY CRUDE UNIT

BACKGROUND

[0001] The world has seen extremely rapid growth of plastics production. According to PlasticsEurope Market Research Group, the world plastics production was 335 million tons in 2016, 348 million tons in 2017 and 359 million tons in 2018. According to McKinsey & Company, the global plastics-waste volume was estimated about 260 million tons per year in 2016, and projected to be 460 million tons per year by 2030 if the current trajectory continues.

[0002] 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 chemical and fuel products. Currently, only a small amount of polyethylene and polypropylene is recycled via chemical recycling, where recycled and cleaned polymer pellets are pyrolyzed in a pyrolysis unit to make fuels (naphtha, diesel), stream cracker feed or slack wax.

[0003] Processes are known which convert waste plastic into hydrocarbon lubricants. For example, U.S. Pat. No. 3,845,157 discloses cracking of waste or virgin polyolefins to form gaseous products such as ethylene/olefin copolymers which are further processed to produce synthetic hydrocarbon lubricants. U.S. Pat. No. 4,642,401 discloses the production of liquid hydrocarbons by heating pulverized polyolefin waste at temperatures of 150-500° C. and pressures of 20-300 bars. U.S. Pat. No. 5,849,964 discloses a process in which waste plastic materials are depolymerized into a volatile phase and a liquid phase. The volatile phase is separated into a gaseous phase and a condensate. The liquid phase, the condensate and the gaseous phase are refined into liquid fuel components using standard refining techniques. U.S. Pat. No. 6,143,940 discloses a procedure for converting waste plastics into heavy wax compositions. U.S. Pat. No. 6,150,577 discloses a process of converting waste plastics into lubricating oils. EP0620264 discloses a process for producing lubricating oils from waste or virgin polyolefins by thermally cracking the waste in a fluidized bed to form a waxy product, optionally using a hydrotreatment, then catalytically isomerizing and fractionating to recover a lubricating oil.

[0004] Other documents which relate to processes for converting waste plastic into lubricating oils include U.S. Patent Nos. 6,288,296; 6,774,272; 6,822,126; 7,834,226; 8,088,961;

8,404,912 and 8,696,994; and U.S. Patent Application Publication Nos. 2019/0161683; 2016/0362609; and 2016/0264885. The foregoing patent documents are incorporated herein by reference in their entirety.

[0005] The current method of chemical recycling via pyrolysis cannot make a big impact for the plastics industry. The current pyrolysis operation produces poor quality fuel components (naphtha and diesel range products), but the quantity is small enough that these products can be blended into fuel supplies. However, this simple blending cannot continue if very large volumes of waste polyethylene and polypropylene are to be recycled to address environmental issues. The products as produced from a pyrolysis unit are of too poor quality to be blended in large amounts (for example 5-20 vol% blending) in transportation fuels.

[0006] In order to achieve 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 polyethylene and polypropylene plastics where the spent waste plastics are recycled effectively back as starting materials for polymers and high value byproducts.

SUMMARY

[0007] Provided is a continuous process for converting waste plastic into naphtha for polyethylene polymerization. The process comprises first selecting waste plastics containing polyethylene and/or polypropylene. These waste plastics are then passed through a pyrolysis reactor to thermally crack at least a portion of the polyolefin waste and produce a pyrolyzed effluent. The pyrolyzed effluent is separated into offgas, a pyrolysis oil and wax comprising a naphtha/diesel fraction and a heavy fraction, and char.

[0008] The incorporation of the process with an oil refinery is an important aspect of the present process, and allows the creation of a circular economy with a single use waste plastic such as polyethylene. Thus, the pyrolysis oil and wax recovered is passed to a crude unit in a refinery. A naphtha fraction (C₅-C₈) is recovered from the distillation column, and the naphtha fraction is passed to a steam cracker for ethylene production.

[0009] The refinery will generally have its own hydrocarbon feed flowing through the refinery units. The flow volume of pyrolysis oil and wax generated from the pyrolysis of waste plastic to the refinery units can comprise any practical or accommodating volume % of the total flow to the refinery units. Generally, the flow of the pyrolysis oil and wax generated from the waste

plastic pyrolysis, for practical reasons, can be up to about 50 vol. % of the total flow, i.e., the refinery flow and the pyrolysis flow. In one embodiment, the flow of the pyrolysis oil and wax is an amount up to about 20 vol. % of the total flow.

[0010] In another embodiment, a continuous process for converting waste plastic comprising polyethylene into a C₃-C₄ stream for polyethylene polymerization is provided. The process comprises selecting waste plastics containing polyethylene and polypropylene. The selected waste plastics are passed through a pyrolysis reactor to thermally crack at least portion of the polyolefin waste and produce a pyrolyzed effluent. The pyrolyzed effluent is separated into offgas, a pyrolyzed oil and wax comprising a naphtha/diesel/heavy fraction, and char. The pyrolysis oil and/or optionally wax is passed to a crude unit distillation column in a refinery. A portion of a propane and butane (C₃-C₄) fraction is recovered from the distillation column, and then passed to a steam cracker for ethylene production.

[0011] Among other factors, it has been found that by adding refinery operations one can upgrade the waste pyrolysis oil and wax to higher value products such as gasoline, and diesel. Also, by adding refinery operations it has been found that clean naphtha (C₅-C₈) or C₃-C₄ can be efficiently and effectively produced from the waste pyrolysis oil and wax for ultimate polyethylene polymer production. Positive economics are realized for the overall process from recycled plastics to a polyethylene product with product quality identical to that of virgin polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 depicts the current practice of pyrolyzing waste plastics to produce fuel or wax (base case).

[0013] FIG. 2 depicts a present process for establishing a circular economy for waste plastics.

[0014] FIG. 3 depicts the plastic type classification for waste plastics recycling.

DETAILED DESCRIPTION

[0015] In the present process, provided is a method to recycle waste polyethylene and/or polypropylene back to virgin polyethylene to establish a circular economy by combining distinct industrial processes. A substantial portion of 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.

[0016] Ethylene is the most produced petrochemical building block. Ethylene is produced in hundreds of millions tons per year via steam cracking. The steam crackers use either gaseous feedstocks (ethane, propane and/or butane) or liquid feed stocks (naphtha or gas oil). It is a noncatalytic cracking process that operates at very high temperatures, up to 850° C.

[0017] Polyethylene is used widely in various consumer and industrial products. Polyethylene is the most common plastic, over 100 million tons of polyethylene resins are produced annually. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Polyethylene is produced in three main forms: high-density polyethylene (HDPE, $\sim 0.940\text{-}0.965\text{ g/cm}^3$), linear low-density polyethylene (LLDPE, $\sim 0.915\text{-}0.940\text{ g/cm}^3$) and low-density polyethylene (LDPE, $< 0.930\text{ g/cm}^3$), with the same chemical formula $(\text{C}_2\text{H}_4)_n$ but different molecular structure. HDPE has a low degree of branching with short side chains while LDPE has a very high degree of branching with long side chains. LLDPE is a substantially linear polymer with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins.

[0018] Low density polyethylene (LDPE) is produced via radical polymerization at 150 – 300° C and very high pressure of 1,000-3,000 atm. The process uses a small amount of oxygen and/or organic peroxide initiator to produce polymer with about 4,000 – 40,000 carbon atoms per the average polymer molecule, and with many branches. High density polyethylene (HDPE) is manufactured at relatively low pressure (10-80 atm) and 80-150° C temperature in the presence of a catalyst. Ziegler-Natta organometallic catalysts (titanium(III) chloride with an aluminum alkyl) and Phillips-type catalysts (chromium(IV) oxide on silica) are typically used, and the manufacturing is done via a slurry process using a loop reactor or via a gas phase process with a fluidized bed reactor. Hydrogen is mixed with ethylene to control the chain length of the polymer. Manufacturing conditions of linear low-density polyethylene (LLDPE) are similar to those of HDPE except copolymerization of ethylene with short-chain alpha-olefins (1-butene or 1-hexene).

[0019] Today, only a small portion of spent polyethylene products is collected for recycling, due to the inefficiencies and ineffectiveness of the recycling efforts discussed above.

[0020] FIG. 1 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), and at times wax. The offgas 4 from the pyrolysis unit is used as fuel to operate the pyrolysis unit 3. An on-site distillation unit (not shown) separates the pyrolysis oil to produce naphtha and diesel products 5 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). The wax can be separated from the heavy fraction 6 and sold to wax markets.

[0021] 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 for ethylene cracker), high quality gasoline and diesel fuel, and/or quality base oil.

[0022] 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-C₄ stream can be fed to the steam cracker. The ethylene is then polymerized to create polyethylene.

[0023] By adding refinery operations to upgrade the waste pyrolysis oil and wax to higher value products (gasoline and diesel) and to produce clean LPG and naphtha for steam cracker for ultimate polyethylene polymer production, one is able to create positive economics for the overall process from recycled plastics to polyethylene product with quality identical to that of the virgin polymer.

[0024] A pyrolysis unit produces poor quality products containing contaminants, such as calcium, magnesium, chlorides, nitrogen, sulfur, dienes, and heavy components, which products cannot be used in large quantity for blending in transportation fuels. It has been discovered that by having these products go through the refinery units, the contaminants can be captured in pre-treating units and their negative impacts diminished. The fuel components can be further upgraded with appropriate refinery units with chemical conversion processes, with the final transportation fuels produced by the integrated process being of higher quality and meeting the fuels quality requirements. The integrated process will generate a much cleaner

naphtha stream for stream cracker feedstock for ethylene generation and for polyethylene production. These large on-spec productions allow “cyclical economy” for the recycle plastics feasible.

[0025] The carbon in and out of the refinery operations are “transparent,” meaning that all the molecules from the waste plastic do not necessarily end up in the exact olefin product cycled back to the polyolefin plants, but are nevertheless assumed as “credit” as the net “green” carbon in and out of the refinery is positive. With the integrated processes, the amount of virgin feeds needed for polyethylene plants will be reduced substantially.

[0026] FIG. 2 shows the present integrated process, integrating refinery operations with recycle for effective polyethylene production. In FIG. 2, 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 at times a 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, 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.

[0027] The pyrolysis unit can be located near the waste plastics collection site, which site could be away from a refinery, near a refinery, or within a refinery. If the pyrolysis unit is located away from the refinery, then pyrolysis product(naphtha/diesel and heavies) can be transferred to the refinery by truck, barge, rail car or pipeline. It is preferred, however, that the pyrolysis unit is within the plastics collection site or the refinery.

[0028] 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 pyrolysis unit for thermal cracking. FIG. 3 depicts the plastic type classification for waste plastics recycling. Classification types 2, 4, and 5 are high density polyethylene, low density polyethylene and polypropylene, respectively. Any combination of the polyethylene and polypropylene waste plastics can be used. For the present process, at least some polyethylene waste plastic is preferred.

[0029] Proper sorting of waste plastics is very important in order to minimize contaminants such as N, Cl, and S. Plastics waste containing polyethylene terephthalate (plastics recycle classification type 1), polyvinyl chloride (plastics recycle classification type 3) and other

polymers (plastics recycle classification type 7) need to be sorted out to less than 5%, preferably less than 1% and most preferably less than 0.1%. The present process can tolerate a moderate amount of polystyrene (plastics recycle classification type 6). Waste polystyrene needs to be sorted out to less than 30%, preferably less than 20% and most preferably less than 5%.

[0030] Washing of waste plastics removes 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 need to be removed to less than 50 ppm, preferentially less than 30 ppm and most preferentially to less than 5 ppm.

[0031] 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.

[0032] 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 olefins and n-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.

[0033] FIG. 2 shows the present integrated process where the entire pyrolysis oil and wax from the pyrolysis unit is sent to a refinery crude unit desalter 28. The crude unit desalter eliminates any contaminants in the pyrolysis product, then the product is sent to a crude unit distillation column (not shown as part of the refinery crude unit). Alternatively, the pyrolysis oil and wax can be treated at the pyrolysis site to remove the contaminants, and then injected directly to the refinery crude distillation unit.

[0034] The refinery crude unit separates crude oil into multiple fractions such as liquefied petroleum gas (LPG), naphtha, kerosene, diesel and gas oil which will be further treated into useful petroleum products. The refinery crude unit has a crude treating section, commonly known as a desalter, and a crude oil distillation or fractionation section. The distillation section typically includes an atmospheric distillation unit and a vacuum distillation unit.

[0035] The pyrolysis oil (and wax) is fed to the desalter which removes the salts and solids contained in the oil to protect downstream equipment from the harmful effects of the contaminants. To remove the salts, water is mixed with the oil and typically heated to temperatures between about 215° F to about 280° F and allowed to separate in the desalter unit.

[0036] The refinery will generally have its own hydrocarbon feed flowing through the refinery units. The flow volume of pyrolysis oil and wax generated from the pyrolysis of waste plastic to the refinery units can comprise any practical or accommodating volume % of the total flow to the refinery units. Generally, the flow of the pyrolysis oil and wax generated from the waste plastic pyrolysis, for practical reasons, can be up to about 50 vol. % of the total flow, i.e., the refinery flow and the pyrolysis flow. In one embodiment, the flow of the pyrolysis oil and wax is an amount up to about 20 vol. % of the total flow. In another embodiment, the flow of the pyrolysis oil and wax is an amount up to about 10 vol. % of the total flow. About 20 vol. % has been found to be an amount that is quite practical in its impact on the refinery while also providing excellent results and being an amount that can be accommodated. The amount of pyrolysis oil and wax generated from the pyrolysis can of course be controlled so that the fraction passed to the refinery units provide the desired volume % of the flow.

[0037] Desalted oil and wax is sent to an atmospheric distillation unit heated to about 340-372° C (644-700° F) at the bottom of the distillation column, and liquid is removed at various points of the fractional distillation column to produce various fuels. The fuels from the crude units can be sent to various upgrading units in the refinery to remove impurities (nitrogen, sulfur) and to catalytically transform the fractions to improve the product properties, such as octane and cetane numbers. The bottom residue from the atmospheric distillation column, also known as atmospheric residue, is typically sent to a vacuum distillation column to produce vacuum gas oil (650 – 1050° F) and vacuum residue. The vacuum gas oil may be used to produce lube oil or further cracked to produce gasoline, jet and diesel fuel. The overall process can produce LPG (<80° F), gasoline (80-400° F), jet fuel (360-500° F), and diesel fuel (300-700° F). The boiling points for these fractions are adjusted depending on the season and local specifications.

[0038] From the refinery crude distillation unit, a C₅-C₈ naphtha stream 29, preferentially a C₅-C₇ naphtha and most preferentially a C₅-C₆ naphtha stream is collected. The light naphtha stream is rich in linear paraffins and is a very good light naphtha feed for a steam cracker 30 to generate ethylene. The ethylene is passed on to a polymerization unit 40 to produce polyethylene. The polyethylene is processed further to produce various polyethylene products 41 to fit the needs of consumer products. The heavy portion of the pyrolysis oil can be combined with hydrocarbon from the crude unit distillation and sent to appropriate refinery units as a heavy naphtha, diesel, atmospheric gas oil stream 31 for upgrading into clean gasoline, diesel, or jet fuel.

[0039] The ethylene polymerization unit is preferably located near the refinery so that the feedstocks (propane, butane, naphtha) can be transferred via pipeline. For a petrochemical plant located away from the refinery, the feedstock can be delivered via truck, barge, rail car or pipeline.

[0040] In another embodiment, a C₃-C₄ fraction 32 is recovered from the refinery crude unit 28. This stream can also be fed to the steam cracker 30 for the production of ethylene. The ethylene is passed on to a polymerization unit 40 to produce polyethylene. The polyethylene is processed further to produce various polyethylene products 41 to fit the needs of consumer products.

[0041] The benefits of a circular economy and an effective and efficient recycling campaign are realized by the present integrated process.

[0042] The following examples are provided to further illustrate the present process and its benefits. The examples are meant to be illustrative and not limiting.

[0043] Example 1: Properties of Pyrolysis Oil and Wax From Commercial Sources

[0044] Pyrolysis oil and wax samples were obtained from commercial sources and their properties are summarized in Table 1. These pyrolysis samples were prepared from waste plastics containing mostly polyethylene and polypropylene via thermal decomposition in a pyrolysis reactor at around 400-600° C, near atmospheric pressure without any added gas or a catalyst. A pyrolysis unit typically produces gas, liquid oil product, optionally wax product, and char. The pyrolysis unit's overhead gas stream containing thermally cracked hydrocarbon was cooled to collect condensate as pyrolysis oil (liquid at ambient temperature) and/or pyrolysis wax (solid at ambient temperature). The pyrolysis oil is the main product of the

pyrolysis units. Some units produce pyrolysis wax as a separate product in addition to the pyrolysis oil.

Table 1
Properties of As-Received Oil and Wax from Pyrolysis of Waste Plastics

	Pyrolysis Oil Sample A	Pyrolysis Oil Sample B	Pyrolysis Oil Sample C	Pyrolysis Oil Sample D	Pyrolysis Wax Sample E
Specific Gravity at 60 °F	0.814	0.820	0.774	-	0.828
<u>Simulated Distillation, °F</u>					
0.5% (Initial Boiling Point)	87	299	18	86	325
5%	179	306	129	154	475
10%	214	309	156	210	545
30%	322	346	285	304	656
50%	421	447	392	421	733
70%	545	585	517	532	798
90%	696	798	663	676	894
95%	772	883	735	743	939
99.5% (Final Boiling Point)	942	1079	951	888	1064
<u>Carlo-Erba Hydrocarbon Analysis</u>					
Carbon, wt%	87.6	84.21	85.46	85.97	85.94
Hydrogen, wt%	12.7	12.25	14.1	14.0	14.15
Sum of C + H, wt%	100.3	96.46	99.5	100.0	100.1
H/C Molar Ratio	1.73	1.75	1.98	1.96	1.98
Bromine Number, g/ 100 g	49	60	40	44	14
<u>Hydrocarbon Type</u>					
Total Aromatics, vol%	23.3	22.8	5.1	8.7	13.3
Total Olefins & Naphthenes, vol%	39.0	50.2	42.4	38.2	42.1
Total Paraffins, vol%	37.7	27	52.5	53.1	44.6
<u>Contaminants</u>					
Total S, ppm	48	29	7.8	99	6.3
Total N, ppm	751	1410	318	353	237
Total Cl, ppm	113	62	41	70	4.7
O in naphtha & distillate, ppm	250	-	574	-	-
<u>Trace Elemental Impurities</u>					
Al, ppm	<1.1	<0.56	0.6	<0.53	<0.68
Ca, ppm	1.4	11.5	<0.5	<0.53	<0.68
Fe, ppm	4.9	11.9	1.6	<1.1	3.1
Mg, ppm	<0.51	1.3	<0.52	<0.53	<0.68
Na, ppm	2.5	<0.54	<1.1	<2.2	<2.7
Ni, ppm	<0.51	<0.54	<0.52	2	<0.68
V, ppm	<0.51	<0.54	<0.52	4	<0.68
P, ppm	8.2	9.9	<1.6	<2.2	20.2
Si, ppm	82.5	49.6	13	17	3.1

[0045] ASTM D4052 method was used for specific gravity measurements. Simulated boiling point distribution curve was obtained using ASTM D2887 method. Carlo-Erba analysis for carbon and hydrogen was based on ASTM D5291 method. Bromine number measurement was based on ASTM D1159 method. Hydrocarbon-type analysis was done using a high resolution magnetic mass spectrometer using the magnet scanned from 40 to 500 Daltons. Total sulfur was determined using XRF per ASTM D2622 method. The nitrogen was determined using a modified ASTM D5762 method using chemiluminescence detection. The total chloride content was measured using combustion ion chromatography instrument using modified ASTM

7359 method. The oxygen content in naphtha and distillate boiling range was estimated using GC by GC/MS measurements with electron ionization detector for m/Z range of 29-500. Trace metal and non-metal elements in oil were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

[0046] Industrial pyrolysis process of sorted plastics, sourced predominantly from polyethylene and polypropylene waste, produced quality hydrocarbon streams with specific gravity ranging 0.7 to 0.9, and a boiling range from 18 to 1100° F as in pyrolysis oil or pyrolysis wax.

[0047] The pyrolysis product is rather pure hydrocarbon made of mostly carbon and hydrogen. The hydrogen to carbon molar ratio varies from 1.7 to near 2.0. The Bromine Number is in the range of 14 through 60 indicating varying degrees of unsaturation coming from olefins and aromatics. The aromatic content is in the range of 5 to 23 volume % with a higher severity unit producing more aromatics. Depending on the process conditions of the pyrolysis unit, the pyrolysis products show paraffinic content ranging from mid-20 vol. % to mid-50 vol. %. The pyrolysis product contains a substantial amount of olefins. Samples A and B, pyrolysis oil produced under more severe conditions such as higher pyrolysis temperature and/or longer residence time, contain higher aromatic and lower paraffinic components, resulting H/C molar ratio of around 1.7 and high Bromine Number of 50-60. Samples C and D were produced at less severe conditions, and the pyrolysis oils are more paraffinic, resulting H/C molar ratio of close to 2.0 and Bromine Number around 40. Sample E, pyrolysis wax, is mostly paraffinic, saturated hydrocarbon with a substantial amount of normal hydrocarbons (as opposed to branched hydrocarbons) with low Bromine Number of only 14.

[0048] The following Examples 2 through 5 show the evaluation of waste plastics pyrolysis oil for transportation fuel.

[0049] Example 2: Fractionation of Pyrolysis Oil for Evaluation As Transportation Fuel

[0050] Sample D was distilled to produce hydrocarbon cuts representing gasoline (350° F⁻), jet (350 – 572° F), diesel (572 – 700° F) and the heavy (700° F⁺) fractions. Table 2 summarizes the boiling point distribution and impurity distributions among the distilled product fractions.

Table 2
Distillation of Pyrolysis Oil into Fuel Fractions

Sample ID	Sample D	Sample F	Sample G	Sample H	Sample I
Intended Fraction		Gasoline Cut	Jet Cut	Diesel Cut	Unconverted
Cut Point Target, °F		350 ⁻	350-572	572-700	700 ⁺
Distillation Actual Yields, wt%		37.2	38.0	15.0	9.3
Simulated Distillation, F					
IBP (0.5 wt%)	86	27	299	539	640
5 wt%	154	98	345	557	684
10 wt%	210	147	365	574	696
30 wt%	304	222	416	597	727
50 wt%	421	270	457	619	758
70 wt%	532	291	492	644	808
90 wt%	676	337	546	674	898
95 wt%	743	347	554	683	953
FBP (99.5 wt%)	888	385	591	711	1140
Total S, ppm	99	52	35	80	320
Total N, ppm	353	215	556	232	467
Total Cl, ppm	70	181	27	12	13

[0051] Example 3: Evaluation of Pyrolysis Oil Cut for Gasoline Fuel

[0052] Sample F, a pyrolysis oil cut for gasoline fuel boiling range, was evaluated to assess its potential to use as gasoline fuel. Sample F has the carbon number range of C5 – C12, typical of the gasoline fuel.

[0053] Due to the olefinic nature of the pyrolysis oil, oxidation stability (ASTM D525) and gum forming tendency (ASTM D381) were identified as the most critical properties to examine. Research octane number (RON) and motor octane number (MON) are also the critical properties for engine performance. The RON and MON values were estimated from detailed hydrocarbon GC analysis.

Table 3
Evaluation of Pyrolysis Oil Naphtha Fraction for Gasoline Fuel

	Oxidation Stability, min	Washed Gum, mg/100 mL	RON	MON
Sample F	90	5.0	71.4	67.7
Reference gasoline	>1440	1	95.8	86.2
4/96 vol.% Blend of Sample F with reference gasoline	>1440	2.0	94.5	85.1
15/85 vol.% Blend of Sample F with reference gasoline	>1440	2.2	91.8	83.1

[0054] Sample F, a pyrolysis oil cut for gasoline fuel boiling range, cannot be used by itself as automotive gasoline fuel due to its poor quality. The gasoline fraction from the pyrolysis oil

showed very poor oxidation stability in that Sample F failed only after 90 min compared to the target stability of longer than 1440 minutes. The pyrolysis gasoline exceeded the wash gum target of 4 mg/ 100 mL suggesting severe gum forming tendency. The pyrolysis gasoline has poor octane numbers compared to the reference gasoline. A premium unleaded gasoline was used as the reference gasoline.

[0055] We also examined the potential of blending of the pyrolysis gasoline cut for a limited amount to the reference gasoline. Our study showed that possibly up to 15 volume % of Sample F can be blended to the refinery gasoline while still meeting the fuels property targets. By integrating the pyrolysis gasoline product with a refinery fuel, the overall product quality can be maintained.

[0056] These results indicate that the as-produced gasoline fraction of pyrolysis oil has limited utility as gasoline fuel. Upgrading in a refinery unit is preferred to convert this gasoline fraction of the pyrolysis oil into hydrocarbon that meets the gasoline fuel property targets.

[0057] Example 4: Evaluation of Pyrolysis Oil Cut for Jet Fuel

[0058] Sample G, a pyrolysis oil cut for jet fuel boiling range, was evaluated to assess its potential to use as jet fuel. Sample G has the carbon number range of C9 – C18, typical of the jet fuel.

[0059] Due to the olefinic nature of the pyrolysis oil, jet fuel thermal oxidation test (D3241) was considered as the most critical test. The pyrolysis oil jet cut as-is, Sample G, had only 36 minutes of oxidation stability suggesting the pure pyrolysis jet cut is unsuitable for use as jet fuel.

[0060] We prepared a 5 volume % blend of pyrolysis jet cut (Sample G) with refinery produced jet. The blend still failed for the jet fuel oxidation test as shown in Table 4.

Table 4
Evaluation of Pyrolysis Oil Jet Fraction for Jet Fuel

	Jet Fuel Thermal Oxidation Test
Reference jet fuel	Passed
5/95 vol.% Blend of Sample G with reference jet fuel	Failed

[0061] These results indicate that the as-produced jet fraction of pyrolysis oil is completely unsuitable for jet fuel, and upgrading in a refinery unit is required to convert this jet fraction of the pyrolysis oil into hydrocarbon that meets the jet fuel property targets.

[0062] Example 5: Evaluation of Pyrolysis Oil Cut for Diesel Fuel

[0063] Sample H, a pyrolysis oil cut for diesel fuel boiling range, was evaluated to assess its potential to use as diesel fuel. Sample H has the carbon number range of C14 – C24, typical of the diesel fuel.

[0064] Sample H contains a substantial amount of normal hydrocarbons. Since normal hydrocarbons tends to exhibit waxy characteristics, cold flow properties such as pour point (ASTM D5950-14) and cloud points (ASTM D5773) were considered as the most critical tests.

[0065] We prepared two blends at 10 and 20 volume % of Sample H with refinery produced diesel fuel. However, both blends still failed for the target pour point of less than -17.8° C (0° F) pour points.

Table 5
Evaluation of Pyrolysis Oil Diesel Fraction for Diesel Fuel

	Cloud Point (°C)	Pour Point (°C)	Pour Point Test
Reference diesel fuel	-17.1	-19.0	Passed
10/90 vol.% Blend of Sample H with reference diesel fuel	-11.1	-12.0	Failed
20/80 vol.% Blend of Sample H with reference diesel fuel	-5.5	-7.0	Failed

[0066] These results indicate that the pyrolysis oil as-is is completely unsuitable for diesel fuel, and upgrading in a refinery unit is required to covert the diesel fraction of pyrolysis oil into hydrocarbon that meets the diesel fuel property targets.

[0067] Examples 6: Coprocessing of Pyrolysis Product to Crude Unit or Desalter Unit

[0068] Results from Table 1 showed that industrial pyrolysis process of sorted plastics, sourced predominantly from polyethylene and polypropylene waste, produced quality pyrolysis oil or pyrolysis wax made of mostly carbon and hydrogen. With good sorting and efficient pyrolysis unit operation, the nitrogen and sulfur impurities are at low enough levels that a modern refinery can handle cofeeding of pyrolysis feedstocks to their processing units with no detrimental impacts.

[0069] However, some pyrolysis oils or wax may still contain high amounts of metals (Ca, Fe, Mg) and other non-metals (P, Si, Cl, O) that could negatively affect the performance of conversion units in a refinery. For pyrolysis products with high impurity levels are preferentially fed to a desalter unit before by the crude unit so that bulk of impurities are removed effectively by the desalter.

[0070] By feeding the entire pyrolysis feedstock to a crude unit or to a desalter unit before the crude unit, the pyrolysis oil and wax will be fractionated into multiple components and then

converted in the subsequent conversion units including paraffin isomerization unit, jet hydrotreating unit, diesel hydrotreating unit, fluid catalytic cracking unit (FCC), alkylation unit, hydrocracking unit and/or coker unit to make gasoline, jet and diesel fuel with satisfactory product properties. The conversion units (FCC or hydrocracking unit) will also convert the heavy cut (corresponding to Sample D) or wax (Sample E) into quality transportation fuels.

[0071] After the crude unit, the pyrolysis oil and wax will be converted further in the subsequent conversion units. The following Examples 7 and 8 demonstrate the conversion of waste plastics pyrolysis product into quality transportation fuel in a refinery conversion unit, using a FCC unit as an example.

[0072] Example 7: Conversion of Pyrolysis Oil in FCC

[0073] To study the impact of coprocessing of waste plastics pyrolysis oil to FCC, series of laboratory tests were carried out with Samples A and C. Vacuum gas oil (VGO) is the typical feed for FCC. FCC performances of 20% blend of pyrolysis oil with VGO and pure pyrolysis oil were compared with that of the pure VGO feed.

[0074] The FCC experiments were carried out on a Model C ACE (advanced cracking evaluation) unit fabricated by Kayser Technology Inc. using regenerated equilibrium catalyst (Ecat) from a refinery. The reactor was a fixed fluidized reactor using N₂ as fluidization gas. Catalytic cracking experiments were carried out at the atmospheric pressure and 900° F reactor temperature. The cat/oil ratio was varied between 5 to 8 by varying the amount of the catalyst. A gas product was collected and analyzed using a refinery gas analyzer (RGA), equipped with GC with FID detector. In-situ regeneration of a spent catalyst was carried out in the presence of air at 1300° F, and the regeneration flue gas was passed through a LECO unit to determine the coke yield. A liquid product was weighted and analyzed in a GC for simulated distillation (D2887) and C₅⁺ composition analysis. With a material balance, the yields of coke, dry gas components, LPG components, gasoline (C₅-430° F), light cycle oil (LCO, 430-650° F) and heavy cycle oil (HCO, 650°F⁺) were determined. The results are summarized below in Table 6.

Table 6
Evaluation of Pyrolysis Oil Cofeeding to FCC

Feed	100% VGO	20/80 vol% blend, Sample A/ VGO	20/80 vol% blend, Sample C/ VGO	100% Sample A	100% Sample C
Cat/Oil, wt/wt	6.0	6.0	6.0	6.0	6.0
Conversion, wt%*	81.3	83.15	83.09	76.1	78.82
<u>WLP Impurity**</u>					
Total O, ppm	81	76	62	54	67
Total N, ppm	27	30	33	50	21
<u>Yields</u>					

Coke, wt%	4.45	4.35	4.20	3.56	2.90
Total Dry Gas, wt%	2.08	1.96	1.93	1.55	1.43
Hydrogen	0.16	0.12	0.12	0.05	0.04
Methane	0.68	0.65	0.64	0.50	0.46
Ethane	0.44	0.43	0.41	0.33	0.28
Ethylene	0.76	0.74	0.72	0.63	0.61
Total LPG, wt%	21.25	21.08	21.50	20.17	24.40
Propane	1.78	1.76	1.72	1.47	1.53
Propylene	5.53	5.51	5.56	5.57	6.75
n-Butane	1.56	1.56	1.54	1.29	1.34
Isobutane	6.61	6.48	6.64	5.43	6.61
C4 olefins	5.77	5.77	6.04	6.41	8.16
Gasoline, wt%	53.53	55.75	55.46	62.53	61.75
LCO, wt%	12.89	12.23	11.93	10.37	8.03
HCO, wt%	5.81	4.63	4.98	1.82	1.50
Octane Number***	88.05	84.57	82.79	73.75	75.41

*: Conversion – conversion of 430°F⁺ fraction to 430°F⁻

**: Impurity level of N and O in whole liquid product in fuels boiling range by GC x GC, ppm

***: Octane number, (R+M)/2, was estimated from detailed hydrocarbon GC of FCC gasoline.

[0075] The results in Table 6 show that up to 20 volume % cofeeding of pyrolysis oil only makes very slight changes in the FCC unit performance indicating coprocessing of pyrolysis oil up to 20% is readily feasible. The 20 volume % blending of Sample A or Sample C led to very slight reduction of coke and dry gas yields, slight increase in gasoline yield and slight decrease in LCO and HCO, which are favorable in most situations. With paraffinic nature of pyrolysis oil, the 20% blends of A and C lowered the Octane number by about 3-5 numbers. With refinery operational flexibility, these octane number debits can be compensated with blending or feeding location adjustments. By cofeeding the pyrolysis oil through the FCC process unit with a zeolite catalyst, the oxygen and nitrogen impurities in the fuel range were reduced substantially, from about 300-1400 ppm N to about 30 ppm N and from about 250-540 ppm O to about 60-80 ppm O. The hydrocarbon composition of all these cofeeding products are well within the typical FCC gasoline range.

[0076] The FCC runs of 100% pyrolysis oil showed substantial debits of Octane numbers by about 13-14 numbers. This shows that coprocessing of pyrolysis oil is preferred over processing of pure 100% pyrolysis oil.

[0077] Example 8: Coprocessing of Pyrolysis Wax in FCC

[0078] To study the impact of coprocessing of waste plastics pyrolysis wax to FCC, series of laboratory tests were carried out with Sample E and VGO. FCC performances of 20% blend of pyrolysis wax with VGO and pure pyrolysis wax were compared with that of the pure VGO feed, similar to Example 7. The results are summarized below in Table 7.

Table 7
Evaluation of Pyrolysis Wax Cofeeding to FCC

Feed	100% VGO	20/80 vol% blend, Sample E/ VGO	100% Sample E
Cat/Oil, wt/wt	6.5	6.5	6.5
Conversion, wt%*	82.75	84.17	91.31
<u>Yields</u>			
Coke, wt%	4.78	4.76	4.26
Total Dry Gas, wt%	2.11	2.05	1.79
Hydrogen	0.16	0.14	0.07
Methane	0.69	0.67	0.58
Ethane	0.44	0.43	0.37
Ethylene	0.78	0.77	0.73
Total LPG, wt%	21.71	23.15	31.79
Propane	1.87	1.93	2.28
Propylene	5.54	5.98	8.59
n-Butane	1.65	1.74	2.15
Isobutane	6.91	7.25	8.88
C4 olefins	5.74	6.25	9.89
Gasoline, wt%	54.16	54.21	53.47
LCO, wt%	12.42	11.59	6.71
HCO, wt%	4.83	4.24	1.99
Octane Number**	89.95	88.38	83.52

*: Conversion – conversion of 430°F⁺ fraction to 430°F⁻

**: Octane number, (R+M)/2, was estimated from detailed hydrocarbon GC of FCC gasoline.

[0079] The results in Table 7 shows that up to 20 volume % cofeeding of pyrolysis wax only makes very slight changes in the FCC unit performance indicating coprocessing of pyrolysis wax up to 20% is readily feasible. The 20 volume % blending of Sample E led to very slight reduction to no change of coke and dry gas yields, noticeable increase in LPG olefin yield, very slight increase in gasoline yield and slight decrease in LCO and HCO, which are all favorable in most situations. With paraffinic nature of pyrolysis wax, the 20% blend of Sample E lowered the Octane number slightly by 1.5 number. With refinery blending flexibility, this octane number debit can be easily compensated with minor blending adjustments.

[0080] The FCC run of 100% pyrolysis wax showed substantial increase in conversion, and debit of the Octane number by 6. This shows that coprocessing of pyrolysis wax is preferred over processing of 100% pyrolysis wax.

[0081] Example 9: Feedstocks of C₃-C₄ and/or Naphtha Generation from Waste Plastics Pyrolysis Product Cofeeding to Refinery Crude Unit

[0082] By feeding of the entire pyrolysis feedstock to a crude unit or to a desalter unit before the crude unit, the pyrolysis oil and wax will be fractionated into multiple components. With the pyrolysis oil cofeeding, the refinery crude unit produces a substantial amounts of clean propane, butane, and naphtha streams, as well as other streams for refinery conversion units.

[0083] Example 10: Feeding of Recycle C₃-C₄ and/or Naphtha to Steam Cracker for Ethylene Production, Followed by Productions of Polyethylene Resin and Polyethylene Consumer Products

[0084] The propane, butane and naphtha streams, produced via cofeeding of pyrolysis products to a crude unit per Example 9, are good feedstocks to cofeed to a steam cracker for production of ethylene with a recycle content. At least a portion of the streams, if not all, are fed to the steam cracker. The ethylene is processed to a polymerization unit to produce polyethylene resin containing some recycled-polyethylene/ polypropylene derived materials while the quality of the newly produced polyethylene is indistinguishable to the virgin polyethylene made entirely from virgin petroleum resources. The polyethylene resin with the recycled material is then further processed to produce various polyethylene products to fit the needs of consumer products. These polyethylene consumer products now contains chemically recycled, circular polymer while quality of the polyethylene consumer products are indistinguishable from those made entirely from virgin polyethylene polymer. These chemically recycled polymer products are different from the mechanically recycled polymer products whose qualities are inferior to the polymer products made from virgin polymers.

[0085] 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.

[0086] All patents and publications referenced herein are hereby incorporated by reference to the extent not inconsistent herewith. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.