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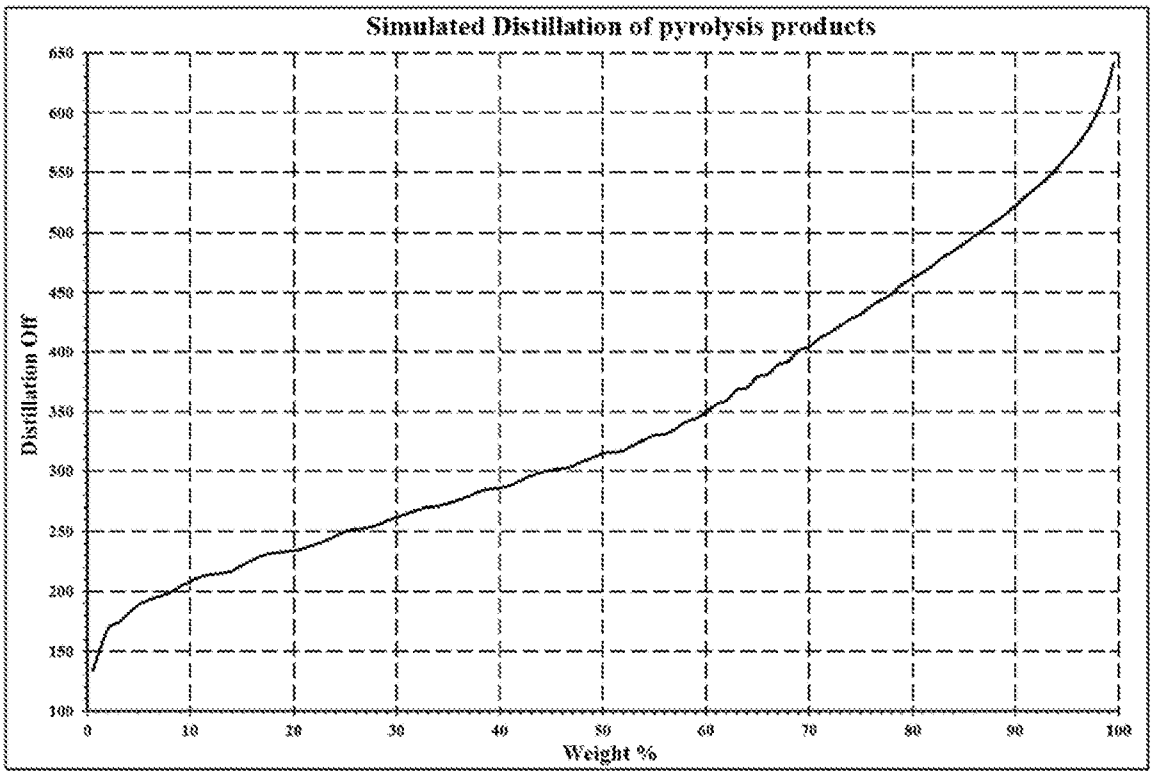


Figure 1

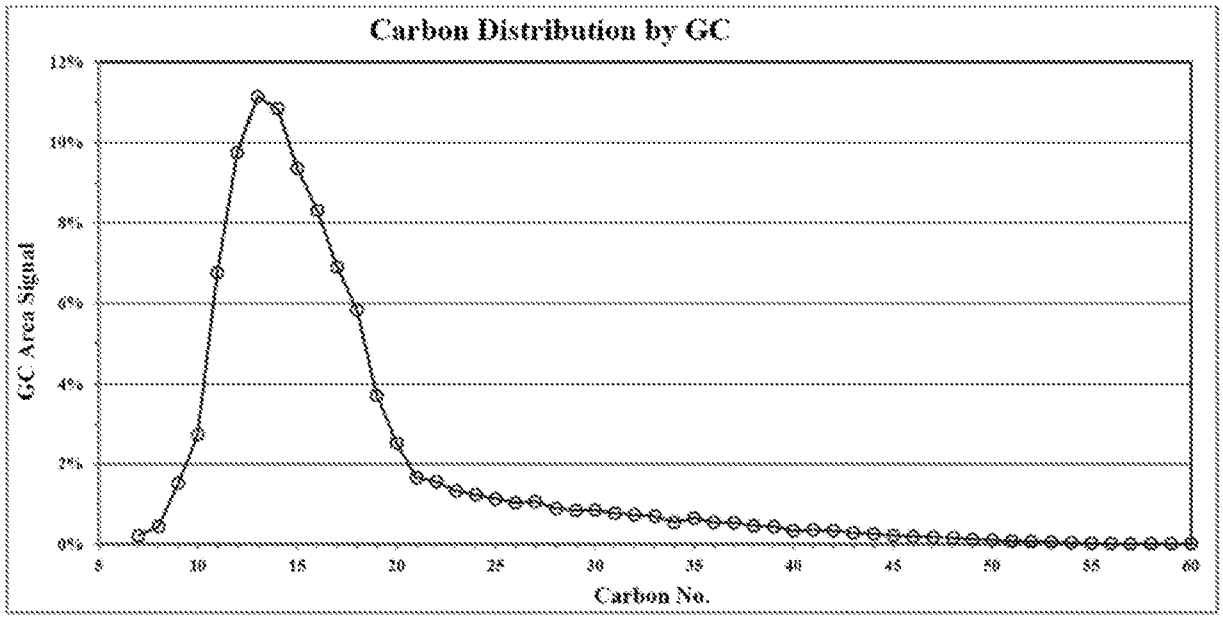


Figure 2

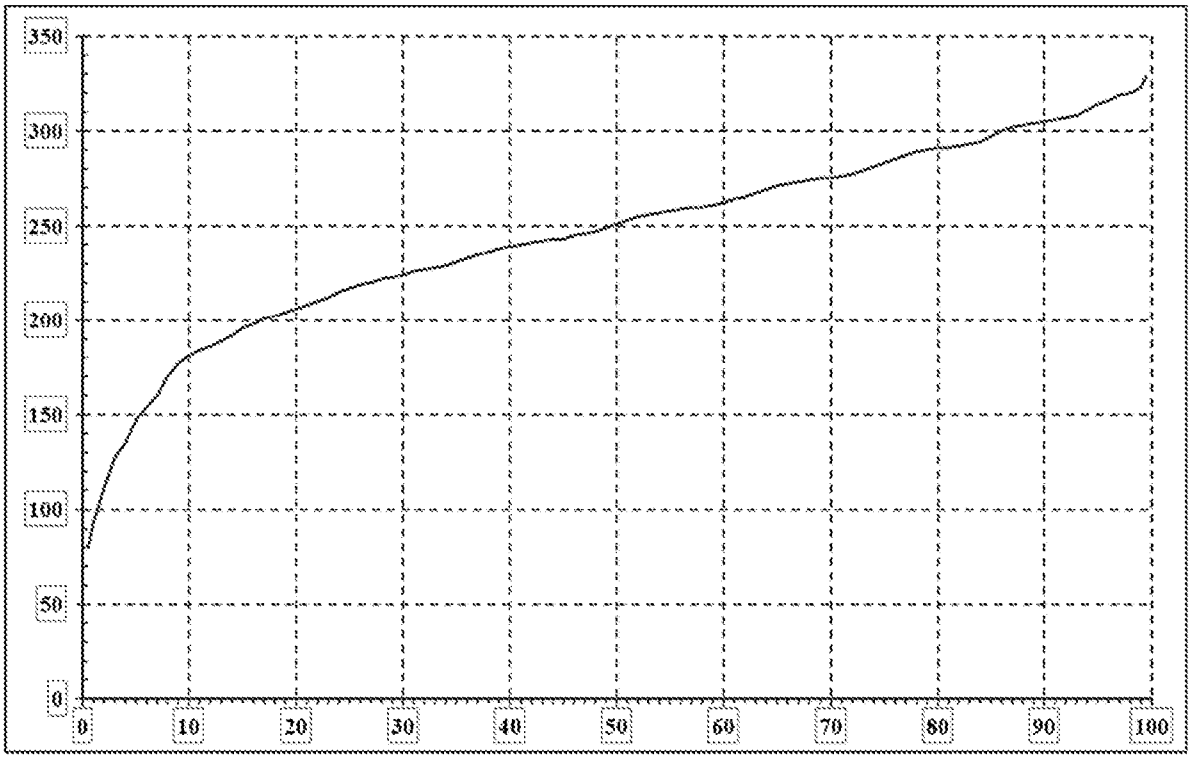


Figure 3

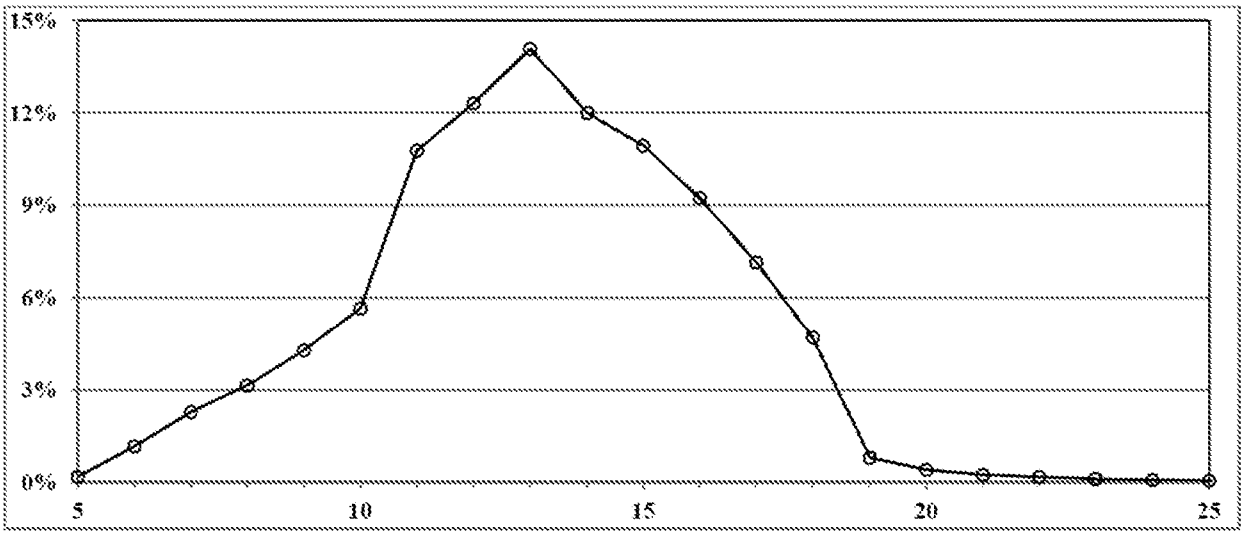


Figure 4

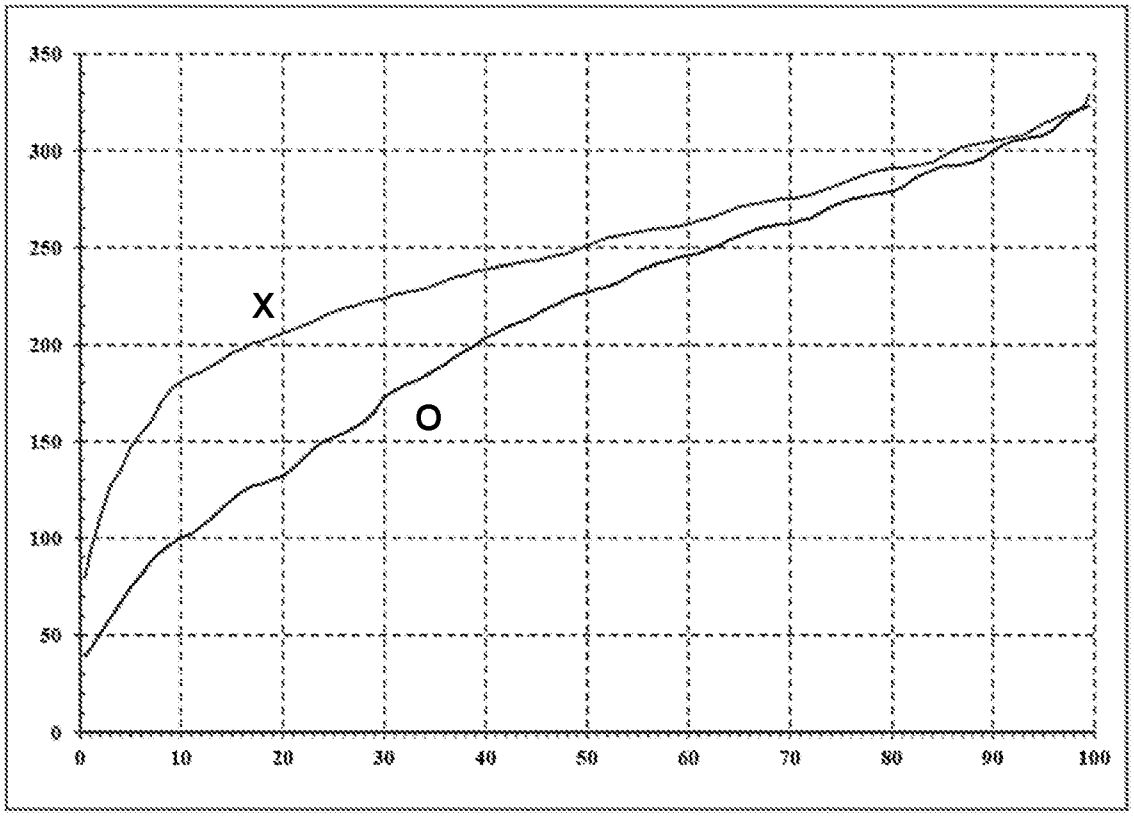
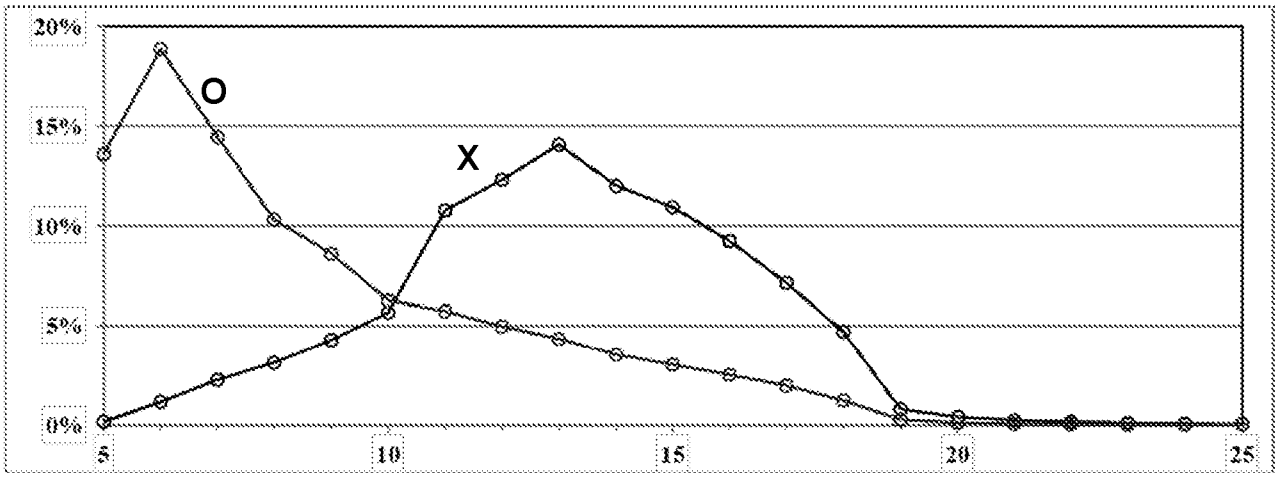


Figure 5



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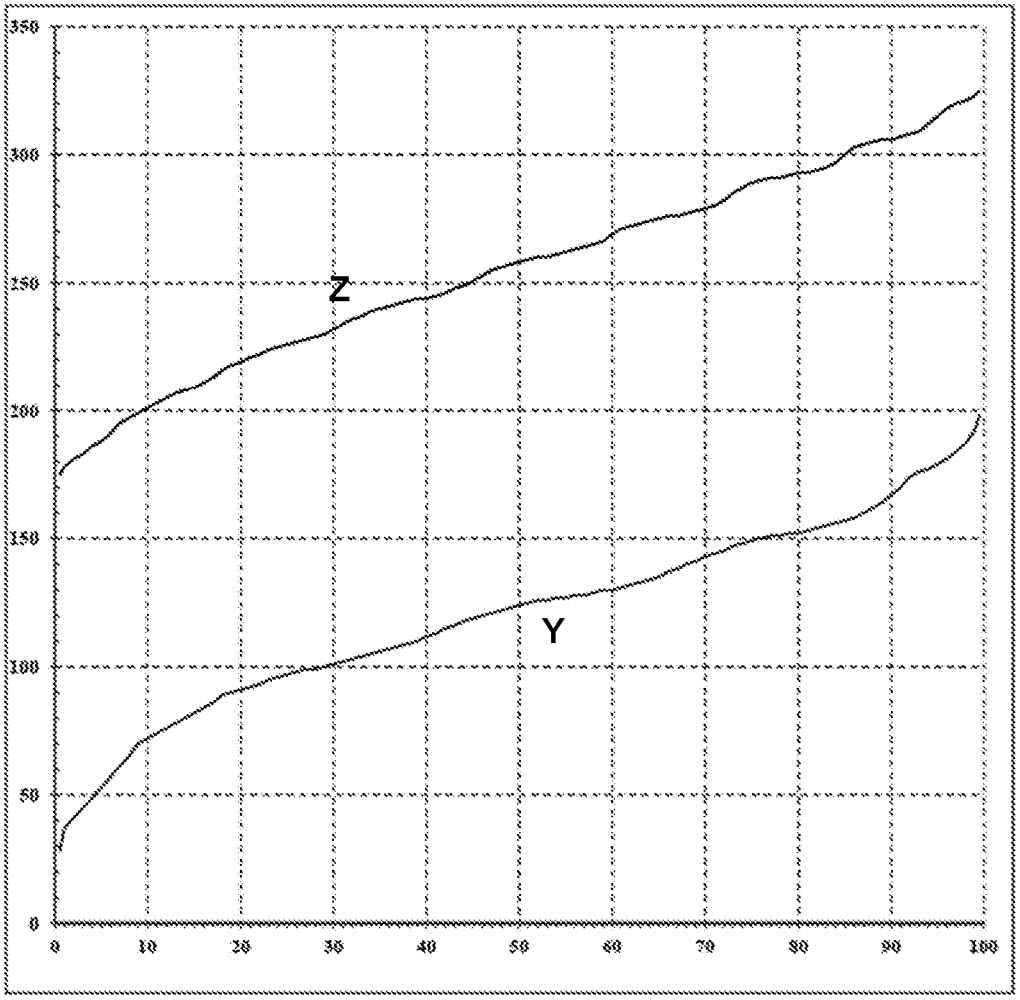

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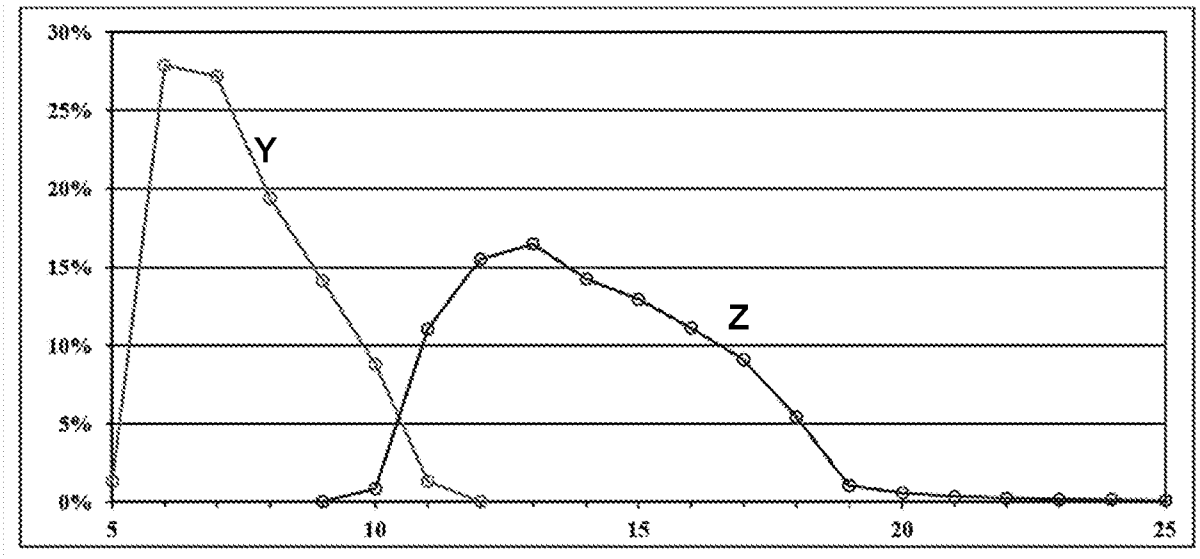

Figure 8

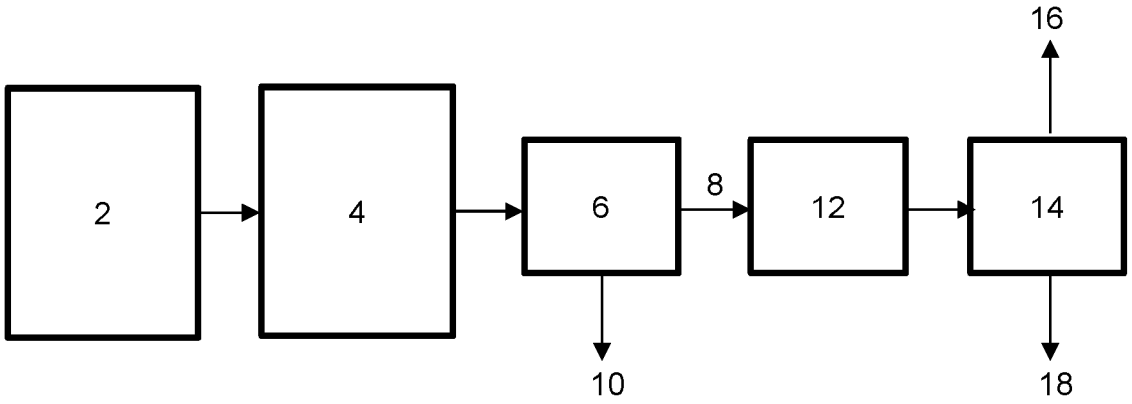

Figure 9

PROCESS FOR PRODUCING NAPHTHA AND DIESEL FROM PYROLYSIS OF PLASTICS

The present invention relates to producing hydrocarbon products from a polymer feed. In particular, the present invention relates to producing naphtha and diesel from a polymer feed by pyrolysis and hydrogenation of a fluid product stream from the pyrolysis.

Background

Plastics are one of the most commonly used materials due to their cheap price and versatility. They are often produced for single-use purposes and making up about 10% of the commercial and household waste produced.

Plastic waste poses a unique challenge as it is not bio-degradable and can persist in the environment for centuries if it is not disposed of using a suitable method. The current widely used methods to handle plastic wastes includes landfilling, incineration and recycling. Most plastic wastes end up in landfills as current recycling and incineration facility capacity is small compared to landfill capacity. This does not align with the current drive towards increased recycling and the use of environmental process.

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Incineration returns some of the energy stored in the plastics in the form of heat energy that can be used to generate steam which can be used to produce electricity. One of the biggest disadvantages of the incineration process is production of carcinogenic furans and dioxins emissions. Another disadvantage of the incineration process is the form of product. Incineration produces heat, which can only be utilized in nearby regions as it loses its energy when transported through long distances.

Plastic wastes can also be recycled to produce new plastics, recovering the plastic material which can be used to produce new plastic products. However, plastic recycling requires time and labour-intensive collection as well as separation, causing the process to have a low technical and economic feasibility. Plastic separation is difficult and cross contaminations are almost always inevitable, producing recycled products that can only be used in low grade applications. Intensive washing is also required before recycling processes take place, producing further waste.

Plastic pyrolysis is one of the most promising plastic disposal methods as it recovers energy from waste plastics in gaseous, liquid and solid form while emitting minimal pollutants. Pyrolysis is the thermal decomposition of materials at elevated temperatures in the absence of oxygen. Thus, no combustion or oxidation takes place. In plastic pyrolysis, the plastic wastes are heated to elevated temperatures to degrade the wastes into combustible gases, liquid and solid products.

Pyrolysis is a tertiary recycling process that is currently considered as a superior way to recover energy from plastic wastes or to produce useful products such as energy sources and chemical feedstock. Compared to incineration, pyrolysis produces fewer toxic gases as well as having a higher energy recovery efficiency. Pyrolysis products are also much more flexible and easy to transport compared to heat energy, which is produced during incineration.

Pyrolysis is also more feasible than plastic recycling as it is not as sensitive to cross plastic contaminations, and therefore does not require an intense separating process. It is considered as a promising green technology as even its gaseous by-product has a significant calorific value that can be reused in the pyrolysis stage to decrease the energy requirement for the pyrolysis plant.

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Pyrolysis of plastics has typically focussed on the conditions applied during pyrolysis in order to maximise the yield of a particular desired product, such as waxes. Little consideration has been given to downstream separation besides to simply fractionate the distribution of products that the pyrolysis process is optimised to obtain. However, while there are many factors that affect different product yields and the composition of products (including the operating temperature, heat rate, retention time, for example), adjusting these typically shifts the distribution towards lighter products, leading to increased losses in non-condensable gas, or towards long carbon-chain waxes produced at the expense of lighter fractions. This leads to compromise in tailoring pyrolysis conditions to shift the product distribution towards a particular desired product, with small amounts of hydrocarbon fractions outside of targeted products that are difficult or too inefficient to separate and collect.

Thus, it is desirable to develop new processes designed to obtain useful product streams more efficiently from the pyrolysis of plastics.

Summary

It has been surprisingly found that by performing controlled pyrolysis in a rotary kiln reactor and hydrogenating pyrolysis products obtained from the reactor prior to additional processing, an improved distribution of hydrocarbon products may be obtained from the pyrolysis process. In particular, the present process has been surprisingly found to result in advantageous yields of naphtha and diesel that may be efficiently separated from each other when hydrocracking of a combined naphtha and diesel containing fraction, separated from heavier hydrocarbon products from the pyrolysis, is performed.

Accordingly, an aspect of the present invention provides a process for producing naphtha and diesel from a polymer feed, the process comprising:

(i) providing a polymer feed comprising at least 80 wt.% of polyolefin polymers;
(ii) melting the polymer feed to provide a molten polymer feed;
(iii) passing the molten polymer feed to a rotary kiln reactor comprising a plurality of sequential heating zones, wherein each zone of the rotary kiln is operated at a temperature of from 300 °C to 800 °C to pyrolyze the molten polymer feed and produce a fluid product stream and a solid char product;
(iv) separating the solid char product from the fluid product stream;
(v) passing a liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons to a hydrogenation reactor and hydrogenating said liquid fraction to produce a hydrogenated hydrocarbon product stream;
(vi) fractionating the hydrogenated hydrocarbon product stream to produce a light hydrogenated fraction comprising C_{5-20} hydrocarbons;
(vii) hydrocracking the light hydrogenated fraction to produce a light hydrocarbon product stream enriched in C_{5-10} hydrocarbons; and
(viii) fractionating the light hydrocarbon product stream from (vii) to produce a naphtha fraction and a diesel fraction.

By providing pyrolysis of plastic polymers in a temperature controlled rotary kiln, and hydrogenating the effluent from the kiln, the process has been found to provide an advantageous distribution of hydrocarbon products. In particular, it has been found that using

the present process an increased yield of a light fraction comprising C_{5-20} hydrocarbons may be obtained, which can be hydrocracked to provide a product enriched in C_{5-10} hydrocarbons. The process allows particularly clean separation of this enriched C_{5-20} stream into a naphtha fraction (C_{5-10}) and a diesel fraction (C_{10-20}).

A further aspect of the present invention provides an apparatus for producing naphtha and diesel from a polymer feed, the apparatus comprising:

(i) means for melting a polymer feed comprising at least 80 wt.% of polyolefin polymers to provide a molten polymer feed;

(ii) a rotary kiln reactor configured to receive the molten polymer feed from part (i), the rotary kiln reactor configured to provide a plurality of sequential heating zones, wherein each zone of the rotary kiln is configured to be operated at a temperature of from 300 °C to 800 °C to pyrolyze the molten polymer feed and produce a fluid product stream and a solid char product;

(iii) means for separating the solid char product from the fluid product stream; and

(iv) a hydrogenation reactor configured to receive a liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons from part (iii) and to hydrogenate said liquid fraction to produce a hydrogenated hydrocarbon product stream;

(v) means for fractionating the hydrogenated hydrocarbon product stream to produce a light hydrogenated fraction comprising C_{5-20} hydrocarbons;

(vi) a hydrocracking reactor configured to catalytically crack the light hydrogenated fraction in the presence of hydrogen to produce a light hydrocarbon product stream enriched in C_{5-10} hydrocarbons; and

(vii) means for fractionating the light hydrocarbon product stream from (vi) to produce a naphtha fraction and a diesel fraction.

Polymer Feed

The polymer feed suitably comprises at least 80 wt.% polyolefin polymers, for example at least 85 wt.% polyolefin polymers. Preferably, the polymer feed comprises at least 90 wt.% polyolefin polymers, preferably at least 95 wt.% polyolefin polymers, for example at least 99 wt.% polyolefin polymers. In some instances, the polymer feed consists essentially of polyolefin polymers, such as polyolefin polymers with only minor amounts of contaminants that do not materially affect the process or the products formed.

Preferably, the polymer feed comprises or consists essentially of waste plastic. Sources of such waste materials include bags, bottles, films, sheets, fibres, textiles, pipes and other moulded or extruded forms.

Other plastic polymers may therefore be present as no more than 20 wt.% of the polymer feed, preferably no more than 10 wt.%, more preferably no more than 5 wt.%, for example no more than 1 wt.%. Other plastic materials may include aromatic plastic polymers, for example polystyrene; halogenated plastic polymers, for example polyvinyl chloride and polytetraflouroethylene; and polyester plastic polymers, for example polyethylene terephthalate. Preferably, these other polymers are limited in the polymer feed as in some instances these polymers can lead to gum formation, disrupting operation and requiring cleaning. Halogen-containing polymers can also cause formation of haloacids during pyrolysis which can lead to corrosion problems or require additional process steps and/or equipment to neutralise or trap the acids.

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As will be appreciated, the polymer feed may in some instances comprise residual contaminants that may be present in waste plastics such as soil, paper, adhesives and piments, for example from labels, or metals. Preferably, such contaminants are present in the polymer feed in an amount of less than 5 wt.%, preferably less than 1 wt.%.

In some embodiments, the process may comprise removing non-polyolefin polymers and/or non-plastic contaminants prior to providing the feed to the present process, for example using magnets to remove metals or an optical sorting process.

Preferably, the polyolefin polymers in the feed comprise or consist essentially of polyethylene and polypropylene, for example wherein the polyolefin polymers comprise at least 90 wt.% polyethylene and polypropylene, preferably at least 95 wt.% polyethylene and polypropylene, for example at least 99 wt.% polyethylene and polypropylene. The polyethylene may be any form of polyethylene but preferably comprises or consists essentially of high-density polyethylene (HDPE) and low-density polyethylene (LDPE). Thus, the polymer feed may comprise or consist essentially of high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene. In some preferred embodiments, the polyolefin polymers in the feed comprise or consist essentially of polyethylene (such as LDPE and HDPE), for example

at least 90 wt.% polyethylene, preferably at least 95 wt.% polyethylene, for example at least 99 wt.% polyethylene. In some preferred embodiments, the polyolefin polymers in the feed comprise at least 40 wt.% polyethylene, preferably at least 50 wt.% polyethylene.

LDPE and HDPE are both polymers of ethylene and have the formula $(CH_2CH_2)_n$. The properties of polyethylene and thus its classification as LDPE or HDPE and its applications depend on factors such as molecular weight, branching and density. LDPE preferably has a molecular weight of from 30,000 to 50,000 g/mol and a density of from 0.910 to 0.925 g/cm^3. HDPE preferably has a molecular weight of from 200,000 to 500,000 g/mol and a density of from 0.941 to 0.980 g/cm^3. LDPE preferably has branching on from 1 to 4 % of carbon atoms, more preferably on 1 to 3 % of carbon atoms, more preferably on 1.5 to 2.5 % of carbon atoms. HDPE preferably has less branching than LDPE, such as on less than 2 % of carbon atoms, preferably less than 1 % of carbon atoms, more preferably less than 0.5 % of carbon atoms, even more preferably less than 0.1 % of carbon atoms. As LDPE generally has more branching than HDPE, the intermolecular forces between the chains are weaker, its tensile strength is lower, and its resilience is higher than HDPE. In contrast, HDPE is known for its high strength-to-density ratio. HDPE is commonly used in the production of many items, including plastic bags, plastic bottles, piping and containers. LDPE is commonly used in parts that require flexibility, such as snap on lids, in trays and containers, and in plastic wraps.

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Polypropylene is a polymer of propylene and has the formula $(CH(CH_3)CH_2)_n$. Preferably, the density of polypropylene is between 0.895 and 0.92 g/cm^3. Polypropylene may have a melting point of from 130 °C to 170 °C, depending on its tacticity. In general, the properties of polypropylene may be considered to be similar to polyethylene, however the methyl group improves mechanical properties and thermal resistance. Generally, polypropylene is tough and flexible with good resistance to fatigue. Therefore, polypropylene may be used in hinges. Polypropylene may also be used in applications requiring high temperatures, such as in medical applications which require the use of an autoclave or kettles.

In addition, polyethylene and polypropylene may be copolymerised with other monomers. The monomers selected will depend on the required properties. For example, PE may be copolymerised with vinyl acetate or with an acrylate. These copolymers may be used in athletic-shoe sole foams and in packaging and sporting goods respectively. In particular, polyethylene and polypropylene maybe copolymerised. For example, a random copolymer of

polypropylene with polyethylene may be used for plastic pipework.

Polyvinyl chlorides (PVCs) are polymers comprising chlorine. The main product of PVC pyrolysis is hydrochloric acid (HCl), with a low pyrolysis oil yield. The toxic and corrosive nature of HCl poses a negative impact to the environment and human health in addition to damaging process equipment. For these reasons, it is particularly preferred that PVC not be used in pyrolysis, or only be used in low amounts. Such small amounts are ideally less than 0.1 wt.% of the polymer feed, preferably less than 0.07 wt.%, more preferably less than 0.05 wt.%. Calcium oxide may be added to the plastic feed material in order to remove hydrochloric acid which may be present/formed during the process. It will be appreciated that the amount of calcium oxide used may be varied depending on the amount of polymers comprising chlorine, such as PVC, in the polymer feed. Calcium oxide may be added in an amount of from 1 wt. % to 5 wt. %, preferably 2 wt. % to 4 wt. %, more preferably 2.5 wt. % to 3.5 wt. % with respect to the plastic feed. Calcium oxide is preferably added to the polymer feed prior to pyrolysis, such as before it is fed to the kiln. For example, calcium oxide may be added to the polymer feed in a melt extruder prior to entering the kiln, such as adding the calcium oxide to a hopper providing the feed plastics to the melt extruder.

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The polymer feed is suitably melted to provide a molten plastic feed for pyrolysis. The polymer feed may be processed prior to melting to change the shape and/or size of the plastic, for example by extruding, chopping and/or shredding. The plastic feed may be in the form of pellets, flakes, threads or fibres, films or may be shredded. Preferably, the plastic feed is processed to increase the surface area, which may aid melting.

Prior to pyrolysis, the polymer feed is suitably melted, for example by melting the plastic feed followed by extrusion or otherwise conveying the molten plastic for pyrolysis in the rotary kiln. For example, the melting is preferably performed in a melt extruder. Alternatively, the polymer feed may be melted at a heated inlet to the rotary kiln or in a melting zone of the kiln prior to heating zones in which pyrolysis takes place. Melting the polymer feed may comprise heating the polymer feed to a temperature of 200 to 400 °C, preferably 250 to 350 °C, more preferably 265 to 325 °C. The melt extruder may suitably comprise a heated screw extruder, which may be heated in any suitable way, for example using electric heaters. In other embodiments, the polymer feed may be melted by microwave heating.

Pyrolysis

Pyrolysis of the polymer feed is carried out by providing the molten polymer feed to a plurality of sequential heating zones of a rotary kiln reactor. Rotary kilns are known to the person skilled in the art and may typically comprise a substantially cylindrical (e.g. tubular) reactor that is configured to be rotated about its longitudinal axis (i.e. an axis extending through the centre of the circular cross-section of the reactor tube along its length). The rotary kiln will typically have an inlet at one end of the reactor and an outlet at the opposite end, though the exact configuration may vary. The molten polymer feed may be fed to the kiln from a melt extruder through any suitable means such as a suitable transfer pipe. The rotary kiln may be inclined to provide a height difference between its ends such that the polymer feed and intermediate pyrolysis products (i.e. pyrolysis products formed from the feed that are still present in the kiln, which may or may not undergo further cracking prior to exiting the kiln) can be moved under gravity from the inlet to the outlet whilst the kiln is rotated. The rotation of the kiln is not particularly limited, but may for example be rotated at a rate of from 0.1 to 5 rpm, for example from 0.1 to 2 rpm.

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The pyrolysis may generally be performed using any suitable conditions, of which the skilled person would be aware, and is performed by heating the polymer feed in the absence of oxygen. The pyrolysis is preferably performed under an inert atmosphere, such as nitrogen or argon, preferably nitrogen. Thus, in preferred embodiments the rotary kiln is maintained under an atmosphere of inert gas, preferably nitrogen.

As described, the rotary kiln comprises plurality of heating zones, preferably 4 or more sequential heating zones, where preferably each heating zone operated at a higher temperature than the preceding zone. Each heating zone of the rotary kiln is suitably operated at a temperature of from 300 °C to 800 °C, preferably each zone of the rotary kiln is operated at a temperature of from 310 °C to 720 °C, for example from 400 °C to 670 °C. In preferred embodiments, the polymer feed experiences increasing temperature as it passes from zone to zone through the kiln. For example, in preferred embodiments the four or more sequential heating zones comprise sequential zones operated at from 310 °C to 600 °C in a first zone to 480 °C to 710 °C in a final zone. Preferably, the final zone of the plurality of zones is heated to a higher temperature then the other heating zones. Heating to a higher temperature in the

final zone has been found to reduce loss of hydrocarbon products with the char, as well as increasing processability of the char, without requiring high temperatures that might cause overcracking of the polymer feed to be maintained throughout the kiln. In some embodiments, the heating zones may comprise at least six sequential heating zones. The heating zones suitably comprise separate discrete heating zones, such that each zone is heated at a predetermined temperature, with each subsequent zone being heated at a higher temperature. The flow of material (i.e. polymer feed and intermediate pyrolysis products) through the kiln may be substantially constant along its length. Thus, by varying the length of each heating zone within the kiln, the residence time in each heating zone may suitably be varied. In some preferred embodiments, each heating zone is of equal length, providing equal residence time within each zone, although this is not essential.

The temperature of the zones as referred to herein will be understood to refer to the temperature of the walls of the rotary kiln in each zone, and it will be appreciated that the exact temperature of polymers or pyrolyzed material inside the reactor may vary.

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By providing a pyrolysis process using a rotary kiln as described, it has been found that an increased proportion of light hydrocarbons (e.g. C_5 to C_{20}) may be produced whilst also minimising non-condensable gas formation due to over-cracking and producing other valuable hydrocarbon fractions and products such as wax and char. In particular, it has been surprisingly found that approximately 60 wt.% of the condensable hydrocarbon products obtained from the kiln (i.e. the condensable liquid separated from the char) are in the diesel range or lighter, i.e. having a boiling point about 350 ° or less. The heavier hydrocarbons in the product advantageously form waxes having a melting point of less than 100 °C, preferably no more than 85 °C. Thus, the liquid hydrocarbon product stream from the kiln can comprise a light hydrogenated fraction comprising $C_{5\text{-}20}$ hydrocarbons and a hydrogenated wax fraction comprising C_{20+} hydrocarbons and having a melting point of less than 100 °C, preferably no more than 85 °C. In some preferred embodiments, the wax fraction may advantageously be further separated to provide three separate wax fractions having respective congealing points in the range of 30-40 °C, 50-60 °C and 70-80 °C (30/40 grade, 50/60 grade and 70/80 grade waxes). The use of the rotary kiln advantageously provides the production of hydrocarbon products in a continuous manner where polymer feed is continuously fed to the inlet of the kiln and products are continuously withdrawn from an outlet.

The pyrolysis vessel may be operated at atmospheric pressure (1 atm), for example approximately 101 kPa. Preferably, the rotary kiln is maintained at a slight negative pressure, such as less than 50 kPa below atmospheric pressure, preferably less than 10 kPa below atmospheric pressure, more preferably less than 0.1 kPa below atmospheric pressure, most preferably less than 0.01 kPa below atmospheric pressure, for example from 90 kPa to 101 kPa or preferably from 95 kPa to 101 kPa. Thus, the rotary kiln is preferably operated at approximately atmospheric pressure or at a slight negative pressure of 0.9 bar absolute or higher, for example 0.95 bar absolute or higher. As will be appreciated, the pressure in the rotary kiln may be controlled by controlling and balancing flow, particularly gas flow into and out from the reactor. In particular, a slight negative pressure in the kiln may only be a result of drawing products through a condensation system from the outlet of the kiln.

Residence time within the reactor may be varied by controlling the flow rate of the polymer feed into the kiln and the flow of products out from the kiln, as well as the configuration of the kiln itself. For example, the physical orientation of the kiln (i.e. the extent to which the kiln is inclined from the horizontal) and/or the rate of rotation of the kiln may be varied in order to provide a desired flow of the feed and intermediate pyrolysis products through the kiln. The use of the rotary kiln having multiple heating zones in the present process allows advantageous control over residence time of the polymer feed and intermediate pyrolysis products in the kiln, and within each heating zone. This can allow the process to be easily adapted to vary the product composition, for example to vary the process in response to a change in the polymer feed to maintain a constant product composition, or to vary the process to change the distribution of different products (e.g. the amounts of different hydrocarbon fractions) to meet demand. As will be appreciated, the residence time may be varied depending on the operating conditions inside the kiln. Preferably, the residence time in the kiln is from 30 minutes to 120 minutes, more preferably from 40 minutes to 70 minutes. As discussed previously, the kiln may comprise a final zone heated to a higher temperature than the preceding zones. Thus, the residence time of the feed inside the kiln may be from 30 to 60 minutes, for example from 40 to 50 minutes, at a temperature of from 310 °C to 600 °C and from 5 to 30 minutes, for example from 10 to 20 minutes, at a temperature of from 480 °C to 710 °C in the final zone. it will be appreciated that residence time refers to the time that the molten feed present in the kiln takes to pass from the inlet to the outlet, while pyrolysis vapours formed during the process may pass out from the kiln in the gas phase more quickly than this. A flow of inert gas, preferably nitrogen, is provided at the inlet of the kiln to provide an inert atmosphere and to provide a gas

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flow to carry pyrolysis vapours to the outlet of the kiln.

Heating of the rotary kiln may be by any suitable means, preferably the rotary kiln is an indirectly heated rotary kiln comprising one or more heaters in which the walls of the kiln are heated from the outside to provide heating to the material within the kiln. For example, the kiln may comprise a rotary kiln enclosed in a furnace or having any suitable heater configured to heat the walls of the kiln. As will be appreciated, the one or more heaters may be separate and arranged to provide heating to each heating zone of the kiln separately, or the one or more heaters may be combined. For example, the heater may comprise a furnace having multiple burners at different points along the length of the kiln, where each burner may be controlled to provide a different heat output (e.g. by controlling fuel flow to the burner), and in some instances the furnace may comprise a common volume surrounding the kiln and a common exhaust outlet for the combustion gases from all burners. Nonetheless, it will be appreciated that any suitable heaters may be provided to provide heating to the heating zones of the kiln.

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The process may suitably comprise cooling and condensing the pyrolysis products following the heating zones. For example, the kiln may comprise one or more condensers at or connected to a vapour outlet of the kiln. For example, the kiln may comprise a vapour outlet for providing gases including pyrolysis vapours to the one or more condensers, and a char outlet for receiving the slid char from the kiln. The means for cooling and condensing the pyrolysis products may comprise any suitable condenser or condenser system. Preferably, one or more condensers may be provided with a gaseous fluid product stream of pyrolysis products from the vapour outlet of the kiln. It will be appreciated that the fluid product stream may be a vapour stream that may comprise liquids or solids (such as fine char particles) as aerosols, where the condenser is configured to provide a liquid fraction comprising C_{5+} hydrocarbons, along with non-condensable gases.. The one or more condensers may for example comprise a quench tower configured to condense the liquid fraction comprising C_{5+} hydrocarbons, and optionally one or more additional condensation stages configured to condense any remaining C_{5+} hydrocarbons in the gaseous effluent from the quench tower and optionally to condense and separate an LPG fraction from the gases. Thus, a condensation system for condensing vapours from the kiln may comprise a first condensation stage, which may comprise a quench tower, that may suitably be operated at about 50 to 70 °C and a second condensation stage, which may comprise for example one or more tube and shell condensers or the like, operated at about 10 to 30 °C. The non-condensable gases, may in some embodiments be used to provide fuel for heating the kiln.

Pyrolysis products

The pyrolysis produces a fluid product stream and a solid char product in the kiln, preferably the pyrolysis products from the kiln consist essentially of the fluid product stream and char. The fluid product stream typically comprises a range of hydrocarbons of varying chain length, including a liquid fraction comprising C_{5+} hydrocarbons and non-condensable gas fraction. The fluid product stream preferably consists essentially of a non-condensable gas fraction and a liquid fraction comprising C_{5+} hydrocarbons, wherein the non-condensable gas fraction is separated from the liquid fraction prior to hydrogenation step (v). For example, the non-condensable gases may suitably be drawn from the fluid product stream during condensation, where the fluid product stream is condensed to provide the liquid fraction and the non-condensable gases can be drawn off. As will be appreciated, the composition of the liquid fraction may depend on the process conditions and how the non-condensable gases are separated. For example, in some instances, the liquid fraction may comprise a small proportion of lighter hydrocarbons such as C_4 hydrocarbons, though preferably less than 1 wt.%, for example less than 0.5 wt.% or less than 0.1 wt.%. Preferably, the non-condensable gases make up less than 30 wt.% of the fluid product stream, more preferably less than 25 wt.%, for example less than 20 wt.%. Preferably, the liquid fraction comprising C_{5+} hydrocarbons makes up at least 60 wt.% of the total effluent from the kiln (the total effluent including the liquid fraction, the non-condensable gases and the char), preferably at least 65 wt.%, more preferably at least 70 wt.%, such as at least 75 wt.%, for example about 80 wt.%.

The non-condensable gas may typically comprise C_1 to C_4 hydrocarbon gas which in some preferred embodiments is recycled to provide heating to the kiln and/or to provide heating to melt the polymer feed. In some embodiments, C_3 and C_4 hydrocarbon gas from the non-condensable gases and C_4 gas recovered from the liquid fraction may be separated and provided as an LPG product stream. If present, any C_{5+} hydrocarbons present in the non-condensable gases from the condensation may be recovered and combined with the liquid fraction or downstream products thereof (for example to the naphtha fraction).

The solid char product preferably comprises no more than 15 wt.% of the effluent from the kiln, preferably no more than 10 wt.%. The solid char product in some embodiments can

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comprise from 10 to 60 wt.% of carbon, for example from 20 to 40 wt.% of carbon, and it will be appreciated that this refers to the carbon content of the char itself, the remainder comprising various non-pyrolysable material present in the polymer feed such as inorganic material and metals.

The process suitably comprises separating the solid char product from the fluid product stream. Such separation may be carried out in any suitable way known for separating solids from a fluid stream. The majority of the char is obtained from the rotary kiln as a solid product stream and is therefore separated from the pyrolysis vapours by providing the char from a char outlet from the kiln separate to the vapour outlet. Nonetheless, some char may be present as an aerosol in the vapours from the kiln that are condensed. Such residual char in the liquid products may be removed in any suitable way. Preferably, the condensed fluid product stream is separated from the residual solid char using a decanter centrifuge or a tricanter centrifuge. For example, liquids from the condenser, for example the quench tower, may be combined with water and separated in a tricanter centrifuge that separates the solid char from the pyrolysis oil liquid fraction and from the water. The liquid fraction may in some embodiments be filtered to remove any residual solids prior to passing to the hydrogenation step.

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As the rotary kiln can continuously withdraw char from the reactor (for example in comparison to stirred tank reactors and the like), the process can be operated continuously without the need to stop the process to remove solid residues such as char or other non-volatile residues from the reactor. This also permits the process to be continuously run in a way that provides a desired range of hydrocarbon products, without needing to eliminate char production to avoid downtime and cleaning (which would be necessary in tank reactors at the like).

The liquid fraction comprising C_{5+} hydrocarbons from the kiln may for example have a congealing point in the range of from 40 °C to 60 °C for example from 45 °C to 55 °C (such as 60 °C or less, or 55 °C or less), and/or may have a density of from 0.6 g/ml to 0.9 g/ml, for example from 0.7 g/ml to 0.8 g/ml. Depending on the polymer feed to the kiln, the liquid hydrocarbon fraction may contain sulfur at a concentration of less than 30 mg/kg (as measured by ASTM (RTM) D5453-19a) but the sulfur concentration may in some instances be at least 5 mg/kg or at least 10 mg/kg. Depending on the feed composition and any steps taken to remove chlorine (e.g. in PVC) from the feed, the liquid hydrocarbon fraction may contain chlorine at a concentration of less than 100 mg/kg (as measured by UOP (RTM) 779-08), preferably less

than 80 mg/kg, but the chlorine concentration may in some instances be at least 10 mg/kg or at least 40 mg/kg, for example at least 60 mg/kg. It will be appreciated that such impurities may in some instances be reduced by treating or controlling the composition of the polymer feed prior to the pyrolysis. The liquid hydrocarbon fraction from the kiln may for example have a bromine index of from 10 to 50 gBr/100g, preferably 10 to 30 gBr/100g, for example 15 to 25 gBr/100g.

Hydrogenation

The liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons from the kiln is hydrogenated to provide a hydrogenated product stream. Suitably, the entire liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons (i.e. all of the pyrolysis products apart from the char and the non-condensable gases) is passed to a hydrogenation reactor and hydrogenated to produce a hydrogenated hydrocarbon product stream.

Hydrocarbon streams, including those derived by pyrolysis of plastics can typically contain as impurities various heteroatoms such as N, S, O which can negatively affect the properties of the hydrocarbon product. Pyrolysis of polyolefin plastics also typically produces a mixture of olefins and saturated hydrocarbons. Olefins and heteroatom-containing hydrocarbons are more chemically reactive than paraffins. By performing hydrogenation of the entire liquid fraction of the fluid product stream from the kiln prior to further fractionation or processing steps, side reactions of olefins or heteroatom-containing hydrocarbons such as polymerisation may advantageously be avoided. In addition, as olefins and heteroatom-containing hydrocarbon molecules vary in boiling point in comparison to saturated hydrocarbons, the presence of heteroatom-containing molecules and olefins may allow cleaner subsequent separation according to carbon number.

The hydrogenation may be performed in any suitable way and suitably comprises passing the liquid fraction of the fluid product stream in contact with a hydrogenation catalyst and hydrogen gas at a temperature of from 250 °C to 400 °C, preferably from 250 °C to 350 °C. it will be appreciated that due to the exothermic hydrogenation reaction, the temperature may suitably increase from the inlet to the hydrogenation reactor to the outlet. Thus, the catalyst bed in the hydrogenation reactor may vary in temperature from 250 °C to 400 °C, preferably from

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250 °C to 350 °C. The pressure in the hydrogenation reactor may suitably be from 3 MPa to 10 MPa, preferably from 4 MPa to 6 MPa (in some instances the pressure may be higher such as up to 20 MPa). The liquid hourly space velocity (LHSV) of the fluid product stream through the reactor may be from 0.5 kg/kg/hr to 10 kg/kg/hr, preferably from 0.5 kg/kg/hr to 4 kg/kg/hr, more preferably from 0.7 kg/kg/hr to 2.5 kg/kg/hr, most preferably from 0.8 kg/kg/hr to 1.5 kg/kg/hr, for example from 0.9 kg/kg/hr to 1.3 kg/kg/hr. The ratio of hydrogen gas to feed liquid in the hydrogenation may suitably be from 300 NV/NV to 1000 NV/NV, preferably from 400 NV/NV to 600 NV/NV, for example from 450 NV/NV to 550 NV/NV. The hydrogen consumption during the hydrogenation step will vary based on the feed to the hydrogenation reactor and the other conditions, but may for example be in the range of 6 to 12 gH_2/kg, such as from 8 to 10 gH_2/kg.

The hydrogenation may be performed in any suitable reactor for contacting the liquid fraction with hydrogen gas. Preferably the hydrogenation reactor comprises a fixed bed reactor. The aspect ratio of the fixed bed reactor may be any suitable ratio, and may for example be from 5:1 to 20:1, preferably from 8:1 to 16:1, for example from 10:1 to 14:1 such as about 12:1. The hydrogenation reactor is preferably a trickle bed reactor. In some embodiments, the hydrogenation reactor may alternatively be a fluid bed reactor or a microchannel reactor.

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The hydrogenation catalyst may be any suitable catalyst and is preferably a metal catalyst. The metal hydrogenation catalyst preferably comprises a metal selected from Group VIII of the periodic table, preferably the catalyst comprises Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and/or Pt, such as a catalyst comprising Ni, Co, Mo, W, Cu, Pd, Ru, Pt. In preferred embodiments, the catalyst is selected from CoMo, NiMo or Ni, preferably NiMo. The hydrogenation catalyst is preferably supported on a carrier such as bauxite, alumina, silica, silica-alumina or zeolite. Preferably the catalyst is supported on alumina. For example, the hydrogenation catalyst may comprise NiMo supported on alumina ($NiMo/Al_2O_3$).

The hydrogenation reactor may comprise a gas recirculation loop to recycle hydrogen through the reactor. The hydrogenation suitably includes hydrodesulphurisation, and the gas phase H_2S concentration in the reactor may be from 0.05 % to 0.5 % such as about 0.1 %. In some embodiments, H_2S may be introduced into the recirculation gas by skimming through CS_2 liquid at ambient temperature and reaction pressure.

In some preferred embodiments, the hydrogenation comprises providing the effluent of the hydrogenation to a second hydrogenation stage, which may be performed under substantially the same conditions as the initial hydrogenation step. The second hydrogenation step may in some instances be performed at a higher initial temperature than the initial hydrogenation step, however due to less of an exotherm the temperature may nonetheless still be in the range of from 250 °C to 350 °C, preferably from 300 °C to 350 °C. The second hydrogenation step may be performed with a longer contact time than the initial hydrogenation step, for example at a liquid space velocity less than the initial hydrogenation step. It has been found that the second hydrogenation step, while having a minimal effect on heteroatom removal, can advantageously reduce the presence of olefins, and particularly olefins in the C_{5-20} range, in the hydrogenated product stream. In some embodiments, the initial and second hydrogenation steps may comprise a combined hydrogenation step equivalent to running the initial and second hydrogenation steps in series. For example, a single hydrogenation step where the contact time through the catalyst bed is increased by lengthening the catalyst bed or lowering the flow rate of the feed through the reactor, or preferably a single hydrogenation step may use a hydrogenation reactor comprising two catalyst beds comprising different catalysts having different activities. In such a hydrogenation step the hydrogen consumption during the hydrogenation step may for example be at least 9 gH_2/kg.

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Following the hydrogenation step, the hydrogenated hydrocarbon product stream may for example have a congealing point in the range of from 40 °C to 60 °C for example from 50 °C to 60 °C, for example 60 °C or less. Congealing point as referred to herein may be measured by ASTM (RTM) D938-12(2017). The hydrogenated hydrocarbon product stream may have a density of from 0.7 g/ml to 0.9 g/ml, for example from 0.75 g/ml to 0.85 g/ml. Depending on the hydrogenation conditions and the sulfur content of the feed to the hydrogenation, the hydrogenated hydrocarbon product stream may contain sulfur at a concentration of less than 15 mg/kg (as measured by ASTM (RTM) D5453-19a), preferably less than 10 mg/kg, more preferably less than 5 mg/kg, such as less than 2 mg/kg. Depending on the hydrogenation conditions and the chlorine content of the feed to the hydrogenation, the hydrogenated hydrocarbon product stream may contain chlorine at a concentration of less than 15 mg/kg (as measured by UOP (RTM) 779-08), preferably less than 10 mg/kg, for example less than 5 mg/kg or less than 2 mg/kg. The hydrogenated hydrocarbon product stream preferably has a bromine index of less than 2 gBr/100g, preferably less than 1 gBr/100g, for example less than

0.7 gBr/100g such as 0.5 gBr/100g or less. As will be appreciated, the conditions of the hydrogenation may be selected so as to provide the above stated bromine index and/or levels of sulfur and/or chlorine. Thus, where necessary, the hydrogenation conditions may be adjusted to increase contact time, increase the ratio of hydrogen gas to feed liquid, or to use a more active catalyst.

Fractionation of hydrogenated hydrocarbon product stream

The present process comprises fractionating the hydrogenated hydrocarbon product stream to produce a light hydrogenated fraction comprising C_{5-20} hydrocarbons. It will also be appreciated that the light hydrogenated fraction may contain small amounts of heavier hydrocarbons up to about C_{25} and small amounts of C_4 hydrocarbons. However, the light hydrogenated fraction preferably contains less than 2 wt.%, for example less than 1 wt.% of C_{21+} hydrocarbons and/or less than 1 wt.%, preferably less than 0.5 wt.% C_4 hydrocarbons, for example the light hydrogenated fraction preferably consists essentially of C_5 to C_{20} hydrocarbons. Preferably, the light hydrogenated fraction comprising C_{5-20} hydrocarbons (e.g. components boiling at up to 350°C) makes up more than 50 wt.% of the hydrogenated hydrocarbon product stream, preferably more than 55 wt.% of the hydrogenated hydrocarbon product stream.

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While it is desired to produce a C_{5-10} naphtha fraction and a C_{10-20} diesel fraction, it has been surprisingly found that increased efficiency can be achieved by initially fractionating the hydrogenated hydrocarbon product stream to provide a light hydrogenated C_{5-20} fraction and a C_{20+} wax fraction. Without wishing to be bound by any particular theory, the present process results in only a small overall (<2 wt.%) proportion of C_{5-8} hydrocarbons in the liquid fraction of the fluid product stream from the kiln, and so separating the hydrogenated hydrocarbon product stream in the described way minimises process losses of naphtha fraction hydrocarbons during this separation step (e.g. compared to initial separation of naphtha as the lighted fraction from the other products, as may typically be done). The subsequent hydrocracking step then provides an advantageous distribution of hydrocarbons to enable a naphtha and diesel fraction to be produced with increased yield and efficiency. Thus, the fractionation step suitably comprises separating the hydrogenated hydrocarbon product stream into a light hydrogenated fraction comprising C_{5-20} hydrocarbons and a C_{20+} wax fraction. In addition, as discussed previously, due to boiling point differences of olefins and heteroatom-containing species

compared to paraffins, performing the fractionation step after the hydrogenation may help to avoid loss of some of the desired C_{5-20} hydrocarbons as non-condensable gases or contamination of the light hydrogenated fraction with longer hydrocarbons.

The fractionation may be performed using any suitable fractionation means, for example a fractionation column or by a fractional condensation. Preferably, fractionating the hydrogenated hydrocarbon product stream comprises fractionating in a fractional distillation column.

The fractionation may preferably comprise providing the hydrogenated hydrocarbon product stream to a vacuum distillation system. The fractionation may comprise using a reboiler configured to improve liquid evaporation, for example equipped with a jet spray evaporation device and forced flow mechanism configured to improve efficiency of liquid evaporation as well as heat exchanging in the reboiler.

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The evaporation temperature of the liquid in the fractionation (for example liquid from a reboiler) may be from 260 °C to 320 °C, preferably from 270 °C to 300 °C, for example from 280 °C to 290 °C. It has been found that minimal degradation of the hydrogenated hydrocarbon product stream can be achieved under such conditions. The evaporation power may for example be from 0.5 kW to 2 kW, for example from 0.9 kW to 1.3 kW. The evaporation pressure may be from 3 to 8 kPa absolute (for example the pressure above the liquid in a reboiler), preferably from 4 to 6 kPa absolute. Condensation of the evaporated products may be performed by cooling to less than around 25 °C, for example about 20 °C. The hydrogenated hydrocarbon product stream may for example be fed to the fractionation at a temperature of from 60 °C to 300 °C, for example from 70 °C to 200 °C, for example from 80 °C to 120 °C, such as around 100 °C. The reflux rate in the fractionation may for example be from 0.5 l/hr to 2 l/hr, for example from 0.8 l/hr to 1.2 l/hr. The vacuum system may suitably comprise a cold trap for preventing loss of light components, for example a cold trap at around −78 °C or less.

Hydrocracking

The process comprises hydrocracking the light hydrogenated fraction to produce a light hydrocarbon product stream enriched in C_{5-10} hydrocarbons.

Despite a major portion of the pyrolysis liquids being made up of the light hydrogenated fraction (i.e. mostly C_{5-20} hydrocarbons), it has been found that this light hydrogenated fraction typically contains too low of a concentration of naphtha range hydrocarbons to make separation of a naphtha fraction efficient. For example, the C_{5-20} fraction may contain less than 15 wt.%, for example less than 10 wt.% C_{5-8} hydrocarbons. However, the level of naphtha range hydrocarbons is enough that the light hydrogenated C_{5-20} fraction cannot be provided as a diesel fraction without removal of lighter hydrocarbons. By hydrocracking the C_{5-20} fraction, it has been found that a readily separable mixture of naphtha and diesel range hydrocarbons may be obtained, addressing the above problems.

The hydrocracking step may be performed in any suitable way using any suitable hydrocracking reactor known in the art. Preferably the hydrocracking is performed in a fixed bed reactor, preferably trickle bed reactor. It is preferred that the reactor is an isothermal reactor. Preferably, the reactor has no gas recirculation loop.

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The hydrocracking catalyst may be any suitable catalyst and is preferably a metal catalyst, particularly a sulfur based hydrocracking catalyst. The metal hydrocracking catalyst preferably comprises a metal selected from Group VIII of the periodic table, preferably the catalyst comprises Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and/or Pt, such as a catalyst comprising Ni, Co, Mo, W, Cu, Pd, Ru, Pt. In preferred embodiments, the metal is selected from NiMo or Pt, preferably NiMo. The hydrocracking catalyst is preferably supported on a carrier such as bauxite, alumina, silica, silica-alumina or zeolite. Preferably the hydrocracking catalyst is supported on zeolite, such as USY or mordenite zeolite. For example, the hydrocracking catalyst may comprise NiMo or Pt supported on zeolite, which can be used in combination with a sulfur agent such as CS_2.

In preferred embodiments, the hydrocracking step comprises contacting the light hydrogenated fraction with a hydrocracking catalyst at a temperature of from 250 °C to 400 °C, preferably from 300 to 350 °C. Preferably, the hydrocracking is performed at a pressure of from 3 to 10 MPa, preferably from 4 to 8 MPa, for example from 5 to 7 MPa.

The liquid hourly space velocity (LHSV) of the light hydrogenated fraction through the hydrocracking reactor may be from 0.5 hr^{-1} to 5 hr^{-1}, preferably from 0.5 hr^{-1} to 3 hr^{-1}, more preferably from 0.7 hr^{-1} to 2 hr^{-1}, most preferably from 0.8 hr^{-1} to 1.5 hr^{-1}, for example from

0.9 hr^{-1} to 1.3 hr^{-1}. The ratio of hydrogen gas to feed liquid in the hydrogenation may suitably be from 100 NV/NV to 500 NV/NV, preferably from 150 NV/NV to 250 NV/NV, for example from 180 NV/NV to 220 NV/NV. The H_2S level in the reactor may be around from 500 to 1500 ppm such as from 800 ppm to 1200 ppm, for example about 1000 ppm. The sulfur level may suitably be maintained using CS_2 mixed with the feed to the hydrocracking reactor.

In some embodiments, the process may comprise washing the light hydrogenated fraction prior to hydrocracking to remove metals and other contaminants, for example a water wash. Optionally, the light hydrogenated fraction may be treated with a H_2S absorber, for example at elevated temperature, for removing H_2S from the light hydrogenated fraction.

It will be appreciated that hydrocracking may produce some non-condensable gas products in addition to the light hydrocarbon product stream enriched in C_{5-10} hydrocarbons. However, preferably the liquid recovery from the hydrocracking is at least 90 wt.%, preferably 95 wt.% or more.

The process further comprises fractionating the light hydrocarbon product stream from the hydrocracking step to produce a naphtha fraction and a diesel fraction. The naphtha fraction suitably comprises C_{5-10} hydrocarbons and preferably comprises at least 90 wt.% C_{5-10} hydrocarbons, preferably at least 95 wt.% C_{5-10} hydrocarbons, for example at least 98 wt.% C_{5-10} hydrocarbons. The diesel fraction suitably comprises C_{10-20} hydrocarbons and preferably comprises at least 90 wt.% C_{10-20} hydrocarbons, preferably at least 95 wt.% C_{10-20} hydrocarbons, for example at least 98 wt.% C_{10-20} hydrocarbons.

The fractionation of the light hydrocarbon product stream may be performed using any suitable apparatus such as distillation columns as are known in the art. Preferably, the fractionation comprises providing the light hydrocarbon product stream to a vacuum distillation system comprising a distillation column. The column may comprise a reboiler, such as an electrically heated reboiler, and a condenser, which may be cooled to around -20 °C to -10 °C, for example about -15 °C. The distillation column may have a bottom temperature of about 200 to 250 °C, preferably 215 to 235 °C, such as 220 to 230 °C, and a top temperature of about 150 to 200 °C, preferably from 160 to 180 °C, for example 165 to 175 °C. The pressure at the top of the distillation column may be 30 to 70 kPa absolute, for example 40 to 60 kPa absolute, such as about 50 kPa absolute. The reflux ratio in the column may be 2:1 to 4:1, preferably 2.5:1 to

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3.5:1, such as about 3:1.

The process therefore produces a naphtha fraction and a diesel fraction that may be provided for downstream use or further processing into other products. In some embodiments, where it is desired to produce an increased proportion of naphtha, the process may comprise a process for producing a naphtha fraction in which the diesel fraction from fractionation of the light hydrocarbon product stream is recirculated and provided to the hydrocracking step with the light hydrogenated fraction. In this way, the diesel fraction separated from the naphtha fraction can be recirculated until completely hydrocracked into naphtha fraction species. As waxes are also produced by the present process as described previously, the process may therefore comprise a process for producing a naphtha fraction and waxes, in which minimal wastage of intermediate diesel fraction hydrocarbons is achieved. In fact, by operating the process in this way, the advantageous production of both waxes and a naphtha fraction can surprisingly be provided by operating a pyrolysis process that produces a liquid effluent comprising a major portion (e.g. more than 50 wt.%) of diesel hydrocarbons.

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It will be appreciated that in general where a C_{x-y} fraction is referred to herein, unless otherwise specified or clear from the context, the fraction will comprise at least 70 wt.% of hydrocarbons falling within the stated range, preferably at least 80 wt.%, more preferably at least 90 wt.%, such as at least 95 wt.% for example at least 98 wt.%. In some preferred embodiments, a C_{x-y} hydrocarbon fraction may consist essentially of hydrocarbon molecules of carbon number between x and y.

For reference, unless otherwise specified or it is obvious that a contrary meaning is intended, all percentages referring to concentrations in the present application are percentage by weight (wt%).

As will be appreciated the process of the present invention may be performed using the various apparatus features as described herein, and the apparatus may be configured to perform process steps described herein.

The present invention is further described by way of the following Examples, which are provided for illustrative purposes and are not in any way intended to limit the scope of the invention as claimed, and with reference to the following figures in which:

Figure 1 shows a simulated distillation curve for the liquid product from the pyrolysis of plastics;

Figure 2 shows carbon number distribution as determined by GC in the liquid product from the pyrolysis of plastics;

Figure 3 shows a simulated distillation curve for the light fraction obtained from fractionation of the pyrolysis products;

Figure 4 shows carbon number distribution as determined by GC in the light fraction obtained from fractionation of the pyrolysis products;

Figure 5 shows a simulated distillation curve comparing before (X) and after (O) hydrocracking of the light fraction;

Figure 6 shows carbon number distribution as determined by GC comparing before (X) and after (O) hydrocracking of the light fraction;

Figure 7 shows a simulated distillation curve comparing the naphtha fraction (Y) and the diesel fraction (Z) after fractionation of the hydrocracked product;

Figure 8 shows carbon number distribution as determined by GC comparing the naphtha fraction (Y) and the diesel fraction (Z) after fractionation of the hydrocracked product; and

Figure 9 shows a schematic process flow for a system configured to perform the present process.

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Examples

Example 1 - Pyrolysis

A waste plastics feed comprising HDPE, LDPE and polypropylene was melted in a melt extruder and the molten feed stream provided to an inlet of a rotary kiln. The feed stream comprised calcium oxide to avoid corrosion due to HCl formation from any unremoved PVC in the feed. The melt extruder was a screw extruder and was heated by electrically powered heaters.

The rotary kiln comprised a rotating stainless steel drum having a length of about 80 feet (24.3 m) and an internal diameter of about 6 feet (1.8 m). The drum was rotated at a speed of from 0.1 to 2 rpm and was operated under an atmosphere of nitrogen at a pressure slightly below atmospheric pressure. The rotary kiln was heated in four sequential heating zones of equal

length, the first three zones were operated at a temperature from 315 °C to 595 °C, and the final heating zone was operated at 480 °C to 705 °C. Heating of the kiln was performed by combustion of natural gas and directing combustion gases into an external jacket surrounding the rotating drum, which is divided into compartments to control heating in each heating zone. The residence time in the kiln was 60 minutes, 45 minutes in the first three zones and 15 minutes in the final zone.

The effluent from the rotary kiln comprised char as well as a fluid product stream comprising a C_{5+} hydrocarbon liquid fraction and non-condensable gases (including C_{1-4} hydrocarbon gases and nitrogen). The fluid product stream was removed from the kiln in the vapour phase via a vapour outlet and passed to a condensation system, while the char was collected from a separate char outlet configured to receive solids from the kiln.

The C_{5+} hydrocarbon liquid fraction of the fluid product stream was separated from the non-condensable gases in the condensation system, with a portion of the non-condensable gases passed to fuel heating of the rotary kiln. The condensation system comprised a quench tower and a tube and two tube and shell condensers arranges in series to receive gases from the quench tower. The fluid product stream is provided to the quench tower above the sump, and then is pulled up through 4 spray headers. Liquid is pumped out of the sump of the quench tower and through cooling heat exchangers (cooled to 60 °C), and then to the spray headers. The quench tower spray headers were configured to spray counter-currently to cool the vapour rising through the tower to condense liquid, that then falls into the sump. The spray also serves to scrub out entrained char and prevents it from moving as an aerosol to the downstream unit operations. A stream of cooled liquid from the quench tower was mixed with water and separated in a tricanter centrifuge to remove entrained char and other solid contaminants before the oil phase is returned to the quench tower or passed downstream to the hydrogenation. Any gas that is not condensed in the quench tower can pass through the tube and shell condensers, the first condenser configured to operate at about 20 °C and to provide a condensate spray to remove entrained char from the first condenser and the pipeline between the quench tower and the condenser. The condensate from the first condenser is provided with the liquids from the quench tower to the hydrogenation. Condensate from the second tube and shell condenser (operated at about 10 °C) can be passed to the hydrogenation with the other liquids or combined with the naphtha fraction downstream. The C_{5+} hydrocarbon liquid fraction can be stored in an intermediate storage tank configured to receive liquids from the condensation system and to

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pass the liquids to the hydrogenation reactor.

The C_{5+} hydrocarbon liquid fraction condensed from the kiln pyrolysis vapours was found to have the following properties:

Congealing Point:	52°C
Density (60°C):	0.779 g/ml
Bromine Index:	20 gBr/100g
Sulfur (ASTM (RTM) D5453-19a):	22 mg/kg
Chlorine (UOP (RTM) 779-08):	79 mg/kg
Silicon (ASTM (RTM) D5185-18):	6 mg/kg
Metal (ASTM (RTM) D5185-18):	<1 mg/kg

Note: a. Tested metals include Cr, Cu, Pb, Ni, Zn, Mn, Cd, As, Co, Sb.
b. Detection limit of ICP of analyzing party was 1 mg/kg.

Simulated distillation of the C_{5+} hydrocarbon liquid fraction was performed and the results are shown in Figure 1. Carbon number distribution as determined by gas chromatography (GC) in the C_{5+} hydrocarbon liquid fraction is shown in Figure 2. As can be seen, the pyrolysis products comprise a significant proportion (around 60 wt.%) of hydrocarbons in the diesel range or lower (boiling point up to about 350 °C). Analysis also showed that the pyrolysis products comprise only a very small proportion of C_{5-8} hydrocarbons in the naphtha range (less than 2 wt.%). GC analysis of the product showed the presence of various isomers as well as n-paraffins in addition to olefins and small amounts of other hydrocarbon species.

Example 2 - Hydrogenation

The C_{5+} hydrocarbon liquid fraction from Example 1 was passed in its entirety to a fixed bed hydrogenation reactor having a catalyst bed aspect ratio of 12:1 and comprising a $NiMo/Al_2O_3$ hydrogenation catalyst. The temperature set at the inlet of the reactor was 260 to 270 °C and the pressure was 5.0 MPa. The feed was provided with a LHSV of 1.1 h^{-1}, and a hydrogen gas to feed ratio of 500 NV/NV. A gas phase H_2S concentration was around 0.1 % introduced by skimming a portion of recirculation gas through CS_2 liquid at ambient temperature and reaction pressure. The temperature at the outlet of the reactor was around 350 °C, giving a temperature rise through the reactor of around 90 °C. The hydrogen consumption was about 8.2 gH_2/kg. No noticeable cracking of the feed was observed during the hydrogenation, neither C_{3-4} (LPG) or

C_{1-2} gases.

The hydrogenated product was found to have a bromine index of 2 gBr/100g, and so the hydrogenated product was passed to a second equivalent hydrogenation in which the initial temperature at the inlet of the reactor was 305 °C and the outlet temperature was 330 °C, and the LHSV was 0.7 h^{-1}. Product recovery over the two hydrogenation steps was more than 95 %.

The twice hydrogenated product was analysed and had the following properties:

Congealing Point:	54°C
Density (60°C):	0.806 g/ml
Bromine Index:	0.5 gBr/100g
Sulfur (ASTM (RTM) D5453-19a):	14 mg/kg
Chlorine (UOP (RTM) 779-08):	12 mg/kg
Silicon (ASTM (RTM) D5185-18):	6 mg/kg
Metal (ASTM (RTM) D5185-18):	<1 mg/kg

Note: Tested metals include Cr, Cu, Pb, Ni, Zn, Mn, Cd, As, Co, Sb, Mo, Al.

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The hydrogenated product was also found by GC to be substantially free of the olefins observed prior to hydrogenation.

Example 3 - Fractionation

The hydrogenated product was then fractionated with a single cut to provide a light hydrogenated C_{5-20} hydrocarbon fraction and a C_{20+} wax fraction. The fractionation was performed in a distillation tower using vacuum distillation. The distillation system included a reboiler equipped with jet spray evaporation device and forced flow mechanism to improve efficiency of liquid evaporation and heat exchange in the reboiler. The distillation was operated under the following conditions:

Evaporation temperature (liquid from reboiler):	~275 °C
Evaporation pressure (above liquid in reboiler):	4~6 kPa (absolute)
Evaporation power:	~1.1 kW
Cooling water temperature:	~20 °C
Pressure at condenser outlet:	~1 kPaA
Sample liquid (~100°C) feed rate:	2~2.5 kg/hr

Reflux rate:	~1 litre/hr
Cold trap temperature (of vacuum pump):	-78°C

The distillation produced a light hydrogenated C_{5-20} hydrocarbon fraction and a C_{20+} wax fraction. The C_{20+} wax fraction was found to contain a portion of diesel length hydrocarbons (mostly C_{18} and C_{19}) and so preferably the temperature of the reboiler may be increased to compensate for this, for example to around 285 °C or higher.

The light hydrogenated C_{5-20} hydrocarbon fraction had a density of 0.803 g/ml at 20 °C and a bromine index of 0.5. The level of residual sulfur in the fraction was 13 mg/kg. The light hydrogenated C_{5-20} hydrocarbon fraction was washed with industrial soft water for removal of water soluble impurities and passed through a H_2S adsorber to remove residual H_2S in the fraction.

Simulated distillation of the light hydrogenated C_{5-20} hydrocarbon fraction was performed and the results are shown in Figure 3. Carbon number distribution as determined by gas chromatography (GC) in the light hydrogenated C_{5+} hydrocarbon fraction is shown in Figure 4. As can be seen, the light hydrogenated C_{5-20} hydrocarbon fraction contains almost all carbon chains within this range, with only a very small proportion of C_{21-25} hydrocarbons present.

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The light hydrogenated C_{5-20} hydrocarbon fraction also contained only a small proportion of C_{5-10} hydrocarbons (less than 10 wt.% components boiling below about 180 °C), making separation of this naphtha fraction from the C_{10-20} diesel fraction an inefficient process. This leads to a suboptimal diesel fraction with too many light hydrocarbons, or inefficiency and waste resulting from separating a very small amount of naphtha fraction hydrocarbons from the diesel.

Example 4 - Hydrocracking

A sample of the light hydrogenated C_{5-20} hydrocarbon fraction from Example 3 was subjected to hydrocracking in an isothermal trickle bed reactor system having a catalyst-loading capacity of 1L and no gas recirculation loop. A commercial grade sulfur based hydrocracking catalyst (NiMo/Zeolite) was used as the catalyst. CS_2 was used as sulfur agent that was mixed with the feed for maintaining the H_2S level in the reactor during the hydrocracking process.

Conditions in the hydrocracking reactor were as follows:

Catalyst loading:	1 L
Reaction pressure:	6 MPa (gauge)
Reactor temperature:	~335 °C
Liquid space velocity:	1.0 V/V/hr
H_2 to oil ratio:	200 NV/NV
H_2S level:	~1000 ppmv

Liquid recovery of the hydrocracked product was 95 %, with only minor loss of gases as LPG or similar volatiles. Tail gas analysis indicated that C_{1-2} generation was less than 0.5 wt% of the feedstock to the hydrocracking. Analysis of the hydrocracked product carbon number distribution indicated diesel conversion (C_{10+}) of 63%.

Simulated distillation of the hydrocracked product was performed and the results are shown in Figure 5, in which the simulated distillation of the hydrocracked product, labelled "O", is compared to the C_{5-20} hydrocarbon fraction from Example 3. Carbon number distribution as determined by gas chromatography (GC) in the hydrocracked product is shown in Figure 6, in which the carbon number distribution of the hydrocracked product, labelled "O", is compared to the C_{5-20} hydrocarbon fraction from Example 3. As can be seen, the hydrocracking redistributed the carbon number distribution to provide a significant enrichment of naphtha range hydrocarbons smaller than C_{10}.

Example 5 – Fractionation of hydrocracked product

The hydrocracked product from Example 4 was separated in a vacuum distillation system using a 40mm ID packed distillation column of theoretical plate number ~40, an electrically heated reboiler and a cold ethanol (-15 °C) cooled condenser.

The distillation was operated under the following conditions:

Tower top pressure:	~50 kPa (absolute)

Tower top temperature:	~168 °C
Feedstock loading:	~2.6 kg/Batch
Reflux ratio:	3:1
Tower bottom temperature:	225 °C

While the separation was performed as a batch distillation, it will be appreciated that the separation may also, and preferably, be performed in a continuous manner.

4.8 kg of the naphtha fraction was collected compared to 4.4 kg of the diesel fraction, demonstrating a much more even split between the naphtha and the diesel fractions following hydrocracking as compared to the distribution of hydrocarbons in the C_{5-20} hydrocarbon fraction from Example 3 before hydrocracking. Total material loss during the fractionation was around 13 wt.%, mainly due to loss of volatiles to the vacuum pump caused by insufficient cooling and could be avoided by providing additional or more efficient cooling.

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Simulated distillation of the two fractions separated from the hydrocracked product was performed and the results are shown in Figure 7, in which the simulated distillation of the naphtha fraction, labelled "Y", is compared to the diesel fraction, labelled "Z". Carbon number distribution as determined by gas chromatography (GC) of the two fractions separated from the hydrocracked product is shown in Figure 6, in which the carbon number distribution of the naphtha fraction, labelled "Y", is compared to the diesel fraction, labelled "Z". As can be seen, the naphtha fraction and the diesel fraction were cleanly separated, with only a very small amount of C_{11+} in the naphtha fraction and only a very small amount of C_{10} or smaller in the diesel fraction.

The naphtha fraction was analysed and the results are shown in Table 1, showing that the naphtha fraction contains mainly n- and iso-paraffins, with some naphthenes and aromatics. The naphtha fraction also contains less than 1% olefins. Analysis of the diesel fraction, which was pretreated with a H_2S absorber at elevated temperature for removal of residue H_2S is shown in Table 2. The diesel fraction has a cetane number of about 64, only 5.5 mg/kg sulfur and minimal other impurities. Therefore, the present process can advantageously produce readily separable naphtha and diesel fractions from pyrolysis of a waste plastic feed.

Table 1:

Test Description	Unit	Test Method	Result
Density @15°C	kg/m^3	ASTM (RTM) D1298-12b(2017)	703.2
Total Sulphur	%(m/m)	ASTM (RTM) D4294-16e1	<0.0150
Existent gum	mg/100mL	ASTM (RTM) D381-19	1.0
Aromatics	%(v/v)	ASTM (RTM) D5134-13	6.29
N-Paraffins	%(v/v)		12.62
ISO-Paraffins	%(v/v)		55.17
Aromatics + Naphthenes	%(v/v)		30.79
Olefins	%(v/v)	ASTM (RTM) D1319-20a	<1.0
Color ,Saybolt	----	ASTM (RTM) D156-15	+30
Lead as Pb	ng/g	SN/T 1410-2004(2012)	<5
Gross Calorific Value	MJ/kg	Calculation	49.53
Distillation			
IBP	°C	ASTM (RTM) D86-20b	28.6
10% Recovery	°C		49.7
30% Recovery	°C		68.1
50% Recovery	°C		89.0
70% Recovery	°C		112.0
90% Recovery	°C		137.1
FBP	°C		156.0
Reid Vapor Pressure @37.8°C	kPa	ASTM (RTM) D323-20a	69.00
Metal Content			
Chromium	mg/kg	ICP	<1
Copper	mg/kg		<1
Lead	mg/kg		<1
Nickel	mg/kg		<1
Silicon	mg/kg		5
Zinc	mg/kg		<1
Manganese	mg/kg		<1
Cadmium	mg/kg		<1
Arsenic	mg/kg		<1
Cobalt	mg/kg		<1
Antimony	mg/kg		<1
Molybdenum	mg/kg		<1
Aluminum	mg/kg		<1
Chloride	mg/kg	ASTM (RTM) D5808-20	<1.0

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Table 2:

Test Description	Unit	Test Method	Result
Cetane Number	--	EN ISO (RTM) 5165:2020	64.3
Cetane Index	--	EN ISO (RTM) 4264:2018	64.4
Density@15°C	kg/L	EN ISO (RTM) 12185:1996	**0.7925**
Sulphur	mg/kg	EN ISO (RTM) 20846:2019	5.5
250°C Recovered	%(v/v)	EN ISO (RTM) 3405:2019	62.6
350°C Recovered	%(v/v)		97.5
95%(v/v) Recovered	℃		291.4
Polycyclic Aromatic	%(m/m)	EN 12916:2019(E)	0.9
Flash Point	℃	EN ISO (RTM) 2719:2016	73.0
Viscosity@40°C	mm^2/s	EN ISO (RTM) 3104:2020	**1.890**
Carbon Residue on 10% distillation residue	%(m/m)	EN ISO (RTM) 10370:2014	<0.10
Copper Strip Corrosion （50°C,3h）	--	EN ISO (RTM) 2160:1998	1a
Ash	%(m/m)	EN ISO (RTM) 6245:2001	0.001
Total Contamination	mg/kg	EN 12662:2014(E)	<12.0
Oxidation Stability	g/m^3	EN ISO (RTM) 12205:1995	3
Lubricity at 60° C	um	EN ISO (RTM)12156-1:2018	**690**
Fatty Acid Methyl Ester	%(v/v)	EN 14078:2014(E)	<0.5
Water	mg/kg	EN ISO (RTM) 12937:2000	89
Cold Filter Plugging Point	°C	EN 116:2015(E)	-18

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Figure 9 shows schematically a process flow of a system for performing the present process. A polymer feed is pyrolyzed in a rotary kiln reactor 2 and the fluid effluent from the kiln comprising all of the condensable liquids from the pyrolysis is provided to a hydrogenation reactor 4. The hydrogenated hydrocarbon stream from the reactor 4 is passed to a fractionation stage 6 to provide a C_{20+} wax fraction 10 and a C_{5-20} hydrocarbon fraction 8 (diesel/naphtha fraction). The C_{5-20} hydrocarbon fraction 8 is passed to a hydrocracking stage 12 in which the C_{5-20} hydrocarbon fraction 8 undergoes hydrocracking to enrich the stream in C_{5-10} hydrocarbons. The hydrocracked stream from 12 is then separated in a naphtha/diesel fractionation stage 14 to provide a naphtha fraction 16 and a diesel fraction 18.

CLAIMS

1. A process for producing naphtha and diesel from a polymer feed, the process comprising:
   (i) providing a polymer feed comprising at least 80 wt.% of polyolefin polymers;
   (ii) melting the polymer feed to provide a molten polymer feed;
   (iii) passing the molten polymer feed to a rotary kiln reactor comprising a plurality of sequential heating zones, wherein each zone of the rotary kiln is operated at a temperature of from 300 °C to 800 °C to pyrolyze the molten polymer feed and produce a fluid product stream and a solid char product;
   (iv) separating the solid char product from the fluid product stream;
   (v) passing a liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons to a hydrogenation reactor and hydrogenating said liquid fraction to produce a hydrogenated hydrocarbon product stream;
   (vi) fractionating the hydrogenated hydrocarbon product stream to produce a light hydrogenated fraction comprising C_{5-20} hydrocarbons;
   (vii) hydrocracking the light hydrogenated fraction to produce a light hydrocarbon product stream enriched in C_{5-10} hydrocarbons; and
   (viii) fractionating the light hydrocarbon product stream from (vii) to produce a naphtha fraction and a diesel fraction.

2. A process according to Claim 1, wherein fractionating the hydrogenated hydrocarbon product stream comprises fractionating in a fractional distillation column.

3. A process according to Claim 1 or Claim 2, wherein the rotary kiln comprises four or more sequential heating zones.

4. A process according to any one of the preceding claims, wherein the rotary kiln is maintained under an atmosphere of nitrogen.

5. A process according to any one of the preceding claims, wherein the rotary kiln is operated at approximately atmospheric pressure or at a slight negative pressure of 0.9 bar absolute or higher, for example 0.95 bar absolute or higher.

6. A process according to any one of the preceding claims, wherein each zone of the rotary kiln is operated at a temperature of from 310 °C to 720 °C, preferably from 400 °C to 650 °C.

7. A process according to any one of the preceding claims, wherein the final zone of the plurality of zones is heated to a higher temperature then the other heating zones, preferably wherein the plurality of heating zones comprise sequential zones operated at from 310 °C to 600 °C in one or more zones and from 480 °C to 700 °C in a subsequent final zone.

8. A process according to any one of the preceding claims, wherein the polymer feed comprises at least 85 wt.% polyolefin polymers, preferably at least 90 wt.% polyolefin polymers, more preferably at least 95 wt.% polyolefin polymers, for example at least 99 wt.% polyolefin polymers.

9. A process according to any one of the preceding claims, wherein the polyolefin polymers comprise or consist essentially of polyethylene and polypropylene, for example wherein the polyolefin polymers comprise at least 90 wt.% polyethylene and polypropylene, preferably at least 95 wt.% polyethylene and polypropylene, for example at least 99 wt.% polyethylene and polypropylene.

10. A process according to any one of the preceding claims, wherein the polymer feed is melted in a melt extruder.

11. A process according to Claim 10, wherein the melt extruder is heated at a temperature of from 250 °C to 350 °C, preferably from 265 °C to 325 °C.

12. A process according to any one of the preceding claims, wherein calcium oxide is added to the polymer feed, preferably in an amount of up to 3 wt.%

13. A process according to any one of the preceding claims, wherein at least a portion of a non-condensable gas fraction is recycled to provide heating to the rotary kiln and/or to melt the polymer feed.

14. A process according to any one of the preceding claims, wherein the solid char product comprises no more than 15 wt.% of the effluent from the kiln, preferably no more than 10 wt.%.

15. A process according to any one of the preceding claims, wherein the hydrogenation reactor in step (v) comprises a fixed bed reactor, preferably a trickle bed reactor.

16. A process according to any one of the preceding claims, wherein the solid char product is separated from the fluid product stream at least in part by a decanter centrifuge or a tricanter centrifuge.

17. A process according to any one of the preceding claims, wherein the fluid product stream comprises a non-condensable gas fraction and a liquid fraction comprising C_{5+} hydrocarbons, wherein the non-condensable gas fraction is separated from the liquid fraction prior to step (v).

18. A process according to any one of the preceding claims, wherein the hydrogenation catalyst is a metal catalyst, preferably wherein the metal hydrogenation catalyst comprises a metal selected from Group VIII of the periodic table, preferably the catalyst comprises Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and/or Pt, such as a catalyst comprising Ni, Co, Mo, W, Cu, Pd, Ru, Pt, and preferably wherein the catalyst is selected from CoMo, NiMo or Ni, more preferably wherein the catalyst is NiMo; and/or wherein the catalyst is supported on a carrier preferably selected from bauxite, alumina, silica, silica-alumina or zeolite, preferably alumina.

19. A process according to any one of the preceding claims, wherein the hydrocracking step comprises contacting the light hydrogenated fraction with a hydrocracking catalyst at a temperature of from 250 °C to 400 °C, preferably from 300 to 350 °C, and/or at a pressure of from 3 to 10 MPa, preferably from 4 to 8 MPa.

20. An apparatus for producing naphtha and diesel from a polymer feed, the apparatus comprising:

(i) means for melting a polymer feed comprising at least 80 wt.% of polyolefin polymers to provide a molten polymer feed;

(ii) a rotary kiln reactor configured to receive the molten polymer feed from part (i), the rotary kiln reactor configured to provide a plurality of sequential heating zones, wherein each zone of the rotary kiln is configured to be operated at a temperature of from 300 °C to 800 °C to pyrolyze the molten polymer feed and produce a fluid product stream and a solid char product;

(iii) means for separating the solid char product from the fluid product stream; and

(iv) a hydrogenation reactor configured to receive a liquid fraction of the fluid product stream comprising C_{5+} hydrocarbons from part (iii) and to hydrogenate said liquid fraction to produce a hydrogenated hydrocarbon product stream;

(v) means for fractionating the hydrogenated hydrocarbon product stream to produce a light hydrogenated fraction comprising C_{5-20} hydrocarbons;

(vi) a hydrocracking reactor configured to catalytically crack the light hydrogenated fraction in the presence of hydrogen to produce a light hydrocarbon product stream enriched in C_{5-10} hydrocarbons; and

(vii) means for fractionating the light hydrocarbon product stream from (vi) to produce a naphtha fraction and a diesel fraction.

21. An apparatus according to Claim 20, wherein the means for fractionating the hydrogenated hydrocarbon product stream comprises a fractional distillation column configured for receiving the hydrogenated hydrocarbon product stream from the hydrogenation reactor.

22. An apparatus according to Claim 20 or Claim 21, wherein the rotary kiln is configured to provide four or more sequential heating zones, preferably wherein the rotary kiln is configured to operate as defined in any one of Claims 4 to 7.

23. An apparatus according to any one of Claims 20 to 22, wherein the means for melting the polymer feed comprises a melt extruder, preferably configured to heat the polymer feed at a temperature of from 250 °C to 350 °C, preferably from 265 °C to 325 °C.

24. An apparatus according to any one of Claims 20 to 23, wherein the apparatus is configured to recycle a gas fraction of the hydrocarbon product stream to provide heating to the rotary kiln and/or to melt the polymer feed.

25. An apparatus according to any one of Claims 20 to 24, wherein the hydrogenation reactor in part (iv) comprises a trickle bed reactor, preferably wherein the catalyst is as defined in Claim 18.

26. An apparatus according to any one of Claims 20 to 25, wherein the means for separating the solid char product from the fluid product stream comprises a decanter centrifuge or a tricanter centrifuge, and/or wherein the means for separating the solid char product from the fluid product stream comprises a char outlet from the rotary kiln and a vapour outlet from the rotary kiln, separate to the char outlet, for receiving the fluid product stream the rotary kiln.