outside of the vessel containing the waste plastic and can therefore suffer from char formation and have hot surfaces that become blocked. Some plastics also decompose producing chemicals that sublime blocking downstream equipment. Heat transfer into polymer masses is also problematic, leading to blockages in plant. Catalytic processes can be sensitive to ash, metals, cellulose (paper), inorganic fillers and additives as impurities in the polymer feed. As a consequence of these problems several waste plastic pyrolysis plants that have attempted to operate commercially have closed down.

A need exists for improved methods and/or devices capable of converting polymeric materials (e.g. plastics) into hydrocarbon feedstock from which new plastic could be manufactured, creating a fully circular economy for plastic.

Summary ~~of the Invention~~

The present ~~invention~~ disclosure addresses one or more problems existing in the prior art by providing improved means to convert polymeric materials such as waste plastics into valuable hydrocarbon products and/or transport fuels and/or other chemicals.

By practising the methods described herein, valuable chemical constituents of end of life plastic can be chemically recycled making hydrocarbon products that could be reused in various applications including, for example, the production of new plastic. The present disclosure ~~invention~~ also offers a solution to the issue of accumulating plastic wastes reducing the consumption of the finite crude oil reserves.

Disclosed herein are methods and apparatuses for treating polymeric material to produce hydrocarbon products.

In some ~~embodiments~~ examples the polymeric material under treatment may be processed by a suitable extruder which may increase the pressure and therefore the temperature of the polymeric material as it exits the extruder. The polymeric material may be further heated by super-critical water upon exiting the extruder to generate a reaction mixture which may comprise polymeric material, water and optionally other component(s). A mixer may be employed to further mix the reaction mixture and/or a heater may be used to further heat the reaction mixer. The reaction mixture comprising the polymeric material and a solvent (e.g. an aqueous solvent), can be received in a reactor apparatus which houses or includes a reaction zone providing pre-determined reaction temperature/s and/or reaction pressure/s. The reaction mixture may be treated in the reaction zone over a period of time suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a product, which may exit the reaction zone in the form of a fluid product stream.

In certain ~~embodiments~~examples, the fluid product stream exiting the reaction zone at elevated temperature and pressure may be rapidly depressurised in a flash vessel in a manner causing vaporizes a large proportion of the fluid product stream generating a vapour comprising hydrocarbon products, steam, and gases, which may be collected in an accumulation apparatus. The present inventors have advantageously identified that fractionation of the vapour into individual components including gas can be enhanced by way of the aforementioned the rapid reduction in fluid product stream pressure and utilising energy of the vapour.

Gas from the vapour may be utilised as energy in the methods of the present disclosure~~invention~~. For example, the gas may be transferred to an apparatus such as a boiler for generating energy to for heating the super-critical water. The energy of the gas may be used for any process of the method.

As described in more detail below, the means by which the present disclosure ~~invention~~ addresses one or more of the shortfalls in the prior art noted above include, without limitation, any one or more of the following features.

Polymeric materials such as waste plastics may be readily prepared by means known in the art for extrusion by a suitable extruder. Polymeric material extrudate exiting the extruder at elevated pressure may be combined with a heated/pressurised aqueous solvent (super-heated water) to provide a mixture with a high concentration of the polymeric material, when compared to an equivalent reaction mixture formed without extruding the polymeric material. The super-heated water phase may provide efficient heat transfer to the polymer melt by virtue of its high diffusivity, and/or the presence of the water may supress char formation. Halogens (e.g. chlorine) present in the reaction mixture may be largely transferred to the aqueous phase as inorganic halides thereby reducing issues around dioxin formation. Cellulose based impurities such as paper may be largely gasified or else converted to oil components. Ash-like components and inorganic fillers may be largely carried through the process and can be separated from the products by means known in the art (e.g. fractional distillation). The design of the extruder-reactor interface and/or the mixing interface for the dilution with supercritical or superheated aqueous solvent (e.g. water) may, for example, be at least in part responsible for providing advantage/s over prior art methods.

One or more collection apparatus/es according to the present disclosure ~~invention~~ may be provided in various configurations. Where substantial energy has been introduced in steps of the method, the energy of the vapour may be used to fractionate the vapour into constituents. For example, a vertical vessel may include various containers in a vertical arrangement which receive constituents as their energy propels them to various heights within the vessel so that they land in a particular container. The container may be associated with a collection pipe to direct the

constituents to their respective reservoirs for further processing. Water may be a constituent and collected for cleaning. Gas may be at least one constituent of a fractionated vapour which is utilised as energy in the method.

Depending upon the energy stored in various constituents of the vapour, the constituents may self-separate to be separately captured. Providing the constituents with the opportunity to self-separate avoids the necessity of additional separation steps which can require re-heating the products, requiring additional energy and time to be expended. The self-separation of constituents of fractionated vapour may be for example, hard wax residue.

The methods and apparatus described herein may be used to process so-called "end-of-life plastics" which have been manufactured with impurities to exhibit various characteristics. The impurities might, for example, might make a plastic opaque and coloured. These impurities might be for example, TiO_2, $CaCO_3$, ZnO and/or NaCl. The heaviness of impurities may cause them to gravitate to the bottom one or more reactor vessels where they may collected. Later, one of various containers of the collection apparatus may include a product useful as bitumen. The methods and apparatus may include means for adding the impurities to one or more bitumen products for safe disposal. As mentioned above, the water constituent of the fractionated vapour may be cleaned wherein impurities may be collected and added to a product useful as bitumen for safe disposal. The bitumen for example, may be used in construction of roads.

As described herein treating the reaction mixture in a reactor apparatus at various reaction temperatures and a reaction pressures over various periods of time suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a fluid product stream may determine the ultimate end products of the fractionated vapour. Depending upon the available feedstock and the desired product output, various parameters may be adjusted.

The methods of the present disclosure ~~invention~~ may include substantially harsh conditions due to high pressure and high temperatures. Therefore, appropriate selection of vessel and piping steel is beneficial. Depending upon the steel selected, the reaction mixture may interact with the steel wherein the steel may act as a catalyst causing various end products to take on characteristics. Depending upon the desired end products additional surfaces may be added to, for example, vessel/s of the reactor apparatus. One such surface may include nickel for example, which may drive certain target reactions to take place.

In one aspect, there is provided a method for treating polymeric material to produce hydrocarbon products, the method comprising: generating a reaction mixture comprising the polymeric material and an aqueous solvent, treating the reaction mixture in a reactor apparatus at a reaction temperature and a reaction pressure over a period of time suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a fluid product stream,

and depressurising the fluid product stream, wherein: the fluid product stream is at a temperature of at least 350°C and a pressure of at least 180 bar immediately prior to the depressurising, the depressurising comprises reducing the pressure of the fluid product stream to less than 25 bar in a flash vessel thereby vaporizing at least a portion of the fluid product stream and generating a vapour comprising constituent parts of hydrocarbon products, steam, and gas, and the vaporizing provides energy to facilitate fractionation of the vapour into the constituent parts; and collecting the fractionated vapour.

In another aspect, there is provided a continuous flow reactor apparatus for treating polymeric material, comprising: an extruder for producing an extrudate comprising a molten stream of the polymeric material; a boiler apparatus for preparing and adding supercritical water to the extrudate; a mechanical mixing device configured for mixing of the extrudate with the supercritical water to thereby form a reaction mixture; a reaction zone in communication with the mechanical mixing device and with indirect heaters, wherein the reaction zone is for treating the reaction mixture at a defined temperature and pressure for a defined residence time to thereby produce a fluid product stream; a pressure let down device for depressurisation of the fluid product stream, wherein the pressure let down device is in communication with the reaction zone and a flash vessel; a fractionation apparatus for separation of vapour generated in the flash vessel; wherein the flash vessel: is coupled directly with the fractionation apparatus; or is an integral part of the flash column; or and the fractionation apparatus are separate product condensers.

The present disclosure ~~invention~~ relates at least in part to the following embodiments:

Embodiment 1. A method for treating polymeric material to produce hydrocarbon products, the method comprising:

- generating a reaction mixture comprising the polymeric material and an aqueous solvent,

CLAIMS

1. A method for treating polymeric material to produce hydrocarbon products, the method comprising:

- generating a reaction mixture comprising the polymeric material and an aqueous solvent,
- treating the reaction mixture in a reactor apparatus at a reaction temperature and a reaction pressure over a period of time suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a fluid product stream, and
- depressurising the fluid product stream, wherein:

the fluid product stream is at a temperature of at least 350°C and a pressure of at least 180 bar immediately prior to the depressurising,

the depressurising comprises reducing the pressure of the fluid product stream to less than 25 bar in a flash vessel thereby vaporizing at least a portion of the fluid product stream and generating a vapour comprising constituent parts of hydrocarbon products, steam, and gas, and

the vaporizing provides energy to facilitate fractionation of the vapour into the constituent parts; and

- collecting the fractionated vapour.

2. The method ofaccording to claim 1, wherein the fluid product stream is at:

(i) a temperature of at least: 380°C, 400°C, 420°C, 450°C, or 470°C, and/or

(ii) a pressure of at least: 200 bar, 220 bar, 240 bar, 260 bar, 280 bar or 300 bar,;

immediately prior to the depressurising.

3. The method according to claim 1 or claim 2, wherein the fluid product stream is at a pressure of at least: 200 bar, 220 bar, 240 bar, 260 bar, 280 bar or 300 bar, immediately prior to the depressurising.

43. The method of any one of claims 1 or claim 2to 3, wherein the flash vessel is coupled directly with the accumulation apparatus, is an integral part of the accumulation apparatus, or is directly coupled to one or more staged product condensers.

~~54~~. The method of~~according to~~ any one of claims 1 to ~~4~~3, comprising fractionating and condensing the vapour into fractions having a maximum atmospheric equivalent boiling point of less than: 400°C, 450°C, 500°C, 550°C or 600°C and collecting a residual fraction with a minimum atmospheric equivalent boiling point of more than 400°C, 450°C, 500°C, 550°C or 600°C

~~65~~. The method of~~according to~~ any one of claims 1 to ~~5~~4, wherein solid fillers and/orinorganic matter and/or metal salts from the depressurized product stream are retained within residue matrix produced by said vaporizing and fractionation.

~~7~~6. The method of any one of claims 1 to ~~6~~5, wherein the depressurising and fractionation enables separation of the aqueous solvent from the hydrocarbon products including separation of the aqueous solvent from:

(i) low boiling hydrocarbons at a temperature below: 10°C, 20°C, 30°C, 40°C, 50°C, or 60°C; or

(ii) low boiling hydrocarbons at a temperature below: 10°C, 20°C, 30°C, 40°C, 50°C, or 60°C, conducted under an effective gravity of 9.8_+/- 0.1 m/s^2.

~~8. The method according to claim 7, wherein the separation of the aqueous solvent from low boiling hydrocarbons is conducted under an effective gravity of 9.8_+/- 0.1 m/s^2.~~

~~9. The method according to claim 7 or claim 8, wherein the separated aqueous solvent comprises a total organic carbon content (TOC) of less than: 15,000 mg/l, 10,000 mg/l, 5000 mg/l, 2500 mg/l, 1000 mg/l, or 500 mg/l.~~

~~10~~7. The method of any one of claims 1 to ~~9~~6, further comprising injecting steam into the flash vessel and contacting the fluid product stream with the steam.

~~11~~8. The method of any one of claims 1 to ~~10~~7, wherein said generating of the reaction mixture comprises:

- providing a molten stream of the polymeric material;
- injecting the aqueous solvent into the molten stream of polymeric material, wherein the aqueous solvent is supercritical prior to said injecting~~,~~; and

- mechanical mixing of the aqueous solvent and the molten stream of polymeric material, wherein the mechanical mixing comprises use of solvent distribution grids in an assembly comprising one or more static mechanical mixing devices.

~~12. The method of claim 11, wherein the aqueous solvent is supercritical prior to said injecting.~~

~~13~~9. The method of claim ~~11 or claim 12~~8, wherein the aqueous solvent is water or substantially water.

~~14. The method of any one of claims 11 to 13, wherein the mechanical mixing comprises use of solvent distribution grids in an assembly comprising one or more static mechanical mixing devices.~~

~~15. The method of claim 12, wherein fluid flow discharged by any said mechanical mixing device has a volume uniformity of greater than about: 94%, 95%, 96 %, 97%, or 98%.~~

~~16. The method of any one of claims 11 to 15, wherein the aqueous solvent is injected into the molten stream of polymeric material through a series of nozzles spanning the circumference of the any said mixing device and solvent distribution grid.~~

~~17. The method of claims 14 to 16, wherein during said generating of the reaction mixture there is a pressure drop across the mixing device of less than: 2 bar, 5 bar, 10 bar, 20 bar, or 30 bar.~~

~~18~~10. The method of ~~any one of~~ claim~~s 12 to 17~~9, wherein the supercritical aqueous solvent is generated in a boiler apparatus comprising a burner fuelled by gas released from the fluid product stream, wherein the supercritical aqueous solvent exits the boiler apparatus at:

(i) a temperature of at least: 450°C, 500°C, or 550°C, and/or

(ii) a pressure of at least 180 bar or at least 200 bar or at least 220 bar or at least 240 bar or at least 250 bar, at least 270 bar, or 290 bar, or 310 bar or 330 bar during generation of the supercritical aqueous solvent.

~~19. The method of claim 18, wherein the supercritical aqueous solvent is generated in a boiler apparatus comprising a burner fuelled by natural gas.~~

~~20. The method of claim 18 or claim 19, wherein the supercritical aqueous solvent exits the boiler apparatus at a temperature of at least: 450°C, 500°C, or 550°C.~~

~~21. The method of any one of claims 18 to 20, wherein the boiler operates at a pressure of at least: least 180 bar or at least 200 bar or at least 220 bar or at least 240 bar or at least 250 bar, at least 270 bar, or 290 bar, or 310 bar or 330 bar during generation of the supercritical aqueous solvent.~~

~~22. The method of any one of claims 18 to 21, comprising heating the gas released from the fluid product stream in the boiler apparatus to a temperature of at least 850°C for at least 2 seconds to thereby destroy halogenated organic compounds including any one or more of: chlorinated dioxins, chlorinated furans, chlorinated biphenyls and other dioxin-like compounds of environmental concern..~~

~~23~~11. The method of any one of claims 1 to ~~22~~10, wherein said treating comprises contacting the reaction mixture with supplementary metal catalysts in addition to those present in any solid state transition metal surface in contact with the reaction mixture during said generating or treating, wherein the supplementary metal catalysts are:

- components of a solid material that is mixed into the reaction mixture to facilitate contact between the fluids and the supplementary metal catalyst, and/or
- a component of any said mixing device.

~~24. The method according to claim 23, wherein the supplementary metal catalysts are solid state transition metal catalysts.~~

~~25. The method according to claim 23 or claim 24, wherein the supplementary metal catalysts are solid state transition metal~~

~~catalysts, and wherein the oxidation state of the transition metal is initially a formal zero valent oxidation state.~~

~~26. The method according to claim 25, wherein the zero valent metal is selected from any of: zero valent iron and nickel.~~

~~27. The method of claims 23 to 26, where the supplementary metal catalysts catalyse the transfer of hydrogen atoms from the aqueous solvent to the hydrocarbon products arising from said treating of the polymeric material.~~

~~28~~12. The method ~~according to~~of any one of claims 1 to ~~27~~11, further comprising removal of solid materials from the reaction mixture during said treating, wherein the solid materials:

- are inorganic materials present within the polymeric material, wherein the inorganic materials:
  - are fillers or contaminants present within the polymeric material prior to conducting the method; and/or
  - have reacted with the aqueous solvent and/or with carbon rich materials formed in small volumes by side reactions during said treating;
- have a greater density than fluids within the reaction mixture and separate from the reaction mixture by gravity during said treating; and
- are removed a reactor apparatus in which said treating is conducted by blowing down into a receiver vessel during said treating by means of remotely operated valves.

~~29. The method according to claim 28, wherein the inorganic materials:~~

- ~~are fillers or contaminants present within the polymeric material prior to conducting the method; and/or~~
- ~~have reacted with the aqueous solvent and/or with carbon rich materials formed in small volumes by side reactions during said treating.~~

~~30. The method according to claim 28 or claim 29, wherein the solid materials are blown down into the receiver vessel with a portion of the hydrocarbon products, waxes, polymer oligomers or partly depolymerized materials.~~

~~31~~13. The method ~~according to~~of any one of claims 1 to ~~30~~12, wherein the method is conducted in a reactor apparatus comprising any one or more of:

- systems for testing pressure levels in valving and a pressure letdown vessel within said reactor apparatus,
- a system allowing cooling of material blown down into a receiver vessel of the reactor apparatus,
- a final collection pot with removable lid for blown down material that is interlocked with its lid and with interconnected pipes and valves to prevent accidental removal of the pot and contents~~.~~,
- venting for release of gases formed during or after said treating,
- providing inert atmospheres comprising nitrogen, argon, carbon dioxide and/or other inert gases preventing ignition and combustion of materials contained within the letdown pot and collection pot,
- sequencing systems to minimise mechanical shock in the reactor apparatus.

~~32. The method of any one of claims 1 to 31, wherein:~~

- ~~one or more heat exchanger/s or a is/are used to indirectly heat the reaction mixture to the reaction temperature;~~
- ~~the one or more heat exchanger/s does not comprise an expansion bellowarrangement; and~~
- ~~the one or more heat exchanger/s comprise a double heated probe type arrangement comprising a steam pipe within a steam pipe and/or an electric powered heater element used to indirectly heat the steam and/or reaction mixture.~~

~~33. The method according to claim 10, comprising utilising a fired superheater to heat the steam prior to injecting the steam into the flash vessel.~~

~~34~~14. The method ~~according to~~of any one of claims 1 to ~~33~~13, wherein the reaction temperature is at least: 380°C, 400°C, 450°C, or 500°C.

~~35~~15. The method of any one of claims 1 to ~~34~~14, wherein the hydrocarbon product comprises any one or more of:

(i) a naphtha component boiling between 10°C and 210°C AEBP, and wherein the naphtha component comprises:

- more than 10%, 20% 30%, 40% by mass olefins; and/or
- more than 10%, 20%, 30% 40% by mass n-paraffins; and/or
- more than 10%, 20%, 30% 40% by mass cycloalkanes or cycloalkenes; and/or
- more than 10%, 20%, 30% 40% by mass aromatics~~.~~;

~~36. The method of any one of claims 1 to 35, wherein the hydrocarbon product comprises~~(ii) a gas oil component boiling between 210°C and 360°C AEBP, and wherein the gas oil component comprises:

- more than 10%, 20% 30%, 40% by mass olefins; and/or
- more than 10%, 20%, 30% 40% by mass n-paraffins; and/or
- more than 10%, 20%, 30% 40% by mass cycloalkanes or cycloalkenes; and/or
- more than 10%, 20%, 30% 40% by mass aromatics~~.~~;

~~37. The method of any one of claims 1 to 36, wherein the hydrocarbon product comprises~~ (iii) a heavy gas oil component boiling between 360°C and 550°C AEBP, and the heavy gas oil component comprises:

- more than 10%, 20% 30%, 40% by mass olefins; and/or
- more than 10%, 20%, 30% 40% by mass n-paraffins; and/or
- more than 10%, 20%, 30% 40% by mass cycloalkanes or cycloalkenes; and/or
- more than 10%, 20%, 30% 40% by mass aromatics.

~~38~~16. The method ~~according to~~of any one of claims 1 to ~~37~~15, wherein:

- the polymeric material used to generate said reaction mixture is a molten polymeric material extrudate;
- the polymeric material extrudate is diverted to a collection vessel prior to generating said reaction mixture;
- the collection vessel is provided with an inert atmosphere avoiding combustion of the molten polymeric material extrudate; and

- the collection vessel is connected to a reactor apparatus by one or more lines providing double valve isolation on each line to prevent reverse flow of the molten polymeric material extrudate from the reactor.

~~39. The method according to claim 14 or claim 15, wherein a system of temperature measurements provides warning of flow back from the mixing device/s towards an extruder apparatus in connection with the mixing device/s, allowing operation of isolation valves thus preventing reverse flow from the mixing device/s.~~

~~40. The method according to any one of claims 1 to 39, wherein the reactor apparatus is a continuous flow reactor apparatus.~~

~~41~~17. The method ~~according to~~of any one of claims 1 to ~~40~~16, wherein:

(i) the treating is performed under conditions of continuous flow; and/or

(ii) ~~.~~

~~42. The method accroding to any one of claims 1 to 41, wherein~~ the polymeric material does not comprise any one or more of: lignocellulosic matter; naturally-occurring carbohydrate polymers; lignin; cellulose; hemicellulose; combinations of any two of lignin, cellulose, hemicellulose; lignite (brown coal); subbituminous coal; any combination thereof.

~~43~~18. A continuous flow reactor apparatus for treating polymeric material, comprising:

- an extruder for producing an extrudate comprising a molten stream of the polymeric material;
- a boiler apparatus for preparing and adding supercritical water to the extrudate;
- a mechanical mixing device configured for mixing of the extrudate with the supercritical water to thereby form a reaction mixture;
- a reaction zone in communication with the mechanical mixing device and with indirect heaters, wherein the reaction zone is for treating the reaction mixture at a defined temperature and pressure for a defined residence time to thereby produce a fluid product stream;

- a pressure let down device for depressurisation of the fluid product stream, wherein the pressure let down device is in communication with the reaction zone and a flash vessel;

- a fractionation apparatus for separation of vapour generated in the flash vessel;

wherein the flash vessel:

- is coupled directly with the fractionation apparatus; or
- is an integral part of the flash column; or
- and the fractionation apparatus are separate product condensers.

~~44. The continuous flow reactor apparatus of claim 43, wherein the indirect heaters are not circumferential.~~

~~45. The continuous flow reactor apparatus of claim 43 or claim 44, wherein the flash vessel:~~

- ~~is coupled directly with the fractionation apparatus; or~~
- ~~is an integral part of the flash column; or~~
- ~~and the fractionation apparatus are separate product condensers.~~

~~46. The continuous flow reactor apparatus of any one of claims 43 to 45, wherein the mechanical mixing device is a static mechanical mixing device.~~

~~47. The continuous flow reactor apparatus of any one of claims 43 to 46, comprising a series of nozzles spanning the circumference of the mechanical mixing device or a portion of thereof, for injection and distribution of the supercritical water into the molten stream of polymeric material.~~

~~48. The continuous flow reactor apparatus of any one of claims 43 to 47, wherein the boiler apparatus comprises a burner in communication with the fractionation apparatus (e.g. a vessel in the fractionation apparatus) for receiving gas.~~

~~49. The continuous flow reactor apparatus of any one of claims 43 to 48, wherein the boiler apparatus comprises a burner in communication with a source of natural gas.~~

~~50~~19. The continuous flow reactor apparatus of ~~any one of~~ claim~~s~~ 18~~43 to 49~~, wherein one or more components of the reaction zone comprises a source of solid state transition metal catalysts for the reaction mixture.

~~51. The continuous flow reactor apparatus of claim 50, wherein the metal catalysts are solid state transition metal catalysts.~~

~~52. The continuous flow reactor apparatus of any one of claims 43 to 51, wherein:~~
~~4. a collection vessel configured to collect the molten polymeric material extrudate prior to generating said reaction mixture is connected to the reactor apparatus by one or more lines;~~
~~4. the one or more lines provide double valve isolation on each line and prevent reverse flow from the reactor;~~

~~5. the collection vessel is provided with an inert atmosphere for avoiding combustion of the extrudate.~~

~~53~~20. The continuous flow reactor apparatus of ~~any one of~~ claim~~s~~ 18 or claim 19~~43 to 52~~, comprising a blow down component for removal of solid materials from the reaction mixture, and a receiver vessel for the solid materials.

~~54. The continuous flow reactor apparatus of any one of claims 43 to 53, comprising means for separating solid residues and/or bottoms formed during pretreatment of the polymeric material and/or the treating of the reaction mixture, and means for combining the solid residues and/or bottoms with the fluid product stream in the flash vessel to thereby vaporize volatile components of the solid residues and/or bottoms.~~

~~55. The continuous flow reactor apparatus of any one of claims 43 to 54, comprising:~~
~~- a heat exchanger for indirectly heating the reaction mixture to the defined temperature at multiple points along a vessel in the reactor apparatus housing the reaction zone through which the reaction mixture flows;~~

~~means for providing supercritical steam generated by a supercritical steam generator to the heat exchanger.~~