leading to blockages in plant. 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 biofuel.

Summary

The present disclosure addresses one or more problems existing in the prior art by providing improved means to convert polymeric materials into biofuels and/or other chemicals.

The means by which the present disclosure 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. The extruder output may then be combined with a heated/pressurised aqueous solvent to provide a mixture of polymeric material/water with a high concentration of the polymeric material compared to an equivalent reaction mixture formed without extruding the polymeric material. The 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.

In one aspect, the present disclosure refers to a method for producing a bio-oil, the method comprising: extruding polymeric material in an extruder to thereby form a melt stream comprising the polymeric material, providing a stream of aqueous solvent that is separate to the melt stream, contacting the melt stream with the stream of aqueous solvent to form a reaction mixture, treating the reaction mixture in a reactor vessel at a reaction temperature and a reaction pressure for a time period suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a product comprising the bio-oil, and depressurising and cooling the product, wherein the stream of aqueous solvent is supercritical prior to said contacting, the reaction temperature is or ranges between 400°C and 600°C, and the reaction pressure is or ranges between 100 bar and 300 bar.

The present disclosure relates to at least the following non-limiting examples:

Example 1. A method for producing a bio-oil, the method comprising:

extruding polymeric material in an extruder to thereby form a melt stream comprising the polymeric material,

providing a stream of aqueous solvent that is separate to the melt stream,

contacting the melt stream with the stream of aqueous solvent to form a reaction mixture,

treating the reaction mixture in a reactor vessel at a reaction temperature and a reaction pressure for a time period suitable for conversion of all or a portion of the polymeric material present in the reaction mixture into a product comprising the bio-oil, and

depressurising and cooling the product.

Example 2. The method according to example 1, wherein the extruder is a single screw extruder, a multiscrew extruder, a counter-rotating multiscrew extruder, a co-rotating multiscrew extruder, a twin screw extruder, a counter-rotating twin screw extruder, a co-rotating twin screw extruder, an intermeshing screw extruder, a radial extruder, or a roll-type extrusion press.

Example 3. The method according to example 1 or example 2, wherein the method further comprises venting gases and/or vapours from one or a series of ports present in a barrel of the extruder.

Example 4. The method according to example 3, wherein the gases and/or vapours comprise any one or more of: hydrogen chloride, hydrogen bromide, hydrogen fluoride, chlorine, ammonia, carbon monoxide, carbon dioxide.

Example 5. The method according to any one of examples 1 to 4, further comprising adding a base to any one or more of: the polymeric material prior to extrusion, the melt stream, the stream of aqueous solvent, and/or the reaction mixture, wherein:

the base is an additional component to the polymeric material and the aqueous solvent,

within the reaction misture the number of moles of the base added per 100 grams of polymeric material is between 0.5 times and 1.5 times the total number of moles of halogens per 100 grams of the polymeric material, and

the base precipitates metal halides in the reaction mixture facilitating their removal.

Example 6. The method according to example 5, wherein the product has a pH of more than 3, 4, 5, 6, 7, 8, or 9 after cooling and depressurising it to ambient temperature and pressure.

Example 7. The method of any one of examples 1 to 6, wherein the melt stream exits from the extruder:

(i) at a pressure of more than 20 bar, more than 50 bar, more than 100 bar, more than 150 bar, more than 200 bar, more than 220 bar, more than 250 bar, or more than 350 bar, or between 220 bar and 300 bar; and/or

(ii) at a temperature of between 200°C and 300°C and a pressure of between 100 bar and 350 bar, or at a temperature of between 220°C and 280°C and a pressure of between 200 bar and 350 bar, or at a temperature of between 280°C and 380°C and a pressure of between 220 bar and 300 bar.

Example 8. The method of any one of examples 1 to 7, wherein the extruder is directly connected to a hydrothermal reactor apparatus in a manner allowing the melt stream to flow into the reactor in a continuous flow.

Example 9. The method according to any one of examples 1 to 8, wherein prior to said extruding the polymeric material is preteated using any one or more of grinding, chipping, pelletisation, granulisation, flaking, powdering, shredding, milling, compression/expansion, agitation, washing, flotation, removing materials comprising halogens optionally by infra-red or x-ray fluorescence detection and compressed gas classification/rejection and/or pulse-electric field (PEF) treatment.

Example 10. The method according to any one of examples 1 to 9, wherein the polymeric material is extruded in the presence of water, and the water constitutes less than 5 wt% (wet basis) of total polymeric material weight.

Example 11. The method according to any one of examples 1 to 10, wherein the polymeric material is selected from the group consisting of: Polyethylene (PE), Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE), Polypropylene (PP), Polyester, Poly(ethylene terephthalate) (PET), poly(lactic acid) PLA, Poly (vinyl chloride) (PVC), Polystyrene (PS), Polyamide, Nylon, Nylon 6, Nylon 6,6, Acrylonitrile-Butadiene-Styrene (ABS), Poly(Ethylene vinyl alcohol) (E/VAL), Poly(Melamine formaldehyde) (MF), Poly(Phenol-formaldehyde) (PF), Epoxies, Polyacetal, (Acetal), Polyacrylates (Acrylic), Polyacrylonitrile (PAN), Polyamide-imide (PAI), Polyaryletherketone (PAEK), Polybutadiene (PBD), Polybutylene (PB), Polycarbonate (PC), Polydicyclopentadiene (PDCP), Polyketone (PK), polycondensate., Polyetheretherketone (PEEK), Polyetherimide (PEI), Polyethersulfone (PES), Polyethylenechlorinates, (PEC), Polyimide, (PI), Polymethylpentene (PMP), Poly(phenylene Oxide) (PPO), Polyphenylene Sulfide (PPS), Polyphthalamide, (PTA), Polysulfone (PSU), Polyurethane, (PU), Poly(vinylidene chloride) (PVDC), Poly(tetrafluoroethylene) PTFE, Poly(fluoroxy alkane) PFA, Poly(siloxanes), silicones, thermosplastics, thermosetting polymers, natural rubbers, tyre rubbers, ethylene propylene diene monomer rubbers EPDM, chloroprene rubbers, acrylonitrile butadiene (nitrile) rubbers, polyacrylate rubbers, Ethylene Acrylic rubbers, Styrene-butadiene rubbers, Polyester urethane rubbers, Polyether urethane rubbers, Fluorosilicone rubbers, silicone

rubbers, and copolymers, synthetic polymeric materials, naturally-occurring polymeric materials, plastics, and mixtures thereof.

Example 12. The method according to any one of examples 1 to 11, wherein the reaction mixture prior to said treating comprises:

(i) at least 1 wt%, at least 2 wt%, at least 3 wt%, at least 4 wt%, at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 5 wt%, at least 30 wt%, at least 35 wt%, at least 40 wt%, at least 45 wt%, at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, or at least 98 wt% of the polymeric material; and/or

(ii) less than 98 wt%, less than 95 wt%, less than 90 wt%, less than 80 wt%, less than 70 wt%, less than 60 wt%, less than 50 wt%, less than 45 wt%, less than 40 wt%, less than 35 wt%, less than 30 wt%, less than 25 wt%, less than 20 wt%, less than 15 wt%, less than 10 wt%, less than 5 wt%, less than 4 wt%, less than 3 wt%, less than 2 wt%, or less than 1 wt%, of the polymeric material.

Example 13. The method according to any one of examples 1 to 12, wherein the reaction mixture prior to said treating comprises:

between 40 wt% and 80 wt% of the polymeric material from the melt stream and between 20 wt% and 60 wt% of the aqueous solvent from the aqueous solvent stream; or

between 50 wt% and 75 wt% of the polymeric material from the melt stream and between 25 wt% and 50 wt% of the aqueous solvent from the aqueous solvent stream.

Example 14. The method according to any one of examples 1 to 13, wherein the polymeric material comprises any one or more of:

less than about 5 wt% nitrogen, less than about 1 wt% nitrogen, less than about 0.5 wt% nitrogen, or less than about 0.1 wt% nitrogen;

less than about 1 wt% total halogens, less than about 1 wt% total halogens, less than about 0.5 wt% total halogens, less than about 0.1 wt% total halogens, or less than about 0.05 wt% total halogens;

a molar ratio of hydrogen to carbon (H/C) of greater than 2.15, greater than 2.0, greater than 1.8, greater than 1.6, greater than 14, greater than 1.2, greater than 1.0, or greater than 0.8.

Example 15. The method according to any one of examples 1 to 14, wherein:

the reaction temperature is or ranges between 300°C and 600°C and the reaction pressure is or ranges between 50 bar and 300 bar; or

the reaction temperature is or ranges between 350°C and 550°C and the reaction pressure is or ranges between 50 bar and 300 bar; or

the reaction temperature is or ranges between 350°C and 600°C and the reaction pressure is or ranges between 20 bar and 350 bar; or

the reaction temperature is or ranges between 375°C and 550°C and the reaction pressure is or ranges between 50 bar and 300 bar; or

the reaction temperature is or ranges between 400°C and 600°C and the reaction pressure is or ranges between 100 bar and 300 bar; or

the reaction temperature is or ranges between 380°C and 500°C and the reaction pressure is or ranges between 200 bar and 300 bar; or

Example 16. The method according to any one of examples 1 to 15, wherein the stream of aqueous solvent is supercritical prior to said contacting.

Example 17. The method of any one of examples 1 to 16, wherein prior to said contacting the stream of aqueous solvent comprises

more than 90% supercritical water, more than 95% supercritical water, or 100% supercritical water; or

more than 90% subcritical water, more than 90% subcritical water, or 100% subcritical water; or

more than 90% steam, more than 95% steam, or 100% steam.

Example 18. The method of any one of examples 1 to 17, wherein prior to said contacting the stream of aqueous solvent comprises between 5 wt% and 40 wt% alcohol, between 1 wt% and 30 wt% alcohol, between 5 wt% and 25 wt% alcohol, between 1 wt% and 20 wt% alcohol, between 2 wt% and 20 wt% alcohol, between 1 wt% and 10 wt% alcohol, or between 2 wt% and 10 wt% alcohol.

Example 19. The method according to example 18 wherein the alcohol is ethanol, methanol, or a mixture comprising ethanol and methanol.

Example 20. The method according to any one of examples 1 to 19, wherein the method comprises

separating one or more of a gaseous, aqueous, bio-oil, and/or wax component from the product, and/or

separating one or more fractions of a bio-oil, and/or one or more fractions of a wax component from the product.

Example 21. The method according to any one of examples 1 to 20, wherein the method comprises separating and recycling into the method one or more fractions of the product having a boiling point:

between 30°C and 140 °C, between 60°C and 160°C, 140°C and 205°C, between 150°C and 300°C, or between 230°C and 350°C.

Example 22. The method according to any one of examples 1 to 21, wherein the method comprises separating and recycling into the method a fraction of the product comprising a wax or a waxy oil having a boiling point above 370°C atmospheric equivalent boiling point (AEBP), above 400°C AEBP, above 450°C AEBP, above 500 °C AEBP, or above 550 °C AEBP.

Example 23. The method according to any one of examples 1 to 22, wherein the method comprises separating and recycling a fraction of the product having a boiling point in the range of a: naphtha boiling range, heavy naphtha boiling range, kerosene boiling range, diesel boiling range, heavy gas oil boiling range, or vacuum gas oil boiling range, and combusting the separated naphtha fraction to provide heat for repeating the method.

Example 24. The method according to any one of examples 1 to 23, wherein the reaction mixture comprises a supplementary catalyst selected from the group consisting of: a base catalyst, an acid catalyst, a water-gas-shift catalyst, an alumino-silicate catalyst, a sulphide catalyst, and any combination thereof, wherein the supplementary catalyst is not derived from any other component of the reaction mixture or a vessel wall of a reactor apparatus, and does not form *in situ* during the method.

Example 25. The method according to example 24, wherein the supplementary catalyst is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium formate, potassium formate, an iron salt, or any combination thereof.

Example 26. The method according to example 24 or example 25, wherein the supplementary catalyst is added to the reaction mixture after the reaction mixture has reached said reaction temperature, or after the reaction mixture after the reaction mixture has reached said reaction temperature and said reaction pressure.

Example 27. The method according to any one of examples 1 to 26, wherein the reaction mixture comprises between 5 wt% and 60 wt%, between 10 wt% and 60 wt%, or between 20 wt% and 60 wt%, of oil, optionally wheerein the oil is recycled from

a bio-oil product previously generated in accordance with the method of any one of examples 1 to 26.

Example 28. The method according to example 27, wherein the oil is selected from the group consisting of paraffinic oil, gas-oil, crude oil, synthetic oil, coal-oil, bio-oil, shale oil, kerogen oil, mineral oil, white mineral oil, and aromatic oil.

Example 29. The method according to any one of examples 1 to 28, wherein the reaction mixture prior to said treating:

(i) comprises less than 10 wt%, less than 5 wt%, less than 4 wt%, less than 3 wt%, less than 2 wt%, or less than 1 wt%, of: lignocellulosic matter, coal, coke, peat, kerogen, tar sand, oil shale, shale tar, asphalt, asphaltine, natural bitumen, or bituminous sand; or

(ii) does not comprise lignocellulosic matter, coal, coke, peat, kerogen, tar sand, oil shale, shale tar, asphalt, asphaltine, natural bitumen, or bituminous sand.

Example 30. The method according to example 29, wherein said lignocellulosic material comprises more than 5 wt% lignin, more than 10 wt% lignin, more than 15 wt% lignin, more than 20 wt% lignin, more than 25 wt% lignin, more than 30 wt% lignin, more than 35 wt% lignin, more than 40 wt% lignin, more than 45 wt% lignin, or more than 50 wt% lignin.

Example 31 The method according to any one of examples 1 to 30, wherein the reaction mixture comprises a solid substrate that is either or both of:

(i) solid or substantially solid at the temperature and the pressure;

(ii) inert or substantially inert at the temperature and the pressure.

Example 32 The method according to example 31, wherein the solid substrate is:

(i) a carbonaceous material comprising at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% by weight carbon; or

(ii) is a non-carbonaceous material comprising no more than 10%, no more than 5%, no more than 1%, or no carbon.

Example 33. The method according to example 31 or example 32, wherein the solid substrate is selected from the group consisting of: coals, anthracitic coal, meta-anthracite, anthracite semianthracite, bituminous coal, subbituminous coal, lignite (i.e. brown coal), coking coal, coal tar, coal tar derivatives, coal char, coke, high temperature coke, foundry coke, low and medium temperature coke, pitch coke, petroleum coke, coke oven coke, coke breeze, gas coke, brown coal coke, semi coke, charcoal, pyrolysis char, hydrothermal char, carbon black, graphite fine particles, amorphous carbon, carbon

nanotubes, carbon nanofibers, vapor-grown carbon fibers, fly ash, a mineral, calcium carbonate, calcite, a silicate, silica, quartz, an oxide, a metal oxide, an insoluble or substantially insoluble metal salt, iron ore, a clay mineral, talc, gypsum, carbonates of calcium, carbonates of magnesium, carbonates of calcium and magnesium, calcite, limestone, dolomite, hydroxides of calcium, hydroxides of magnesium, oxides of calcium, oxides of magnesium, hydrogen carbonates of calcium, hydrogen carbonates of magnesium.

Example 34. The method according to any one of examples 31 to 33, wherein the reaction mixture comprises more than 0.5 wt%, more than 1 wt%, more than 3 wt%, more than 5 wt%, more than 10 wt%, more than 15 wt%, more than 20 wt%, more than 25 wt%, or more than 30 wt%, of the solid substrate.

Example 35. A product obtained or obtainable by the method according to any one of examples 1 to 34.

Brief Description of the Figures

A preferred embodiment of the present invention will now be described, by way of an example only, with reference to the accompanying figures wherein:

Figure One provides an exemplary schematic of a method and apparatus according to embodiments of the present invention.

Figure Two provides a further exemplary schematic of a method and apparatus according to embodiments of the present invention.

Figure Three provides a non-limiting example of a reactor apparatus (part a) and a series of three such reactors (part b) according to embodiments of the present invention. each reactor including a blow down valve at the base leading to a drain pot.

Figure Four provides pictorial representations of an exemplary supercritical aqueous solvent injection manifold according to embodiments of the present invention. 1: supercritical water injection barrel, c/w welded nozzles to accept injecton spigots, 2: butt weld coupling hub, 3: weld-on tube fitting, bored through, 4: supercritical water injection spigot, 5:tube ftting, elbow, 6: channeling breaker insert, 7: tube fitting, tee, 8: supercritical water delivery tubing.

Figure Five shows a representative process flow diagram of a flash distillation process according to an embodiment of the present invention.

Figure Six shows a representative process flow diagram of a flash distillation process with two condenser stages according to an embodiment of the present invention.