

A method for the storage or transport of pyrolysis oil

- The present invention relates to a method for the storage or transport of a pyrolysis oil. In particular, the method mitigates problems with the formation of solids and films which can render the storage or transport vessel unusable, except with costly and time-consuming cleaning. This is a particular issue arising with the pyrolysis oil obtained from pyrolysis of end-of-life plastics, since they are especially unstable due to the presence of contaminants and unsaturated material.
- End-of-life plastic chemical recycling is an emerging technology designed to recycle mixed waste-plastics into a variety of liquid hydrocarbon products. The waste plastics for use in such a process may, for example, include low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and/or polypropylene (PP).
- Plastic waste is currently a major problem in the world and is causing a significant number of environmental issues. Pyrolysis of waste plastics is commonly accepted as a highly promising solution for this problem.

- Pyrolysis treatments are known for converting these waste plastics into the liquid hydrocarbon products by heating and then pumping the plastic feed in molten form into reactor vessels. The reactor vessels are heated by combustion systems to a temperature in excess of 350°C. This produces rich saturated hydrocarbon vapour from the molten plastic. This flows out of the reactor vessels through contactor vessels and will condense the heavier vapour fractions to maintain a target outlet temperature set point which is determined by the end-product specification. This is then distilled at near-atmospheric pressures in a downstream condensing column. This process obtains a so-called pyrolysis oil.

- WO2021123822 discloses a method for pyrolysing plastic material. The method comprises the steps of: heating and densifying plastic material; conveying the plastic material to one or more reactors; and pyrolysing the plastic material in the one or more reactors. The plastic material is maintained in a heated state during the conveying step.

- WO2016030460 discloses a pyrolysis reactor system suitable for the treatment of end-of-life plastics.

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WO2011077419 also discloses a process for treating waste plastics material to provide at least one on-specification fuel product. Plastics material is melted (4) and then pyrolysed in an oxygen-free atmosphere to provide pyrolysis gases. The pyrolysis gases are brought into contact with plates (13) in a contactor vessel (7) so that some long chain gas components
5 condense and return to be further pyrolysed to achieve thermal degradation. Short chain gas components exit the contactor in gaseous form; and proceed to distillation to provide one or more on-specification fuel products. There is a pipe (12) directly linking the pyrolysis chamber (6) to the contactor (7), suitable for conveying upwardly-moving pyrolysis gases and downwardly-flowing long-chain liquid for thermal degradation. There is a vacuum
10 distillation tower (26) for further processing of liquid feeds from the first (atmospheric) distillation column (20). It has been found that having thermal degradation in the contactor and pyrolysis chamber and by having a second, vacuum, distillation column helps to provide a particularly good quality on-specification liquid fuel.

15 By pyrolysing plastic, it is broken down into a hydrocarbon rich oil. This oil can then be used to produce monomeric species via the refining process. Once in the monomeric state, the molecules can then be polymerised to form virgin grade plastic. This effectively closes the loop on the plastic production process, reducing waste and environmental impact. In addition, all of these foregoing methods and processes are suitable for obtaining a pyrolysis
20 oil which can be used as a fuel, especially for transportation purposes.

While it is desirable for the pyrolysis oil to be used in these applications, it is not always possible for the pyrolysis oil to be used immediately. This is particularly the case where the treatment of the plastics waste is distributed or performed in a batchwise manner. On the
25 other hand, a cracking reactor may be supplied by those multiple distributed production sites, or may also be run on a batchwise basis which does not align with the pyrolysis treatment. This means that it is often necessary to store the pyrolysis oil until it can be used, or to transport it between sites.

30 It is known that oil materials can suffer from the formation of films on contacting surfaces or the development of suspended solids. These issues are referred to herein as the formation of "sediment", although this is not strictly in accordance with the usual meaning of this term. It is known that pyrolysis oil can be washed with water to reduce the formation of sediments during the cracking process. This helps to avoid reactor downtime and improves the viability
35 of the process.

US10760012 describes a system for conversion of crude oil to petrochemicals and fuel products integrating steam cracking and conversion of naphtha into chemical rich reformat. This contemplates water washing of the kerosene product.

- 5 EP0502404 describes a method for decreasing the level of contamination of fuels by performing a washing and centrifugation step on the fuel, such as crude oil.

It is also known to include stabilisers in certain fuels to prevent sediment formation.

- 10 US5711767 discusses the use of monophenols as stabilizers for the prevention of gum formation in gasoline.

US20070289203 discloses an antioxidant additive for biodiesel fuels.

- 15 US5169410 discloses methods for stabilizing gasoline mixtures using antioxidants.

- GB2589936 discloses a method for pyrolysing plastic material. The method comprises the steps of: heating and densifying plastic material; transporting the plastic material to one or more reactors; and pyrolysing the plastic material in the one or more reactors. The plastic is delivered sequentially to one reactor at a time. The plastic material is maintained in a heated state during the transporting step. A system for pyrolysing plastic material is also provided.

- CN106906007 discloses an electronic waste pyrolysis gas purification system and a method for treating electronic waste pyrolysis gas.

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CN108148605 discloses a combined heating type biomass continuous cascade pyrolysis carbon gas co-production system.

- Accordingly, it is an object of the present invention to provide a method for the storage or transport of pyrolysis oil which tackles the problem of sediment formation, or at least to tackle problems associated therewith in the prior art, or provide a commercially viable alternative thereto.

- According to a first aspect the present invention provides a method for the storage or transport of pyrolysis oil, the method comprising:

- 35 (i) providing a holding vessel for the storage or transport of pyrolysis oil;

- (ii) flushing the holding vessel with an inert gas and maintaining the vessel under an inert atmosphere;
- (iii) providing a pyrolysis oil obtained from the pyrolysis of end-of-life plastics material;
- (iv) contacting the pyrolysis oil with water in a wash column, wherein the water is present in amount of at least 50wt% relative to the amount of pyrolysis oil; and
- (v) filling the pyrolysis oil into the holding vessel for storage or transport with a minimum time in the holding vessel of at least 24 hours.

The present disclosure will now be described further. In the following passages different aspects/embodiments of the disclosure are defined in more detail. Each aspect/embodiment so defined may be combined with any other aspect/embodiment or aspects/embodiments unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous. It is intended that the features disclosed in relation to the product may be combined with those disclosed in relation to the method and vice versa.

The present inventors have found that there are particular issues with the use of pyrolysis oils obtained from pyrolysis of end-of-life plastics when seeking to use the pyrolysis oil as a feedstock for a cracking process, or even when using the oil as a transportation fuel. In particular, compared to natural oil materials, the pyrolysis oil obtained from end-of-life plastics has unacceptably high levels of mercury and phosphorous, as well as the typical sulphur and chlorine contaminants. Without wishing to be bound by theory, it is considered that the level of these impurities is a direct result of contaminants mixed with the plastics from their original lifetime use.

It is often the case that the pyrolysis oil may not be produced on a site equipped with a cracking plant, or it may be that the relative scale of the processes favours temporary storage of the pyrolysis oil. The inventors have now found that a pyrolysis oil obtained from end-of-life plastics is particularly unstable on storage or transport. The pyrolysis oil can form sediment or film on the holding vessel, reducing the quality of the oil and rendering the holding vessel unsuitable for further use without cleaning. There is therefore a desire to mitigate these problems.

The problems of sediment formation are particularly severe for pyrolysis oils obtained from end-of-life plastics. This is because there is a large amount of unsaturated material present in the oil which can cross-link, and this is further exacerbated by the presence of the

contaminants carried through from the original materials. The contaminants can catalyse the cross-linking, leading to increased sediment formation. Moreover, when the pyrolysis oil is stored or transported, the sediment can reach such levels that its utility is significantly reduced and the vessel stored or transported can also be fouled to the point that costly,
5 timely or intensive cleaning is required.

The inventors have therefore sought an optimised method for addressing the sediment formation during storage and transport. This is typically encompassing a period from production to use of at least 24 hours, during which time ageing occurs. The inventors have
10 now found that the use of the inert atmosphere, coupled with the water washing and, ideally, a BHT additive, they can address these issues to the point that the transport and storage of the pyrolysis oil becomes commercially viable. In particular, these elements can work together to enable stable storage of the pyrolysis oil until it can be used.

15 The present invention describes a process which allows for the reduction of sediment formed during the ageing of a pyrolysis oil when it is initially washed using water and then left under an inert atmosphere. Employing these techniques in series has been shown to reduce the sediment formation by up to 40%. When further coupled to the presence of an additive, the formation can be reduced by over 80%.

20 Reducing the sediment formation of the pyrolysis oil will also be beneficial when the pyrolysis oil is taken into the petrochemical refining process as it will minimise the formation of these sediments on the cracking equipment. This will prevent the need for cleaning and downtime of the equipment.

25 The present invention provides a method for the storage or transport of pyrolysis oil. The pyrolysis oil will be held in the holding vessel for storage or transport with a minimum time in the holding vessel of at least 24 hours, preferably at least 36 hours and more preferably at least 48 hours. The holding time is preferably less than 1 month, preferably less than 1 week
30 and most preferably less than 3 days.

By storage it is meant the static retention of the oil in a holding vessel, such as a tank. By transport, it is meant that the oil is held in a vessel which is itself conveyed. When transported the oil is subjected to a degree of agitation which may exacerbate the sediment
35 formation.

The method comprises providing a holding vessel for the storage or transport of pyrolysis oil. For static storage the holding vessel is generally a large capacity tank. For transport purposes, the holding vessel will generally be the holding tank on a liquid-transporting truck or train truck.

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- The method comprises flushing the holding vessel with an inert gas and maintaining the vessel under an inert atmosphere. The inert gas is preferably selected from the group consisting of nitrogen, carbon dioxide and noble gases, such as argon, and mixtures of two or more thereof. The use of nitrogen and/or carbon dioxide is advantageous due to the low production costs. It is believed that the absence of atmospheric moisture and oxygen achieved by these steps serves to reduce the sediment formation. Preferably the holding vessel, prior to the addition of the pyrolysis oil, has an oxygen content of less than 1 vol%, more preferably less than 0.1%.
- 15 Preferably the method further comprises a step of washing and drying the holding vessel before the step of flushing the holding vessel with an inert gas. This helps to remove the presence of material which can act as a seed for the growth and formation of further sediment.
- 20 The method comprises providing a pyrolysis oil obtained from the pyrolysis of end-of-life plastics material. End-of-life or contaminated plastic waste feedstock, for plastic chemical recycling, may be received from, for example, municipal recovery facilities, recycling factories, or other plastic collection sources. During a pre-treatment process, the feedstock may be refined such that it only contains plastics suitable for the chemical recycling process,
- 25 such as low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and/or polypropylene (PP). Unsuitable materials, such as metals, paper and card, and glass, as well as humidity from the plastic waste, may be removed.

- The end-of-life plastics material may be obtained from a common source or from mixed sources, including mixed plastic waste obtained from municipal or regional sources and/or from waste streams of polyethylene terephthalates (PET), high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polypropylene, and/or polystyrene. Furthermore, the waste may include thermoplastic elastomers and thermoset rubbers, such as from tires and other articles made from natural rubber,
- 30 polybutadiene, styrene-butadiene, butyl rubber and ethylene propylene diene monomer rubber (EPDM). The waste may include one or more plastics classified as plastic

identification code (PIC) 1 to 7 by the Society of the Plastics Industry. For example, the waste may include one or more of the following plastics: polyethylene terephthalate classified as PIC 1; high-density polyethylene classified as PIC 2; polyvinyl chloride classified as PIC 3; low-density polyethylene classified as PIC 4; polypropylene classified as PIC 5; polystyrene classified as PIC 6; and polycarbonate and other plastics classified as PIC 7.

A pyrolysis oil is obtained by the thermal treatment of these plastics materials. WO2021123822 discloses an optimised process for this pyrolysis and the contents of this document are incorporated herein in their entirety by reference. This sort of pyrolysis oil, because of its source, contains a number of impurities, including: Sulphur; Chlorine; Phosphorus; Metals: especially mercury, but also arsenic, lead, nickel and the like; Silica; Oxygen and Nitrogen. As will be appreciated, the elements, in particular the metals, may be present in their elemental form though will typically be present as compounds such as salts and/or organic impurities comprising said elements (i.e. organosulphur impurities and so forth).

The method comprises contacting the pyrolysis oil with water in a wash column, wherein the water is present in amount of at least 50wt% relative to the amount of pyrolysis oil. Wash columns are known in the art and any suitable design may be employed. Wash columns provide good contact between the oil and the water, whereby soluble contaminants may be removed from the pyrolysis oil.

The water wash unit may include mixing the pyrolysis oil with water for selective transfer of certain solutes from the pyrolysis oil to the water, thus extracting contaminants from the pyrolysis oil. The pyrolysis oil and the water may then be allowed to separate producing a water phase and a phase of a purified pyrolysis oil.

The contact of the pyrolysis oil and water in the water wash unit can occur at any of a variety of suitable conditions to achieve a desirable level of contaminant reduction. For example, the contact may occur at a weight ratio of pyrolysis oil to water of about 2:1 to about 1:2. Preferably the water is present in amount of from 50wt% to 200wt%, relative to the amount of pyrolysis oil, more preferably about 100 to 125wt%. Preferably the contact may occur at temperature of about 10°C to about 100°C. By way of further example, the contact may occur at a pressure of about ambient to about 2100 kPa. Preferably the pyrolysis oil is

contacted with the water for an average contact time of at least 10 minutes, more preferably 20 minutes to 1 hour.

5 The water used in the water wash unit may be any suitable water for removing contaminants from the pyrolysis oil, including but not limited to, fresh water, deionized water, and demineralized water, among others. The water may have a neutral or basic pH. For example, the water may have a pH of about 7 to about 13, about 7 to about 12, about 7 to about 10, or about 7 to about 9. Preferably, the water may be neutral with pH of about 7.

10 The water wash unit may have any of a variety of configurations suitable for liquid-liquid extraction. For example, the water wash unit may utilize a mixer-settler, a column, or a centrifugal contactor. The water wash unit may include any of a variety of different equipment to facilitate contact between the water and recycled pyrolysis oil, including, but not limited to, mixers, tanks, centrifugal contactors, vessels, columns, valves, sensors, and
15 piping, among others.

Any suitable mixing device may be used for facilitating contact between the water and the recycle pyrolysis oil, including, but not limited to, paddle mixers and inline mixers, among others.

20 The method comprises filling the pyrolysis oil into the holding vessel for storage or transport. Filling may be by any conventional technique associated with the specific design of the holding vessel. Critically, the filling must maintain the inert atmosphere in the holding vessel, or fill the vessel to the point that there is no remaining atmosphere included.

25 Preferably the method further comprises adding an alkylphenol derived antioxidant to the pyrolysis oil before step (v) of filling the pyrolysis oil into the holding vessel. Preferably the alkylphenol derived antioxidant comprises one or more antioxidants selected from the group comprising butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT),
30 t-butylhydroquinone (TBHQ), and propyl gallate.

Preferably the alkylphenol derived antioxidant is added in an amount of from 250 to 1000mg per litre of pyrolysis oil, more preferably 500 to 750mg per litre of pyrolysis oil. These levels of addition are particularly suitable for the stabilisation of the pyrolysis oil.

35 Preferably the pyrolysis oil is obtained in a method comprising:

- (I) providing end-of-life plastics material;
- (II) melting the end-of-life plastics material to form a molten plastics material;
- (III) pyrolysing the molten plastics material in an oxygen-free atmosphere to provide pyrolysis gases and a char material;
- 5 (IV) condensing the pyrolysis gases to provide the pyrolysis oil.

More details of this method are provided in the description below.

10 Preferably the end-of-life plastics material is melted in step (II) in a heated extruder at a temperature of from 250 to 350°C. Preferably the pyrolysis of step (III) is conducted in an optionally agitated pyrolysis reactor at a temperature of from 350 to 450°C.

Preferably before step (IV), the method further comprises:

15 passing the pyrolysis gases from step (III) into a contactor having a bank of condenser elements so that some long chain gas components condense on said elements to provide a condensed long chain material;

returning said condensed long chain material to step (III) to be further pyrolysed; and

allowing short chain gas components to exit from the contactor in gaseous form before condensing in step (IV).

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Preferably step (IV) comprises distilling said pyrolysis gases from the contactor in a distillation column.

25 Methods for pyrolysis end-of-life plastics are well known in the art, including, for example, in WO2021123822, WO2016030460 and WO2011077419 which are each incorporated herein by reference. The preferred method of pyrolysis will now be described further in more detail.

Preferably the method for pyrolysis end-of-life plastics involves the steps of:

30 melting a waste plastics material,

pyrolysing the molten material in an oxygen-free atmosphere to provide pyrolysis gases;

bringing the pyrolysis gases into a contactor having a bank of condenser elements so that some long chain gas components condense on said elements,

returning said condensed long-chain material to be further pyrolysed to achieve

35 thermal degradation, and allowing short chain gas components to exit from the contactor in gaseous form; and

distilling said pyrolysis gases from the contactor in a distillation column to provide one or more fuel products.

5 The end-of-life plastic (ELP) from the walking floor silo is discharged into the extruder hopper, which is designed to deliver heated ELP to the reactors. The extruder is supplied with variable speed drives that permit lower flow rates to be fed to the reactors, if required, during start-up and shutdown of an extruder. The extruder heats up the plastic from ambient conditions to the target set temperature using shear force generated by the rotation of the extruder screw. The high temperatures on the outlet of the extruder is required to ensure that
10 the plastic temperature, which is lower than the reactor operating temperature, does not adversely affect the thermal performance of the reactor when loaded in.

The extruder barrel can be electrically heated, especially during start-up. During normal operation, the electric heating function is not used because the shear force from the auger
15 screw will provide sufficient heat to melt the plastic.

Plasticised ELP is expelled from the extruder under high pressure into a melt feed line that connects the extruder to three Reactors via a header pipe. Multiple instruments monitor pressure and temperature along the melt feed line during feeding to assure flow.
20 The plant has multiple jacketed reactors that form the core of the process. Each conical based reactor is enclosed by a reactor jacket which provides the heat required to decompose the ELP and generate the desired hydrocarbon vapour. Each reactor is physically located above a char receiver and below a contactor (condenser elements).
25 Each individual reactor is provided with an agitator designed to maintain thermal efficiency of the process by minimising char build up on the walls of the reactor by maintaining close steel to steel clearance with the vessel walls; suspend any char produced during pyrolysis in the plastic mass to prevent build-up on the internal surfaces of the reactor; and homogenise the molten ELP in the reactor during processing; and remove char once pyrolysis is complete
30 and the char is dry.

The agitator homogenises the vessel mass by pushing ELP down the walls of the reactor, to the centre of the vessel and up the agitator shaft when running in forward. When operating in reverse, it pushes medium down the agitator shaft and from the centre of the vessel to
35 vessel walls. This promotes char removal through a bottom outlet nozzle located at the lowest point of the vessel conical dished end.

An individual reactor is designed to process 5 tonnes of ELP every day. Future generations may have a higher capacity. Reactors are grouped in threes and each trio of reactors is fed sequentially such that only one of each trio of vessels is being fed with fresh ELP at any one
5 time whilst the other two are either completing pyrolysis or processing char.

ELP is fed into a reactor vessel by its respective Extruder. The reactor is operated at 380 to 450°C and up to 0.5 barg in an inerted oxygen free environment. At these temperatures the ELP polymer chains decompose into shorter hydrocarbon chains and are vaporised to form
10 a rich saturated hydrocarbon vapour. This vapour exits the vessel via an outlet located on the top of the vessel which leads to the reactors' respective contactor.

The reactor is designed to operate on a cycle. Each cycle consists of three periods. The first is a ELP feed period known as "charging" in which ELP is loaded to the reactor and
15 pyrolysed. In the second period, pyrolysis is completed and the non-pyrolysable material (char) in the reactor is dried to allow for easy handling after removal from the reactor in anticipation of the next charge of ELP. This stage is called "cooking". The third stage is called "removal" and involves removing char from the reactor by opening the reactor bottom outlet valve and then reversing the reactor's agitator which in turn forces char out of the
20 reactor into the char receiver below it. Once all the char is removed the bottom outlet valve is closed and plastic feeding can recommence.

Char is formed primarily of carbonaceous material, plastic polymer-forming additives, pigmentation and ELP contamination. Char continually forms in the reactor throughout
25 pyrolysis and must be removed prior to commencement of another charge else the effective volume of the reactor reduces.

Char is removed through the bottom outlet nozzle and valve (BOV). When char removal is required the bottom outlet valve is opened to the char receiver below. The agitator is then
30 set to reverse to assist char removal. Char should fall out of the chamber under gravity because of the conical shape of the reactor however if it does not, the agitator has been designed to assist it by breaking up char lumps which may have formed in the nozzle.

Preferably the contactor elements comprises a plurality of plates forming an arduous path for
35 the pyrolysis gases in the contactor. Moreover, preferably the plates are sloped downwardly for runoff of the condensed long-chain hydrocarbon, and include apertures to allow upward

progression of pyrolysis gases. In one embodiment, the contactor elements comprise arrays of plates on both sides of a gas path. Preferably the contactor element plates are of stainless steel. The contactor may be actively cooled such as by a heat exchanger for at least one contactor element.

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Alternative cooling means may comprise a contactor jacket and cooling fluid is directed into the jacket. There may be a valve linking the jacket with a flue, whereby opening of the valve causing cooling by down-draught and closing of the valve causing heating. The valve may provide access to a flue for exhaust gases of a combustion unit of the pyrolysis chamber.

10

Preferably there is a pipe directly linking the pyrolysis chamber to the contactor, the pipe being arranged for conveying upwardly-moving pyrolysis gases and downwardly-flowing long-chain liquid for thermal degradation.

15 Preferably infeed to the pyrolysis chamber is controlled according to monitoring of level of molten plastics in the chamber, as detected by a gamma radiation detector arranged to emit gamma radiation through the chamber and detect the radiation on an opposed side, intensity of received radiation indicating the density of contents of the chamber.

20 Preferably the pyrolysis chamber is agitated by rotation of at least two helical blades arranged to rotate close to an internal surface of the pyrolysis chamber. Optionally, the pyrolysis chamber is further agitated by a central auger. Advantageously, the auger can be located so that reverse operation of it causes output of char via a char outlet.

25 Preferably the temperature of pyrolysis gases at an outlet of the contactor is maintained in the range of 240°C to 280°C. The contactor outlet temperature can be maintained by a heat exchanger at a contactor outlet.

A bottom section of the distillation column is preferably maintained at a temperature in the
30 range of 200°C to 240°C, preferably 210°C to 230°C. The top of the distillation column is preferably maintained at a temperature in the range of 90°C to 110°C, preferably approximately 100°C.

Optionally there is further distillation of some material in a vacuum distillation column. Heavy
35 or waxy oil fractions are drawn from the bottom of the vacuum distillation column and can be recycled back to the pyrolysis chamber. Desired grade on-specification pyrolysis oil can be

drawn from a middle section of the vacuum distillation column. Light fractions are drawn from a top section of the vacuum distillation column and are condensed.

Examples

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The invention will now be described further in relation to the following non-limiting Examples.

Example 1 - Benefits of water washing

- 10 Pyrolysis oil obtained from the pyrolysis of end-of-life plastics was prepared by vacuum filtration through a 0.8 micron nitrocellulose filter. During which, a borosilicate container was prepared by thoroughly cleaning and drying to remove any residues and dust that may affect the ageing results. For the inert atmosphere samples, the borosilicate containers were then filled with an inert gas and left to purge for 10 minutes to displace all the air in the container,
- 15 atmospheric samples were just left to thoroughly dry.

For the water washed samples, 500 mL of the waste plastic pyrolysis oil was then placed into a separation funnel and washed with different amounts of water. The ratio of water:pyrolysis oil is highlighted in Table 1 below.

20

Table 1. Table of samples prepared for ageing study.

Sample	Water: Pyrolysis Oil Ratio
1	None (Air Atmosphere)
2	None (Air Atmosphere)
3	None (Air Atmosphere)
4	None (Inert Atmosphere)
5	None (Inert Atmosphere)
6	None (Inert Atmosphere)
7	0.5:1
8	0.5:1
9	0.5:1
10	1:1
11	1:1
12	1:1
13	2:1
14	2:1
15	2:1

The pyrolysis oil and water were then left to separate for 20 minutes to form 2 distinct layers. 500 mL of the pyrolysis oil layer was then tapped off into the borosilicate glassware.

The samples were then purged with an inert gas for a further 15 minutes and sealed with airtight lids.

- For the blank samples, no water washing was conducted. The blank samples stored under an inert atmosphere were prepared as described above without the water washing step. The blank atmospheric samples were placed into the borosilicate containers and fitted with an airtight lid which contained a breathing tube. Samples were aged for 4 weeks under ambient temperature and pressure and then assessed for their filterable and adherent insolubles. Results are shown below in Table 2.

Table 2. Ageing Results.

Sample	Mass of Oil (g)	Filterable Insolubles Mass (mg)	Adherent Insolubles Mass (mg)	Total Insolubles Mass (mg)	Total Insolubles Mass (mg/kg)
1	392.13	25.4	70.8	96.2	245.33
2	391.52	25.5	70.7	96.2	245.71
3	391.85	29.2	91.2	120.4	307.26
4	393.24	29.1	44.6	73.7	187.42
5	392.56	29.0	38.3	67.3	171.44
6	393.88	27.3	56.8	84.1	213.52
7	391.60	55.0	23.1	78.1	199.44
8	393.19	49.7	19.3	69.0	175.49
9	390.27	40.2	17.1	57.3	146.82
10	390.39	51.3	5.8	57.1	146.26
11	393.04	53.0	18.3	71.3	181.40
12	391.36	50.5	17.1	67.6	172.73
13	391.34	41.5	10.4	51.9	132.62
14	392.44	47.1	16.2	63.3	161.30
15	393.12	51.6	22.4	74.0	188.24

Sample	Average Total Insolubles (mg/kg)	Average Percentage Change from Average Air Blank (%)	Average Percentage Change from Average Inert Blank (%)
1	266.10	0.00%	+39.47%
2			

3			
4	190.79	-28.30%	0.00%
5			
6			
7	173.92	-34.64%	-8.84%
8			
9			
10	166.80	-37.32%	-12.57%
11			
12			
13	160.72	-39.60%	-15.76%
14			
15			

As is shown in Table 2, by storing the pyrolysis oil under only an inert atmosphere (1-3), a sediment reduction of almost 30% is achieved when compared to the sample stored in contact with air. With the extra processing step of water washing, this further reduces the sediment by up to an additional 15%.

In addition, it has also been shown that increasing the ratio of water to oil helps with the reduction in the sediment formation. This is largely observed by significant reduction of adherent insolubles.

Example 2 - Benefits of additive

The pyrolysis oil was prepared by vacuum filtration through a 0.8 micron nitrocellulose filter. During which, a borosilicate container was prepared by thoroughly cleaning and drying to remove any residues and dust that may affect the ageing results. For the inert atmosphere samples, the borosilicate containers were then filled with an inert gas and left to purge for 10 minutes to displace all the air in the container. 500 mL of the pyrolysis oil was then placed into the borosilicate containers with different concentrations of Alkylphenol derived antioxidant, Table 1.

Table 1. Table of samples prepared for ageing study.

Sample	Additive	Concentration (mg/L)	Atmosphere
1	None	0	Ambient
2	None	0	Ambient
3	None	0	Inert
4	None	0	Inert

5	None	0	Inert
6	>99% purity BHT	250	Inert
7	>99% purity BHT	250	Inert
8	>99% purity BHT	250	Inert
9	>99% purity BHT	500	Inert
10	>99% purity BHT	500	Inert
11	>99% purity BHT	500	Inert
12	>99% purity BHT	1,000	Inert
13	>99% purity BHT	1,000	Inert
14	>99% purity BHT	1,000	Inert
15	>99.8% purity BHT	1,000	Inert
16	>99.8% purity BHT	1,000	Inert
17	>99.8% purity BHT	1,000	Inert
18	>99.9% purity BHT	1,000	Inert
19	>99.9% purity BHT	1,000	Inert
20	>99.9% purity BHT	1,000	Inert

The inert samples were then purged with an inert gas for a further 15 minutes and sealed with airtight lids. The ambient samples were fitted with a lid and a breathing tube to allow contact with air without the chance of any dust settling in the pyrolysis oil over the ageing period.

All samples were then heated to 40°C for 15 minutes to dissolve any additive. The samples without additive were also heated to make sure all the pyrolysis oil was treated similarly.

10 Samples were aged for 4 weeks under ambient conditions and then assessed for their filterable and adherent insolubles. Results are shown in Table 2.

Table 2. Ageing Results.

Sample	Mass of Oil (g)	Filterable Insolubles Mass (mg)	Adherent Insolubles Mass (mg)	Total Insolubles Mass (mg)	Total Insolubles Mass (mg/kg)
1	389.56	12.2	137.8	150.0	385.05
2	389.15	11.8	155.4	167.2	429.66

3	392.35	17.9	49.1	67.0	170.77
4	392.31	17.6	72.7	90.3	230.18
5	391.67	16.8	71.3	88.1	224.94
6	392.40	19.0	42.8	61.8	157.49
7	392.30	14.1	44.9	59.0	150.39
8	392.36	15.8	11.3	27.1	69.07
9	392.19	12.1	45.4	57.5	146.61
10	391.90	14.5	56.6	71.1	181.43
11	391.17	12.7	15.2	27.9	71.33
12	391.93	9.8	84.0	93.8	239.33
13	391.71	15.6	76.1	91.7	234.10
14	391.44	20.2	17.9	38.1	97.33
15	391.32	23.7	27.1	50.8	129.82
16	391.39	12.0	18.1	30.1	76.91
17	391.48	16.6	43.0	59.6	152.24
18	386.20	15.4	82.0	97.4	252.20
19	390.10	18.5	41.5	60.0	153.81
20	389.14	15.0	15.9	30.9	79.41

Sample	Average Total Insolubles (mg/kg)	Percentage Change from Air Blank (%)	Percentage Change from Inert Blank (%)
1	407.35	0.0	95.3
2			
3	208.63	-48.8	0.0
4			
5			
6	125.65	-69.2	-39.8
7			
8			
9	133.12	-67.3	-36.2
10			
11			

12	190.25	-53.3	-8.8
13			
14			
15	119.66	-70.6	-42.6
16			
17			
18	161.81	-60.3	-22.4
19			
20			

As is shown in Table 2, by storing the pyrolysis oil under an inert atmosphere, a sediment reduction of almost 50% is observed. With the extra addition of an alkylated phenol antioxidant at 1000 mg/L, this further reduces the sediment by up to 70%. It has also been shown that an alkylated phenol at 250 and 500 mg/L addition can lead to further sediment reductions than just storing under an inert atmosphere.

Purity of the BHT does not seem to greatly affect the sediment reduction.

The term “comprising” as used herein can be exchanged for the definitions “consisting essentially of” or “consisting of”. The term “comprising” is intended to mean that the named elements are essential, but other elements may be added and still form a construct within the scope of the claim. The term “consisting essentially of” limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. The term “consisting of” closes the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith.

The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

For the avoidance of doubt, the entire contents of all documents acknowledged herein are incorporated herein by reference.

Claims:

1. A method for the storage or transport of pyrolysis oil, the method comprising:
 - (i) providing a holding vessel for the storage or transport of pyrolysis oil;
 - 5 (ii) flushing the holding vessel with an inert gas and maintaining the vessel under an inert atmosphere;
 - (iii) providing a pyrolysis oil obtained from the pyrolysis of end-of-life plastics material;
 - (iv) contacting the pyrolysis oil with water in a wash column, wherein the water is present in amount of at least 50wt% relative to the amount of pyrolysis oil; and
 - 10 (v) filling the pyrolysis oil into the holding vessel for storage or transport with a minimum time in the holding vessel of at least 24 hours;wherein the method further comprises adding antioxidant comprising one or more selected from the group comprising butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), t-butylhydroquinone (TBHQ), and propyl gallate to the pyrolysis oil
- 15 before step (v) in an amount of from 250 to 750 mg per litre of pyrolysis oil.
2. The method according to claim 1, wherein the water is present in amount of from 100wt% to 200wt%, relative to the amount of pyrolysis oil.
- 20 3. The method according to claim 1 or claim 2, wherein the pyrolysis oil is contacted with the water for an average contact time of at least 10 minutes.
4. The method according to any preceding claim, wherein the method further comprises a step of washing and drying the holding vessel before the step of flushing the holding
- 25 vessel with an inert gas.
5. The method according to any preceding claim, wherein the pyrolysis oil is obtained in a method comprising:
 - (I) providing end-of-life plastics material;
 - 30 (II) melting the end-of-life plastics material to form a molten plastics material;
 - (III) pyrolysing the molten plastics material in an oxygen-free atmosphere to provide pyrolysis gases and a char material;
 - (IV) condensing the pyrolysis gases to provide the pyrolysis oil.
- 35 6. The method according to claim 5, wherein the end-of-life plastics material is melted in step (II) in a heated extruder at a temperature of from 250 to 350°C.

7. The method according to claim 5 or 6, wherein the pyrolysis of step (III) is conducted in an optionally agitated pyrolysis reactor at a temperature of from 350 to 450°C.
- 5 8. The method according to any of claims 5 to 7, wherein, before step (IV), the method further comprises:
- passing the pyrolysis gases from step (III) into a contactor having a bank of condenser elements so that some long chain gas components condense on said elements to provide a condensed long chain material;
- 10 returning said condensed long chain material to step (III) to be further pyrolysed; and allowing short chain gas components to exit from the contactor in gaseous form before condensing in step (IV).
9. The method according to any of claims 5 to 8, wherein step (IV) comprises distilling
- 15 said pyrolysis gases from the contactor in a distillation column.