

Method for Processing a
Phosphorus-containing Hydrocarbon Stream

The present invention relates to a method for processing a phosphorus (P)-containing hydrocarbon stream.

In refinery processes, material flows of different origins are used, which can be contaminated with different impurities. Silicon (Si) and phosphorus (P) play an important role in this. For example, material flows may be contaminated by silicone oils used as lubricants and sealants in refinery systems. Silicone oils are sometimes also used as process additives or anti-foaming agents, for example in cokers or Thermal Gasoil Units (TGU). P compounds are also often used as additives, for example as corrosion inhibitors, which can manifest themselves in P-containing impurities.

Such impurities are particularly important in connection with synthetic crude oils. Synthetic crude oil, sometimes also referred to as Syncrude, can be obtained from different processes. For example, synthetic crude oil may be shale oil, which is obtained from oil shale by pyrolysis. Another source is hydrocarbons obtained from oil sand, in particular bitumen, from which synthetic crude oil can be obtained by upgrading. In addition, synthetic crude oil can also be produced from plastic material, for example plastic waste, by cracking. Another source of synthetic crude oils are biomass, wood and other biological raw materials, which may already contain organic P compounds from natural sources (such as phospholipids and nucleic acids) and to which Si and P compounds are often added in the form of impregnations and surface treatments (such as flame retardants, surface improvement by silicones, silicone adhesives, etc.). Synthetic crude oils typically contain different impurities, which may have adverse effects on refining processes and refinery systems or can make the crude oil completely unsuitable for certain refining processes. The type and content of the impurities can vary greatly depending on the source and method for obtaining the synthetic crude oil. However, Si and P play an important role.

Si and P can cause problems in connection with different

processes in refinery systems. For example, Si and P compounds can be harmful to catalysts in hydrogenation systems and lead to vitrification. Typically, Si and P must therefore be removed before such a process. Separation usually takes place by means of elaborate guard beds. However, guard beds incur running costs and must be replaced regularly, which in turn requires the system to be shut down. When large amounts of hydrocarbon streams are used, guard beds are quickly overloaded even at low Si or P contents and must be replaced frequently.

There is therefore a need for new and better methods to utilize Si and/or P-containing hydrocarbon streams. It is an object of the present invention to provide such methods.

The present invention therefore relates to a method for processing a phosphorus (P)-containing hydrocarbon stream, the method comprising the following steps:

- providing the hydrocarbon stream;
- separating a P-rich fraction from the hydrocarbon stream, wherein the P-rich fraction has a boiling range with a lower end of at least 350 °C and a P content of at least 10 ppm;
- processing the P-rich fraction in a Fluid Catalytic Cracking (FCC) unit.

In a preferred embodiment, the hydrocarbon stream is a phosphorus (P)- and silicon (Si)-containing hydrocarbon stream, wherein an Si-rich fraction is separated from the hydrocarbon stream in addition to the P-rich fraction, wherein the Si-rich fraction has a boiling range with a lower end of at least 120 °C and a Si content of at least 10 ppm, and wherein the P-rich fraction and the Si-rich fraction are processed in the FCC unit.

To date, the prior art has generally assumed that impurities must be removed from hydrocarbon streams prior to refinery processes such as FCC. For example, WO 2021/201932 A1 describes a method for the pyrolysis of plastic waste, in which the entire liquid fraction from the pyrolysis is fed to an FCC unit. It is expressly pointed out that impurities - in addition to numerous others also P compounds and silica - must be removed in the plastic waste to as much as possible below 5 ppm (WO 2021/201932 A1, [0036]). If this is not achieved, a separate guard bed must

be provided to remove the impurities (WO 2021/201932 A1, [0037]). In addition, a pretreater unit can be provided in front of the FCC unit to remove sulfur, nitrogen, phosphorus, silica, dienes and metals (WO 2021/201932 A1, [0014]).

In the course of the present invention, it has now surprisingly been found that, in the case of Si and P compounds, it is not necessary to remove them before an FCC process. What's more - surprisingly, an FCC unit can even be used specifically to remove such compounds. This is convincingly shown by the examples contained herein, wherein hydrocarbon streams overdosed with silicone oil or organic P compounds could still be treated without problems in an FCC unit even at concentrations of 1 % by weight (i.e. 10,000 ppm). Si and P were efficiently removed even at these high concentrations.

Without being bound to a theory, the inventors explain this by the fact that, during the FCC process, any organic components of Si and P compounds are cleaved, formally forming SiO_2 or PO_4^{3-} groups. In contrast to hydrogenation systems, in which the uppermost catalyst layer can vitrify, the SiO_2 or PO_4^{3-} groups do not harm the FCC process. Instead, they can even expand the backbone of FCC catalysts. In FCC processes, zeolites, which consist of a silicate skeleton and which can be modified with phosphate groups in the active centre, are regularly used as catalysts. According to the inventors, the SiO_2 or PO_4^{3-} groups formed in the process can accumulate on existing catalysts and subsequently act as catalysts themselves or at least not negatively influence the catalyst activity. This effect is particularly favorable if a zeolite is already used as the starting catalyst; however, the use of other catalysts is also possible.

In connection with the invention, "P-containing" is preferably understood to mean a P content of at least 0.1 ppm, preferably at least 1 ppm, in particular at least 10 ppm.

The hydrocarbon stream preferably contains organic P compounds, preferably triaryl phosphites and/or triaryl phosphates. Triaryl phosphites are used, for example, as additives in plastics, e.g. as flame retardants. In the pyrolysis of plastic material, triaryl phosphites can be partially converted into stable triaryl phosphates. Therefore, synthetic crude oils obtained

from the depolymerization of plastic, for example, may contain significant amounts of triaryl phosphites and/or triaryl phosphates. It is therefore also preferred if the hydrocarbon stream is produced from the depolymerization of plastic material containing triaryl phosphites. The triaryl phosphites are preferably tris(2,4-di-tert-butylphenyl)phosphite, trisphenyl phosphite and/or tristolyl phosphite. It is particularly preferred if the triaryl phosphite is tris(2,4-di-tert-butylphenyl)phosphite (CAS Registry Number 31570-04-4). The concentration of organic P compounds, in particular of said preferred organic P compounds, in the hydrocarbon stream is preferably at least 0.1 ppm, preferably at least 1 ppm, in particular at least 10 ppm.

The P-rich fraction preferably has a P content of at least 20 ppm, preferably at least 30 ppm, more preferably at least 40 ppm, more preferably at least 50 ppm, more preferably at least 60 ppm, more preferably at least 70 ppm, more preferably at least 80 ppm, more preferably at least 90 ppm, more preferably at least 100 ppm. It is particularly preferred if the P content is between 10 and 10,000 ppm, more preferably between 15 and 2000 ppm, more preferably between 20 and 800 ppm, more preferably between 30 and 700 ppm, more preferably between 40 and 600 ppm, more preferably between 50 and 550 ppm, more preferably between 60 and 500 ppm, more preferably between 70 and 450 ppm, more preferably between 80 and 400 ppm, more preferably between 90 and 350 ppm, more preferably between 100 and 300 ppm.

Preferably, by processing the P-rich fraction in the FCC unit, a P-poor FCC product is obtained.

"P-poor" is preferably understood here to mean a lower P content than "P-rich", i.e. the P-poor FCC product has a lower P content than the P-rich fraction. Preferably, the P-poor FCC product has a P content of less than 10 ppm, preferably less than 5 ppm, more preferably less than 1 ppm, more preferably less than 0.5 ppm.

Within the scope of the invention, it has been found that P compounds can typically be present, in particular, in hydrocarbon fractions with boiling ranges from 350 °C. This also applies in particular to the above-mentioned triaryl phosphites and triaryl phosphates. Therefore, if the P-rich fraction has a boiling

range with a lower end of at least 350 °C, a large portion of the P compounds can be separated from the hydrocarbon stream without entraining valuable lighter fractions with boiling ranges below 350 °C. These lighter fractions can therefore advantageously be utilized elsewhere. It is therefore preferred if the P-rich fraction has a boiling range with a lower end of at least 350 °C, preferably at least 360 °C, more preferably at least 370 °C, more preferably at least 380 °C, more preferably at least 385 °C, more preferably at least 390 °C, more preferably at least 395 °C, more preferably at least 400 °C.

In order to ensure that the most important P compounds are separated with the P-rich fraction, on the other hand, it is also advantageous if the lower end of the boiling range of the P-rich fraction is not too high. The lower end of the boiling range is therefore preferably between 350 °C and 500 °C, preferably between 360 °C and 480 °C, more preferably between 370 °C and 470 °C, more preferably between 380 °C and 460 °C, more preferably between 385 °C and 450 °C, more preferably between 390 °C and 440 °C, more preferably between 395 °C and 430 °C, more preferably between 400 °C and 420 °C.

In embodiments of the method according to the invention, it is also preferred if the P-rich fraction has a boiling range with an upper end of at most 1000 °C, preferably at most 900 °C, more preferably at most 800 °C, more preferably at most 700 °C, more preferably at most 600 °C, more preferably at most 500 °C. The upper end of the boiling range is preferably between 450 °C and 1000 °C, more preferably between 500 °C and 900 °C, more preferably between 600 °C and 800 °C. By providing a boiling range with a lower and an upper end as indicated, those fractions with the most important P compounds can be cut out of the hydrocarbon stream in a targeted manner.

Within the scope of the invention, it has proven advantageous for the P-rich fraction to be subjected to a solids depletion before processing in the FCC unit. Preferably, therefore, the solids-depleted P-rich fraction is processed in the FCC unit. It has been shown that the P-rich fraction may often contain solids, for example inorganic salts. Such solids can have a negative impact on the FCC unit and damage the FCC catalyst. This applies in particular if the hydrocarbon stream is a

synthetic crude oil stream, for example a synthetic crude oil stream obtained from the depolymerization of plastic material. Plastic material may often contain fillers and similar additives, which can result in higher solids contents in the synthetic crude oil stream and subsequently in the P-rich fraction.

A solids depletion is preferably understood herein to mean a reduction in the solids content. The solids content of the P-rich fraction processed in the FCC unit is preferably less than 3 % by weight, more preferably less than 1 % by weight, even more preferably less than 0.5 % by weight, even more preferably less than 0.3 % by weight, even more preferably less than 0.2 % by weight, even more preferably less than 0.1 % by weight. The solids content is preferably determined according to the standard ASTM D5631-21.

The solids depletion may take place before or after separating the P-rich fraction from the hydrocarbon stream, i.e. the P-rich fraction can also have passed through the solids depletion as part of the hydrocarbon stream. In addition, further steps may take place between the solids depletion and the processing of the P-rich fraction in the FCC unit, e.g. further fractions can also be separated from the solids-depleted P-rich fraction.

In order to minimize negative effects on the FCC process and the FCC catalyst, it is preferred if the P-rich fraction processed in the FCC unit has an ash content of less than 0.1 % by weight, preferably less than 0.05 % by weight, more preferably less than 0.02 % by weight, more preferably less than 0.01 % by weight. The ash content may preferably be determined in accordance with the ISO 6245:2002 standard.

In order to minimize negative effects on the FCC process and the FCC catalyst, it is also preferred if the P-rich fraction processed in the FCC unit has low coke formation. The P-rich fraction preferably has a CCR (Conradson Carbon Residue) of less than 0.5 % by weight, preferably less than 0.2 % by weight, more preferably less than 0.1 % by weight, more preferably less than 0.05 % by weight. The CCR may preferably be determined according to the standard ASTM D189-06(2019).

In a preferred embodiment, the solids depletion comprises the following steps: adding a solvent to the P-rich fraction to

form a mixture; separating solids from the mixture. The addition of a solvent to the P-rich fraction has the advantage that waxes present in the P-rich fraction can be at least partially dissolved in the solvent and can thus be separated particularly well from the undesirable solids.

The solvent can be added to the P-rich fraction by means of an introduction device. The introduction device may have a metering device, such as a metering pump. To add the solvent, the P-rich fraction can be fed to a container to which the introduction device can be connected. The container may be heatable so that the dissolving of wax contained in the P-rich fraction in the solvent can take place at a certain temperature.

The mixture preferably has a temperature of at least 80 °C, more preferably at least 100 °C, even more preferably at least 120 °C, even more preferably 140 °C, even more preferably at least 160 °C. If the mixture has such a high temperature, waxes present in the P-rich fraction can be dissolved even better and solids can be removed even more efficiently. In particular, it is preferred if the mixture has a temperature in the range from 80 to 240 °C, more preferably from 100 to 160 °C, even more preferably 100 to 140 °C.

The mixture may preferably be subjected to a pressure in the range from 1 to 25 bar, in particular in the range from 5 to 16 bar. As a result, the method can be further improved and rapid dissolution of wax in the solvent can be achieved.

The solvent may preferably have a boiling temperature (or boiling range) in the range from 20 to 270 °C, more preferably from 20 to 250 °C, even more preferably from 35 to 200 °C, even more preferably from 50 to 150 °C. This has proven to be particularly beneficial for the efficient dissolution of wax and also enables efficient subsequent separation of the solvent. The boiling temperature (or boiling range) of the solvent may be determined according to the standard ASTM D5399-09:2017 or ASTM D2887-22:2022.

In a preferred embodiment, the solvent comprises at least 10 % by weight, more preferably at least 20 % by weight, even more preferably at least 50 % by weight, even more preferably at least 70 % by weight, even more preferably at least 90 % by

weight, of an aliphatic hydrocarbon, based on the total weight of the solvent. The solvent preferably consists of an aliphatic hydrocarbon, or of a mixture consisting of two or more aliphatic hydrocarbons. As the proportion of aliphatic hydrocarbon increases, not only can the solvent's ability to dissolve wax improve, but the solubility of solids in the solvent can also be reduced. In the case of a high proportion of aromatics in the solvent, however, certain solids, for example asphaltenes or tar, can partially dissolve in the solvent, which can make separation difficult.

The aliphatic hydrocarbon is preferably selected from the group of aliphatic hydrocarbons having up to 15 carbon atoms per molecule, in particular from 4 to 12 carbon atoms per molecule. N-pentane, n-hexane, n-heptane, iso-dodecane, n-tetradecane or a mixture thereof have proven to be particularly suitable.

The mass ratio between the P-rich fraction and the solvent may preferably be in the range of 3:1 to 1:5, more preferably in the range of 1:1 to 1:3. This allows the waxes to dissolve in the solvent quickly and as completely as possible.

The separation of the solids from the mixture can take place using any separation method, preferably by gravimetric separation, filtration and/or centrifugal force separation. Gravimetric separation may include sedimentation and/or decantation. In particular, the separation can take place using filtration. The filtration may be carried out with a filter medium, which may comprise an activated carbon or a bleaching earth. As a result, any polar components (e.g. a tar or a polyphenol) dissolved in the solvent together with the wax can be well separated and adsorbed by the filter medium. Even small particles can be easily removed during filtration.

The solids may preferably comprise inorganic salts, ceramic raw materials, asphaltenes, tar, and/or coke. In particular, the solids may comprise talc, iron oxide (e.g., ferric oxide), aluminum oxide, titanium dioxide, magnesium oxide, and/or calcium carbonate. If the hydrocarbon stream is a synthetic crude oil stream, in particular from the depolymerization of plastic material, the solid may comprise an additive contained in the plastic material. For example, the additive may comprise a filler, a

color pigment, and/or an additive.

In a preferred embodiment, after separating the solids from the mixture, at least a portion of the solvent is separated from the mixture. The separating of the solvent preferably takes place before processing in the FCC unit. This separation makes it possible to reduce the amount of material processed in the FCC unit, thus increasing the efficiency of the process.

Separating the solvent may include evaporation or extraction under pressure. The separation of the solvent is preferably carried out at a temperature in the range from 50 to 280 °C, more preferably from 80 to 150 °C, even more preferably from 100 to 130 °C. The separation of the solvent is preferably carried out at a pressure in the range from 0.1 to 2.5 bar, preferably from 0.5 to 1 bar.

In a preferred embodiment, at least a portion of the separated solvent is reused for the solids depletion. Before being recycled into the method, the solvent may preferably be additionally purified, preferably by evaporation, in particular by rotary evaporation.

In a preferred embodiment, the hydrocarbon stream is a phosphorus (P)- and silicon (Si)-containing hydrocarbon stream, wherein an Si-rich fraction is separated from the hydrocarbon stream in addition to the P-rich fraction, wherein the Si-rich fraction has a boiling range with a lower end of at least 120 °C and a Si content of at least 10 ppm, and wherein the P-rich fraction and the Si-rich fraction are processed in the FCC unit. Preferably, a P- and Si-poor FCC product is obtained from the processing of the P-rich fraction and the Si-rich fraction.

Also disclosed is a method for processing a silicon (Si)-containing hydrocarbon stream, the method comprising the following steps: providing the hydrocarbon stream; separating an Si-rich fraction from the hydrocarbon stream, wherein the Si-rich fraction has a boiling range with a lower end of at least 120 °C and a Si content of at least 10 ppm; and processing the Si-rich fraction in a Fluid Catalytic Cracking (FCC) unit. This method can also be used independently of the above-described method for processing a P-containing hydrocarbon stream.

A preferred embodiment relates to a method for processing a

phosphorus (P) and silicon (Si)-containing hydrocarbon stream, the method comprising the following steps:

- providing the hydrocarbon stream;
- separating a P-rich fraction from the hydrocarbon stream, wherein the P-rich fraction has a boiling range with a lower end of at least 350 °C and a P content of at least 10 ppm;
- separating an Si-rich fraction from the hydrocarbon stream, wherein the Si-rich fraction has a boiling range with a lower end of at least 120 °C and a Si content of at least 10 ppm;
- processing the P-rich fraction and the Si-rich fraction in a Fluid Catalytic Cracking (FCC) unit.

Preferably, a P-poor and Si-poor FCC product is obtained from the processing of the P-rich fraction and the Si-rich fraction.

In connection with the invention, "Si-containing" is preferably understood to mean a Si content of at least 0.1 ppm, preferably at least 1 ppm, in particular at least 10 ppm. The hydrocarbon stream preferably contains organic Si compounds, preferably silicone oils or siloxanes, more preferably dimethylsiloxanes, in particular cyclic dimethylsiloxanes, preferably selected from the group consisting of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane. The concentration of organic Si compounds, in particular of said preferred organic Si compounds, in the hydrocarbon stream is preferably at least 0.1 ppm, preferably at least 1 ppm, in particular at least 10 ppm.

The Si-rich fraction preferably has a Si content of at least 20 ppm, preferably at least 30 ppm, more preferably at least 40 ppm, more preferably at least 50 ppm, more preferably at least 60 ppm, more preferably at least 70 ppm, more preferably at least 80 ppm, more preferably at least 90 ppm, more preferably at least 100 ppm. It is particularly preferred if the Si content is between 10 and 10,000 ppm, more preferably between 15 and 2000 ppm, more preferably between 20 and 800 ppm, more preferably between 30 and 700 ppm, more preferably between 40 and 600 ppm, more preferably between 50 and 550 ppm, more preferably between 60 and 500 ppm, more preferably between 70 and 450 ppm,

more preferably between 80 and 400 ppm, more preferably between 90 and 350 ppm, more preferably between 100 and 300 ppm.

Preferably, by processing the Si-rich fraction in the FCC unit, an Si-poor FCC product is obtained. "Si-poor" is preferably understood here to mean a lower Si content than "Si-rich", i.e. the Si-poor FCC product has a lower Si content than the Si-rich fraction. Preferably, the Si-poor FCC product has a Si content of less than 10 ppm, preferably less than 5 ppm, more preferably less than 1 ppm, more preferably less than 0.5 ppm.

Within the scope of the invention, it has been found that Si compounds can typically be present, in particular, in hydrocarbon fractions with boiling ranges from 120 °C. If the hydrocarbon stream is, for example, a synthetic crude oil stream produced from a starting material containing Si polymers - for example, a hydrocarbon stream obtained from the depolymerization of plastic material - the hydrocarbon stream may contain large amounts of cyclic dimethylsiloxanes, which are formed from the Si polymers in the course of the pyrolysis. These can be, in particular, the following compounds:

- Hexamethylcyclotrisiloxane (boiling point: 134-135 °C);
- Octamethylcyclotetrasiloxane (boiling point: 171-175 °C);
- Decamethylcyclopentasiloxane (boiling point: 210 °C);
- Dodecamethylcyclohexasiloxane (boiling point: 245 °C).

Silicone oils, which are used as anti-foaming agents or as lubricants and sealants, often also have boiling points of > 200 °C.

Therefore, if the Si-rich fraction has a boiling range with a lower end of at least 120 °C, a large portion of the Si compounds can be separated from the hydrocarbon stream without entraining valuable lighter fractions with boiling ranges below 120 °C. These lighter fractions can therefore advantageously be utilized elsewhere. It is preferred if the Si-rich fraction has a boiling range with a lower end of at least 125 °C, preferably at least 130 °C, more preferably at least 135 °C, more preferably at least 140 °C, more preferably at least 145 °C, more preferably at least 150 °C, more preferably at least 155 °C, more preferably at least 160 °C, more preferably at least 170 °C. In

this way, the Si compound can be separated in an even more targeted manner and even larger boiling ranges can be utilized elsewhere.

In order to ensure that the most important Si compounds are separated with the Si-rich fraction, on the other hand, it is also advantageous if the lower end of the boiling range of the Si-rich fraction is not too high. The lower end of the boiling range is therefore preferably between 120 °C and 230 °C, preferably between 130 °C and 220 °C, more preferably between 140 °C and 210 °C, more preferably between 145 °C and 205 °C, more preferably between 150 °C and 200 °C, more preferably between 155 °C and 195 °C, more preferably between 160 °C and 190 °C, more preferably between 165 °C and 185 °C, more preferably between 170 °C and 180 °C.

In embodiments of the method according to the invention, it is also preferred if the Si-rich fraction has a boiling range with an upper end of at most 500 °C, preferably at most 450 °C, more preferably at most 400 °C, more preferably at most 350 °C, more preferably at most 300 °C, more preferably at most 280 °C, more preferably at most 270 °C, more preferably at most 260 °C, more preferably at most 255 °C, more preferably at most 250 °C, more preferably at most 245 °C, more preferably at most 240 °C, more preferably at most 235 °C, more preferably at most 230 °C, more preferably at most 225 °C. The upper end of the boiling range is preferably between 205 °C and 500 °C, more preferably between 210 °C and 400 °C, more preferably between 215 °C and 300 °C, more preferably between 220 °C and 280 °C, more preferably between 225 °C and 260 °C, more preferably between 230 °C and 250 °C, more preferably between 235 °C and 245 °C. By providing a boiling range with a lower and an upper end as indicated, those fractions with the most important Si compounds can be cut out of the hydrocarbon stream in a targeted manner. This applies in particular to the above-mentioned cyclic dimethylsiloxanes. It is therefore particularly advantageous to provide the specified boiling ranges if the hydrocarbon stream is a synthetic crude oil stream, in particular a hydrocarbon stream obtained from the depolymerization of plastic material.

In a preferred embodiment of the method according to the invention, a light fraction is separated from the hydrocarbon

stream in addition to the Si-rich fraction. Preferably, the light fraction is a naphtha fraction. The light fraction preferably has a boiling range with an upper end of at most 200 °C, preferably at most 190 °C, more preferably at most 180 °C, more preferably at most 170 °C, more preferably at most 160 °C. The choice of such a boiling range for the light fraction has the advantage that significant Si compounds are generally not contained therein, and the light fraction can thus be further used without additional separation of Si compounds, for example as a valuable naphtha fraction, e.g. in a naphtha hydrotreating system.

In a preferred embodiment, the light fraction has a Si content of less than 20 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, more preferably less than 1 ppm. It is also preferred if the light fraction has a P content of less than 20 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, more preferably less than 1 ppm.

Within the scope of the invention, it has proven to be advantageous if the Si-rich fraction is washed with at least one aqueous wash solution before processing in the FCC unit. Thus, the washed Si-rich fraction is preferably processed in the FCC unit. Such washing can remove unwanted compounds, which may be present in the Si-rich fraction and which can have negative effects on the FCC unit. Thus, hydrocarbon streams often contain basic compounds, e.g. amines, which can partially deactivate the typically acidic FCC catalyst. This is particularly the case if the hydrocarbon stream is a synthetic crude oil stream. For example, amines from polyamide contained in plastic material or from biomass can enter the Si-rich fraction. With an aqueous wash, such basic compounds, especially amines, can be removed before the FCC unit. The scrubbing with the at least aqueous wash solution may take place before or after the separation of the Si-rich fraction from the hydrocarbon stream, i.e. the Si-rich fraction may also pass through the scrubbing as part of the hydrocarbon stream. In addition, further steps may take place between the washing of the Si-rich fraction and the processing in the FCC unit, e.g. further fractions can also be separated from the washed Si-rich fraction.

It is particularly preferred in this context if the pH of

the at least one aqueous wash solution is less than 8, preferably less than 7, more preferably less than 6, more preferably less than 5, more preferably less than 4, even more preferably less than 3, even more preferably less than 2, most preferably less than 1. This enables particularly efficient removal of basic compounds. It is particularly preferred if the pH of the aqueous wash solution is in the range from 0 to 8, preferably 0.5 to 7, more preferably 1 to 6, more preferably 1 to 5, more preferably 2 to 4, most preferably 2.5 to 3.5.

In a preferred embodiment, the at least one aqueous wash solution contains sulfuric acid. The concentration of sulfuric acid is preferably between 0.5 and 10 % by weight, in particular between 1 and 5 % by weight.

The washing with the at least one aqueous wash solution preferably takes place at a temperature of at least 20 °C, preferably at least 30 °C, more preferably at least 40 °C, more preferably at least 50 °C, more preferably at least 60 °C, more preferably at least 70 °C. The provision of such a high temperature enables a particularly thorough removal of the undesired basic compounds. It is particularly preferred if the washing takes place at a temperature in the range from 20 °C to 120 °C, preferably from 30 °C to 110 °C, more preferably from 40 °C to 100 °C, even more preferably from 50 °C to 90 °C, even more preferably from 60 °C to 80 °C.

Typically, scrubbing the Si-rich fraction with an aqueous wash solution includes mixing the Si-rich fraction with the aqueous wash solution, followed by separating the scrubbed Si-rich fraction. Preferably, the washing is carried out in a mechanical mixer, in a static mixer and/or in a mixer-settler. It has proven to be particularly advantageous if the washing is carried out in a mixer-settler. Typically, mixer-settlers comprise a continuously operated mixing zone and a continuously operated settling zone and therefore allow the mixing with the aqueous wash solution, as well as the subsequent settling process to separate the phases and separate the purified Si-rich fraction in a continuous process.

Particularly suitable washing processes for the Si-rich fraction are known from WO 2023/041680 A1.

The Si-rich fraction and the P-rich fraction may be mixed in the FCC unit prior to processing so that a mixture containing the Si-rich fraction and the P-rich fraction is processed in the FCC unit. Alternatively, the Si-rich fraction and the P-rich fraction can also be processed separately in the FCC unit. In a preferred embodiment, the Si-rich fraction and/or the P-rich fraction is mixed with another hydrocarbon stream prior to processing in the FCC unit. This is particularly advantageous since the Si-rich fraction and/or the P-rich fraction can thus be processed as a co-feed in an existing FCC process.

In connection with the method according to the invention, processing in an FCC unit is preferably understood as bringing into contact with an FCC catalyst at a temperature of at least 400 °C, preferably at least 450 °C, more preferably at least 480 °C, wherein hydrocarbons contained in the Si-rich fraction and/or in the P-rich fraction are preferably cracked, i.e. preferably longer hydrocarbon chains are converted into shorter hydrocarbon chains. The contacting preferably takes place in a fluidized-bed reactor. The FCC catalyst is preferably a silicate or an aluminate, particularly preferably a zeolite.

In a preferred embodiment, the FCC unit comprises a catalyst comprising zeolites. As explained at the beginning, zeolites are particularly suitable for the removal of Si and P according to the method according to the invention, since the free Si=O or Si-OH groups of the catalyst can react with Si and/or P groups, whereby the catalyst can grow by the respective number of Si or P atoms from the impurities. The organic residue of organic Si and P compounds can be removed under FCC conditions.

Particularly preferred catalysts are zeolites which are modified with phosphate groups. The zeolites may also be modified with rare earth elements. For example, the catalyst may be zeolite Y.

Preferably, the FCC unit has a riser nozzle. In particular, a riser nozzle enables lighter fractions to be better introduced into the FCC unit. Preferably, the Si-rich fraction and the P-rich fraction are introduced into the FCC unit via separate riser nozzles. This facilitates the processing of fractions with different boiling ranges.

Preferably, the FCC product comprises ethylene and/or propylene.

In a preferred embodiment, the hydrocarbon stream is a synthetic crude oil stream. In connection with the invention, a "synthetic crude oil stream" is preferably understood to mean a material flow containing a synthetic crude oil or a fraction of a synthetic crude oil. Preferably, the synthetic crude oil stream consists of synthetic crude oil or a fraction thereof. Within the scope of the invention, it is particularly preferred if the synthetic crude oil stream comprises, in particular consists of, a pyrolysis oil or a fraction thereof. The pyrolysis oil is preferably a pyrolysis oil obtained from biomass, in particular wood, and/or plastic. As mentioned at the onset, pyrolysis oils from biomass or wood may already contain organic P compounds (such as phospholipids and nucleic acids) of natural origin and often still contain Si and P compounds in the form of impregnations and surface treatments (such as flame retardants, surface improvement by silicones, silicone adhesives, etc.). The method according to the invention has proven to be particularly suitable if the synthetic crude oil stream is a hydrocarbon mixture obtained from the depolymerization of biomass or plastic material, in particular plastic material. The synthetic crude oil stream is therefore preferably a plastic pyrolysate or a fraction thereof, or a biomass pyrolysate, in particular wood pyrolysate, or a fraction thereof. However, the method according to the invention is also well suited for other synthetic crude oils and fractions thereof. In further preferred embodiments, the synthetic crude oil stream therefore comprises, preferably consists of, shale oil or upgraded bitumen.

In a particularly preferred embodiment, the synthetic crude oil stream is therefore produced by depolymerization of plastic material, in particular plastic waste. The person skilled in the art is familiar with the production of a synthetic crude oil stream by depolymerization of plastic material. Such methods are known, for example, from WO 2012/149590 A1 and US 6,060,631 A. Preferably, the plastic material comprises polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamide (PA), styrene-acrylonitrile (SAN), and/or acrylonitrile-butadiene-styrene (ABS).

In a preferred embodiment, the plastic material comprises Si compounds, preferably organic Si compounds, preferably silicones, in particular polyorganosiloxanes. Silicones typically contain O-Si(CH₃)-O dimethylsiloxane units. Silicones (oils and plastics) are typically produced industrially from dimethyldichlorosilane or via the cyclic siloxanes (e.g. octamethylcyclotetrasiloxane). Due to the pyrolysis, cyclic siloxanes can be formed again from the straight-chain silicone for stability reasons. These have the property of binding to inorganic SiO₂ units under a ring opening. This reaction is favored by the conditions in an FCC unit, particularly elevated temperatures and a formally acidic environment. The dimethyl groups can be cleaved in the FCC process, which can result in the elimination of CO₂ SiO₂.

In a preferred embodiment, the Si content in the plastic material is at least 1 ppm, preferably at least 10 ppm, more preferably at least 100 ppm, even more preferably at least 1000 ppm, even more preferably at least 10,000 ppm. Preferably, the Si content is between 1 ppm and 10,000 ppm, preferably between 5 ppm and 1000 ppm, more preferably between 10 ppm and 100 ppm. The Si content in the plastic material is preferably determined according to ASTM D7111-16 (2021).

The Si content of organic Si compounds, in particular silicones, in the plastic material is preferably at least 1 ppm, preferably at least 10 ppm, more preferably at least 100 ppm, even more preferably at least 1000 ppm, even more preferably at least 10,000 ppm. Preferably, the Si content is between 1 ppm and 10,000 ppm, preferably between 5 ppm and 1000 ppm, more preferably between 10 ppm and 100 ppm. The Si content of organic Si compounds or silicones refers to the concentration of Si in the plastic material that is present as part of organic compounds or silicones. The determination may take place, for example, by manually separating the plastic material. If, for example, the Si content is to be determined from organic Si compounds, inorganic Si sources (filler material, glass, etc.) can be removed manually in a sample of the plastic material and the Si content in the remaining material can be determined by means of ASTM D7111-16 (2021) and extrapolated to the total weight of the sample taken. If the Si content is to be determined from silicones, a similar procedure can be followed by removing all

Si-containing components except silicones from a sample and determining the Si content in the remaining material by means of ASTM D7111-16 (2021) and extrapolating it to the total weight of the sample taken.

In a preferred embodiment, the plastic material comprises P compounds, preferably organic phosphites, more preferably triaryl phosphites. As stated above, triaryl phosphites are often used as additives in plastics, e.g. as flame retardants. Triaryl phosphites or triaryl phosphates formed therefrom in the course of a pyrolysis can be removed particularly efficiently with the method according to the invention.

All parameters mentioned herein refer, unless otherwise indicated, to SATP conditions according to IUPAC ("Standard Ambient Temperature and Pressure"), in particular to a temperature of 25 °C and a pressure of 101,300 Pa.

Unless otherwise indicated, all percentages (%) herein refer to percentages by weight.

Information in "ppm" herein refers, unless otherwise indicated, to parts per million on a mass basis (ppmw). 1 ppm as used herein corresponds to 0.0001 % by weight.

The person skilled in the art is familiar with the determination of Si and P contents in hydrocarbon streams. Unless otherwise indicated, all Si contents and P contents specified herein are preferably determined in accordance with ASTM D7111-16(2021).

The person skilled in the art is also familiar with the determination of boiling ranges of hydrocarbon fractions. Unless otherwise indicated, all boiling ranges specified herein are determined according to ISO 3924:2019, preferably according to method A or method B as defined in this standard.

The present invention is illustrated by the following Figure and the following examples, to which, of course, it is not limited.

Figure 1 shows a method flow diagram of a preferred embodiment of the method according to the invention.

In the embodiment shown in Figure 1, a Si and P-containing hydrocarbon stream 1 is produced by depolymerization of plastic

material. The plastic material is compacted, degassed and melted in an extruder 2. The plastic melt emerging from the extruder 2 is mixed in a static mixer 3 with an external solvent 4, preferably heavy oil, and/or with already cracked plastic material, which is recycled as recycling stream 5, in order to reduce the viscosity of the plastic melt. The resulting mixture is introduced into a depolymerization reactor 6, in which the plastic material is depolymerized, preferably at a temperature between 350 °C and 450 °C. The pyrolysis product obtained is a Si and P-containing hydrocarbon stream 1, which is fed to a hydrocyclone 7 downstream of the pyrolysis reactor 6. In the hydrocyclone 7, the hydrocarbon stream 1 is separated into a light stream 8, the recycling stream 5 and a P-rich fraction 9. A hydrocyclone 8 suitable for this purpose is described, for example, in WO 2023/036751 A1.

The P-rich fraction 9 may have a boiling range with a lower end of 400 °C and a P content of at least 10 ppm. In the embodiment shown, the P-rich fraction is subjected to a solids depletion. The P-rich fraction 9 is fed to a cooling unit 11 for cooling to a temperature in the range from 80 to 240 °C. Subsequently, a solvent 13 comprising at least 20 % by weight of an aliphatic hydrocarbon is added to the P-containing fraction 9 in a container 12 to form a mixture 14. The mass ratio of the P-rich fraction to the solvent is in the range of 1:1 to 1:3. The container 12 is heated. Wax contained in the P-rich fraction 9 is dissolved in the solvent at a temperature in the range from 80 to 240 °C, which facilitates separation of the solids contained in the P-rich fraction 9. In a separating device 15 comprising a filter, the solids 16 are at least partially separated from the mixture 14 and removed. The separating device 15 is followed by an evaporator 17, which enables a portion of the solvent 13 used to be separated and the separated solvent 18 to be returned to the container 12. The solids-depleted P-rich fraction 19 is fed to an FCC unit 20.

The light stream 8 from the hydrocyclone 7 is separated in a column 21 into a gas stream 22, a naphtha fraction 23 and an Si-rich fraction 24. The naphtha fraction 23 may have a boiling range with an upper end of 160 °C and may be further processed in a naphtha hydrotreating system, for example. The Si-rich

fraction 24 may have a boiling range with a lower end of 160 °C and an upper end of 240 °C and a Si content of at least 10 ppm. In the embodiment shown, the Si-rich fraction 24 is washed prior to processing in the FCC unit 20. The Si-rich fraction 24 is mixed with an aqueous wash solution 25 in a mixing zone of a mixer-settler 26, preferably in a volumetric mixing ratio of 1:1 and at a temperature of at least 40 °C. The aqueous wash solution is preferably aqueous sulfuric acid with a pH of less than 7. In a settling zone of the mixer-settler 26, the one purified oil phase is separated from a water phase. The water phase is removed as wastewater stream 27. The oil phase is supplied as a washed Si-rich fraction 28 to the FCC unit 20.

The washed Si-rich fraction 28 and the solids-depleted P-rich fraction 19 are processed in the FCC unit 20 and converted into an Si-poor and P-poor FCC product 29.

Example 1 Removal of Si and P compounds using FCC

The influence of high Si and P contents on FCC processes was investigated. For this purpose, a vacuum gas oil was used as the hydrocarbon stream to be processed. Either 10,000 ppm (= 1 % by weight) of silicone oil or 10,000 ppm (= 1 % by weight) of tris(2,4-di-tert-butylphenyl)phosphite were added to the vacuum gas oil. The resulting mixtures were processed in an FCC system and the FCC products were analyzed for their Si and P content according to the ASTM D7111-16 (2021) standard.

The following results were obtained:

FCC input material	P in FCC product	Si in FCC product
Vacuum gas oil	< 1 ppm	< 1 ppm
Vacuum gas oil + 10000 ppm tris(2,4-di-tert-butylphenyl)phosphite	< 1 ppm	7.7 ppm
Vacuum gas oil + 10000 ppm silicone oil	< 1 ppm	1.6 ppm

From these results it can be seen that even in the case of an overdose with Si and P compounds (10000 ppm), the FCC process can still be carried out successfully and a product with a low Si and P content can be obtained. Both Si and P are virtually

completely removed – the small amounts of Si partially observed are not due to the silicone oil used, but to catalyst fines, which can be seen from the fact that they also occur in the experiment without silicone oil. This shows that Si and P compounds can be efficiently removed by treatment in an FCC unit.

Example 2: Si and P concentrations in boiling cuts from synthetic crude oil

Experiments were carried out to investigate which boiling cuts in synthetic crude oils have particularly high Si and P concentrations and can therefore advantageously be provided for processing in an FCC unit. For this purpose, pyrolysis oils were produced from various waste plastics (silicone additive, pyrolysis of plastics from the electronics industry, real mixtures from sorting systems, residual waste sorting, etc.) and separated by subsequent distillation for pilot-scale experiments. The pyrolysis was carried out as described in connection with Figure 1. The Si and P content in the individual boiling cuts was determined in accordance with the standard ASTM D7111-16 (2021).

The following tables show the results of two distillations carried out separately with a pyrolysis oil from a plastic waste sorting:

Experiment 1:

Fraction (boiling range)	P [ppm]	Si [ppm]
Naphta SB-175 °C	1.8	9.8
Kero 175-225 °C	1	22.5
Gas oil 225-350 °C	0.5	5.2
Spindle oil 350-410 °C	0.8	2.1
+410 °C	32.1	1.2

Experiment 2:

Fraction (boiling range)	P [ppm]	Si [ppm]
Naphta SB-175 °C	1.2	7.2

Kero 175-225 °C	0.9	21.3
Gas oil 225-350 °C	0.6	4.5
Spindle oil 350-410 °C	2.9	2.4
+410 °C	30.4	1

From the results of these experiments, it can be seen that the Si concentrations are highest in the kero fractions with boiling ranges in the range of 175 to 225 °C. The P concentrations are highest in the heavy fractions, especially with boiling ranges from 410 °C.

Claims:

1. A method for processing a phosphorus (P)-containing hydrocarbon stream (1), the method comprising the following steps:
 - providing the hydrocarbon stream (1);
 - separating a P-rich fraction (9) from the hydrocarbon stream (1), wherein the P-rich fraction (9) has a boiling range with a lower end of at least 350 °C and a P content of at least 10 ppm;
 - processing the P-rich fraction (9) in a Fluid Catalytic Cracking (FCC) unit (20).
2. The method according to claim 1, wherein the P-rich fraction (9) is subjected to a solids depletion prior to processing in the FCC unit (20).
3. The method according to claim 2, wherein the solids depletion comprises the steps of:
 - adding a solvent (13) to the P-rich fraction (9) to form a mixture (14);
 - separating solids (16) from the mixture (14).
4. The method according to claim 3, wherein the solvent (13) comprises at least 20 % by weight of an aliphatic hydrocarbon, based on the total weight of the solvent (13).
5. The method according to claim 3 or 4, wherein the mixture (14) has a temperature of at least 80 °C.
6. The method according to any one of claims 3 to 5, wherein after separating the solids (16) from the mixture (14), at least a portion of the solvent (13) is separated from the mixture (14).
7. The method according to claim 6, wherein at least a portion of the separated solvent (18) is reused for the solids depletion.
8. The method according to any one of claims 1 to 6, wherein the hydrocarbon stream (1) is a phosphorus (P)- and silicon

(Si)-containing hydrocarbon stream (1),

wherein an Si-rich fraction (24) is separated from the hydrocarbon stream (1) in addition to the P-rich fraction (9), wherein the Si-rich fraction (24) has a boiling range with a lower end of at least 120 °C and a Si content of at least 10 ppm;

and wherein the P-rich fraction (9) and the Si-rich fraction (24) are processed in the FCC unit (20).

9. The method according to claim 8, wherein the Si-rich fraction (24) has a boiling range with an upper end of at most 280 °C.

10. The method according to claim 8 or 9, wherein a naphtha fraction (23) is separated from the hydrocarbon stream (1) in addition to the Si-rich fraction (24), preferably wherein the naphtha fraction (23) has a boiling range with an upper end of at most 200 °C.

11. The method according to any one of claims 8 to 10, wherein the Si-rich fraction (24) is washed with at least one aqueous wash solution (25) prior to processing in the FCC unit (20).

12. The method according to claim 11, wherein the washing with the at least one aqueous wash solution (25) takes place at a temperature of at least 40 °C.

13. The method according to claim 11 or 12, wherein the pH of the aqueous wash solution (25) is less than 8.

14. The method according to any one of claims 1 to 13, wherein the FCC unit (20) comprises a catalyst comprising zeolites.

15. The method according to any one of claims 1 to 14, wherein the hydrocarbon stream (1) is produced by depolymerization of plastic material, in particular plastic waste.