

Method for Purifying a Synthetic Crude Oil Stream

The present invention relates to methods for purifying a synthetic crude oil stream.

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.

Synthetic crude oils typically contain different impurities, which can 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.

A particularly big problem in the further processing of synthetic crude oils is the so-called gum formation. Pyrolysis oils usually contain different chemical compounds that can tend to form deposits. Such deposits can subsequently clog or otherwise damage refinery systems, increase the cleaning effort and shorten the service life of systems.

The problem of gum formation in connection with synthetic crude oils has not yet been satisfactorily solved. There is still a need for methods to reduce the tendency of synthetic crude oils to form gum. It is therefore an object of the present invention to provide methods for reducing the gum formation of synthetic crude oils.

The present invention therefore relates to a method for purifying a synthetic crude oil stream, the method comprising the following steps:

- providing the synthetic crude oil stream, wherein the synthetic crude oil stream contains aromatic compounds;
- contacting the synthetic crude oil stream with a carbonyl stream containing at least one carbonyl compound selected from

an aldehyde and a ketone to form a mixture, thereby crosslinking at least a portion of the aromatic compounds to condensation products; and

- separating the condensation products from the mixture in order to obtain a purified synthetic crude oil stream.

A further aspect of the invention relates to a method for producing a purified synthetic crude oil stream from a plastic material, comprising the following steps:

- providing the plastic material, wherein the plastic material contains a carbonyl source;

- pyrolyzing the plastic material to obtain a synthetic crude oil stream containing aromatic compounds, wherein at least one carbonyl compound selected from an aldehyde and a ketone is released from the carbonyl source, and wherein the at least one carbonyl compound crosslinks at least a portion of the aromatic compounds to condensation products; and

- separating the condensation products in order to obtain a purified synthetic crude oil stream.

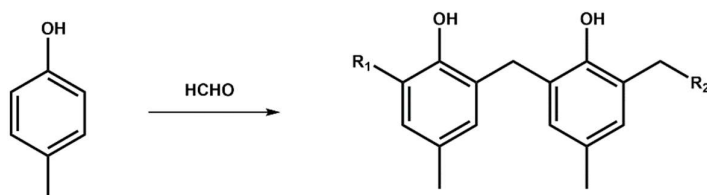
It has been found that certain aromatic compounds can contribute significantly to the formation of deposits in synthetic crude oils. This applies in particular to phenols, heteroaromatics, diaromatics, triaromatics and polyaromatics. In connection with the present invention, it has been found that these aromatic compounds in synthetic crude oils can be crosslinked via treatment with aldehydes or ketones to form condensation products, which can be easily separated and removed as insoluble solids. The gum formation is thus brought about in a targeted manner in the method according to the invention and the "gum" - i.e. the insoluble condensation products - are separated. The purified synthetic crude oil stream therefore has a lower aromatics content and is therefore less likely to form deposits, which can protect systems and in particular also reactive surfaces that comprise catalysts.

The aromatic compounds are preferably present in dissolved form in the synthetic crude oil stream. In the mixture, the aromatic compounds are preferably crosslinked by the at least one carbonyl compound to form insoluble condensation products. These

precipitate as insoluble solids and can thus be easily separated. Thus, treatment with a carbonyl compound can achieve spontaneous precipitation of undesirable components. "Condensation products" herein means the reaction products of the carbonyl compounds and the aromatic compounds. As an alternative to the term "condensation products", the term "reaction products" may also be used.

The aromatic compounds are preferably selected from phenols, heteroaromatics, diaromatics, triaromatics and polyaromatics. It is particularly preferred if the aromatic compounds are phenols. These have a strong tendency to form deposits and at the same time can be removed particularly well with the method according to the invention.

A possible condensation reaction of phenols is subsequently shown as an example with formaldehyde (HCHO) as the carbonyl compound:

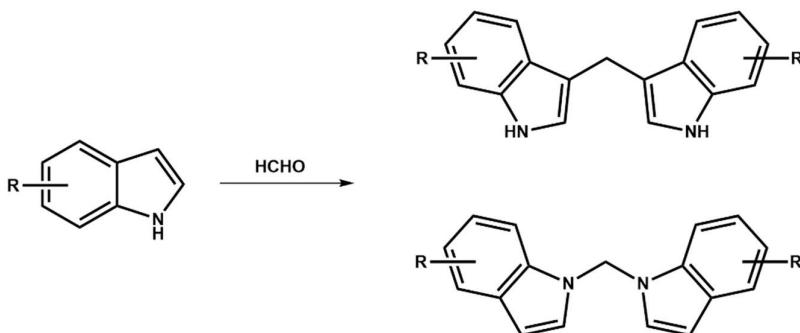


In a first step, the reaction with formaldehyde leads to a crosslinking of two phenols with the elimination of water. The reaction product of this first condensation reaction may subsequently react with other starting products and/or reaction products to form polymers. The polymers can precipitate as solids and be easily separated. The reaction can proceed analogously with other aldehydes and ketones.

In connection with the invention, it is particularly preferred if the aromatic compounds are nitrogen heteroaromatics (N-heteroaromatics), in particular pyridines and/or indoles. In addition to forming deposits, these compounds can have a significant effect on catalysts, in particular by being able to deactivate acidic FCC or HDT catalysts due to their basicity. Since N-heteroaromatics generally have a higher nucleophilicity than carbocyclic aromatics, they react particularly efficiently with carbonyl compounds and can therefore be removed particularly well with the method according to the invention. Catalysts in

refinery plants can thus be protected particularly well.

The following are examples of possible condensation reactions of indoles with formaldehyde:



The dimeric methylene compounds shown are already insoluble in the synthetic crude oil stream and can thus be easily removed. With other aldehydes and ketones, the reaction can proceed analogously. Of course, condensation reactions between different types of aromatics are also possible.

The synthetic crude oil stream preferably has an aromatics content of at least 10 % (w/w), more preferably at least 12 % (w/w), more preferably at least 14 % (w/w), more preferably at least 16 % (w/w), more preferably at least 18 % (w/w), more preferably at least 20 % (w/w). It is preferred if the synthetic crude oil stream has an aromatics content of 10 % (w/w) to 50 % (w/w), more preferably from 12 % (w/w) to 45 % (w/w), more preferably from 14 % (w/w) to 40 % (w/w), more preferably from 16 % (w/w) to 35 % (w/w), more preferably from 18 % (w/w) to 30 % (w/w), more preferably from 20 % (w/w) to 25 % (w/w).

Preferably, the purified synthetic crude oil stream has a lower aromatics content than the synthetic crude oil stream. The method according to the invention can therefore lead to a reduction in the aromatics content. The aromatics content in the purified synthetic crude oil stream is preferably less than 20 % (w/w), more preferably less than 18 % (w/w), more preferably less than 16 % (w/w), more preferably less than 14 % (w/w), more preferably less than 12 % (w/w), more preferably less than 10 % (w/w). Preferably, the aromatics content in the purified

synthetic crude oil stream is lower by at least 1 percentage point (% (w/w)) than in the synthetic crude oil stream (e.g., if the aromatics content in the synthetic crude oil stream is 20 % (w/w), it is preferred if the aromatics content in the purified synthetic crude oil stream is 19 % (w/w) or less). Preferably, the aromatics content in the purified synthetic crude oil stream is lower by at least 2 percentage points (% (w/w)), more preferably by at least 3 percentage points (% (w/w)) than in the synthetic crude oil stream.

The aromatics content is preferably determined according to the ASTM D6591-19 standard. Alternatively or in addition to this, the aromatics content may also be determined in accordance with ASTM D5134-21.

It has proven advantageous if the contacting of the synthetic crude oil stream with the carbonyl stream takes place at a temperature of at least 50 °C, preferably at least 60 °C, more preferably at least 70 °C, more preferably at least 80 °C, more preferably at least 100 °C, more preferably at least 120 °C. In particular, it is preferred if the contacting of the synthetic crude oil stream with the carbonyl stream takes place at a temperature in the range from 50 to 450 °C, more preferably from 60 to 350 °C, more preferably from 70 to 250 °C, more preferably from 80 to 180 °C, more preferably from 100 to 170 °C, more preferably from 120 to 160 °C. A higher temperature can promote the reaction between the aromatic compounds and the carbonyl compounds and therefore lead to an even more efficient removal of undesirable aromatic compounds.

In a preferred embodiment, the contacting of the synthetic crude oil stream with the carbonyl stream takes place for a period of at least 0.5 minutes, preferably at least 1 minute, more preferably at least 2 minutes, even more preferably at least 5 minutes, most preferably at least 12 minutes. The provision of a longer duration allows a more complete course of the reactions, so that the content of the undesirable aromatic compounds can be reduced even more. In particular, it is therefore preferred if the duration is between 0.5 and 180 minutes, preferably between 1 and 120 minutes, more preferably between 2 and 60 minutes, even more preferably between 5 and 30 minutes, most preferably between 12 and 20 minutes. The duration is preferably the

average period of time between the first contacting of the synthetic crude oil stream with the carbonyl stream and the separation of the condensation products from the mixture in order to obtain the purified synthetic crude oil stream. If the method is carried out as a continuous process, the duration preferably corresponds to the average residence time in a washing device used, e.g. in a mixer-settler.

In a preferred embodiment, the contacting of the synthetic crude oil stream with the carbonyl stream takes place in a pressure vessel. Providing a pressure vessel allows treatment at higher pressures and temperatures and may facilitate condensation reactions. This is particularly preferred if the carbonyl stream is an aqueous solution and/or if the mixture formed by the synthetic crude oil stream and the carbonyl stream contains water. As described in more detail below, the presence of water can favor the condensation reactions. Providing increased pressure in this case may allow the water in the mixture to remain in a liquid state.

Preferably, the contacting of the synthetic crude oil stream with the carbonyl stream takes place at a pressure of more than 2 bar, preferably more than 3 bar, more preferably more than 5 bar, even more preferably more than 7 bar, most preferably more than 10 bar. It is particularly preferred that the contacting takes place at a pressure in the range from 2 bar to 50 bar, preferably from 3 bar to 35 bar, more preferably from 5 bar to 25 bar, even more preferably from 7 bar to 20 bar, most preferably from 10 bar to 18 bar.

In a preferred embodiment, the carbonyl stream is an aqueous solution. This has the advantage, among other things, that the condensation reactions between the undesirable aromatic compounds and the carbonyl compounds are favored. Specifically, acidic or basic catalysis of the reactions can take place due to the protons and hydroxide ions present in the water.

This advantageous effect can be further enhanced or achieved to an even greater extent if an acid or a base is added to the mixture. The more acid or base is present, the faster and more efficient the reaction can be. In a preferred embodiment, the carbonyl stream has a pH of at least 8, more preferably at least

9, more preferably at least 10, more preferably at least 11, more preferably at least 12. The pH value is preferably in the range from 8 to 14, preferably from 10 to 13. This enables efficient basic catalysis of the condensation reactions. In an alternative embodiment, which is likewise preferred, the carbonyl stream has a pH of at most 6, more preferably at most 5, more preferably at most 4, more preferably at most 3, more preferably at most 2. The pH value is preferably in the range from 0 and 6, preferably between 1 and 5. This enables efficient acidic catalysis of the condensation reactions.

In a particularly preferred embodiment of the method according to the invention, the contacting of the synthetic crude oil stream with the carbonyl stream takes place in the presence of an acid or a base and/or an acid or a base is added to the mixture of the synthetic crude oil stream and the carbonyl stream. This is preferably an aqueous acid or an aqueous base. Thus, the desired condensation reactions can be favored by acidic or basic catalysis, as described above.

In connection with the method according to the invention, any type of aldehyde or ketone can be used as the carbonyl compound. Preferably, the at least one carbonyl compound is selected from formaldehyde, acetaldehyde, propionaldehyde, propenaldehyde, butyraldehyde, crotonaldehyde, acetone, ethyl methyl ketone, and/or pentanone.

It has proven to be particularly advantageous if the at least one carbonyl compound is an aldehyde. Without being bound by any theory, the inventors suspect that this is due, on the one hand, to the higher electrophilicity of aldehydes compared to ketones and, on the other hand, to the lower steric hindrance when the carbonyl group is terminal. Both factors favor the desired reactions with aromatic compounds. Since these factors apply to the highest degree to formaldehyde, it is particularly preferred if the at least one carbonyl compound is formaldehyde. The advantages of aldehydes over ketones in general and the advantages of formaldehyde in particular can also be seen from the data contained in Example 1, in which a more marked reduction in the aromatics content was found by formaldehyde than by acetone.

The concentration of the carbonyl compounds in the carbonyl

stream is preferably at least 1 % (w/w), more preferably at least 5 % (w/w), more preferably at least 10 % (w/w), more preferably at least 15 % (w/w), more preferably at least 20 % (w/w), more preferably at least 25 % (w/w). The concentration is preferably between 1 % (w/w) and 100 % (w/w), more preferably between 5 % (w/w) and 80 % (w/w), more preferably between 10 % (w/w) and 60 % (w/w), more preferably between 15 % (w/w) and 50 % (w/w). The use of such high concentrations favors the reaction with the aromatic compounds contained in the synthetic crude oil stream.

Based on the total mass of the synthetic crude oil stream and the carbonyl stream, it is preferred if the concentration of the carbonyl compounds is at least 0.01 % (w/w), more preferably at least 0.02 % (w/w), more preferably at least 0.05 % (w/w), more preferably at least 0.1 % (w/w), more preferably at least 0.2 % (w/w). The concentration of the carbonyl compounds, based on the total mass of the synthetic crude oil stream and the carbonyl stream, is preferably from 0.01 % (w/w) to 5 % (w/w), preferably from 0.02 % (w/w) to 2 % (w/w), more preferably from 0.05 % (w/w) to 0.5 % (w/w).

In a preferred embodiment, the volumetric mixing ratio between the synthetic crude oil stream and the carbonyl stream is from 10:1 to 1:5, more preferably from 5:1 to 1:2.5, more preferably from 1.5:1 to 1:1.5. Such mixing ratios have proven to be particularly good for treating the synthetic crude oil stream.

In a preferred embodiment, the mixture formed from the synthetic crude oil stream and the carbonyl stream has a polar phase and a non-polar phase, the condensation products being predominantly present in the polar phase. Preferably, the separation of the condensation products from the mixture is achieved by separating the polar phase. If the carbonyl stream is an aqueous solution, the polar phase may be an aqueous phase. The condensation products can thus be separated in a particularly simple manner.

It has proven to be particularly advantageous if the contacting with the carbonyl stream and the subsequent separating of the polar phase 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 carrying out of the mixing of the synthetic crude oil stream with the carbonyl stream, as well as the subsequent settling process for separating the phases and separating the purified synthetic crude oil stream in a continuous process.

In an advantageous embodiment, the separated polar phase is at least partially recycled and reused at least as a portion of the carbonyl stream. It has been found that the separated polar phase often still contains a significant proportion of unconsumed carbonyl compounds. If the wastewater stream is partially circulated, the carbonyl compound can therefore be better used. For example, the circulation may comprise from 1 to 25 revolutions. This recirculation can have energy advantages and lead to lower costs and also enables a smaller version of the system. The proportion of chemicals consumed can also be compensated by dosing fresh medium into the circuit.

In a preferred embodiment of the method according to the invention, the purified synthetic crude oil stream is washed with an aqueous wash solution to obtain a second purified synthetic crude oil stream. By means of such an additional washing step, impurities contained in the synthetic crude oil stream can be removed even more thoroughly.

The aqueous wash solution is preferably an acidic aqueous wash solution. In particular, it is preferred if the pH of the aqueous wash solution is less than 6, preferably less than 5, more preferably less than 4, more preferably less than 3.5. Such a pH value is particularly preferred if the carbonyl stream has a basic pH value. Thus, a basic wash in the form of treatment with the carbonyl stream may be followed by an acid wash.

Washing the purified synthetic crude oil stream with an acidic wash solution can improve the removal of basic compounds such as amines, pyridines and other basic impurities. If the carbonyl stream has a basic pH, especially if it is an aqueous stream, a basic hydrolysis of neutral compounds may have taken place by treatment with the carbonyl stream. In this case, additional basic hydrolysis products, e.g. amines, can be removed by the acid wash. In particular, polycyclic amines can also be efficiently removed by this step. Polycyclic amines can be present

to a greater extent in synthetic crude oils, in particular in pyrolysis oils. They can form, for example, in cracking processes in the presence of a nitrogen source, for example additives or polymers such as polyamide (PA), polyacrylonitrile (PAN) or acrylonitrile-butadiene-styrene copolymer (ABS). Polycyclic amines may be, for example, polycondensed - saturated, mono- and polyunsaturated or aromatic ring systems. They may be partially dissolved in the synthetic crude oil or suspended in the colloidal area and often result in undesirable deposits and thus in difficult cleaning of the system. In addition, they can lead to a laying of active surfaces of catalysts in subsequent applications. In addition, they can dissolve undesirable compounds such as salts, chloride, heavy metals or sulfides in the organic product phase. It has been shown that polycyclic amines can be efficiently removed by the acidic washing step. For the removal of polycyclic amines, it has proven advantageous if the acidic washing step takes place at a temperature of at least 20 °C. The removal is particularly efficient if the temperature is at least 50 °C.

However, it has been found to be advantageous if the temperature in the acidic washing step is not too high, in particular lower than the temperature of the contacting with the carbonyl stream. It has been shown that high temperatures in the acidic washing step can lead to a reduction in product yield and the formation of impurities. It has therefore proven advantageous to carry out the acidic washing step at a temperature of less than 120 °C. In particular, these adverse effects can be minimized if the temperature is less than 100 °C, even more preferably less than 95 °C.

An additional advantage of the lower temperature in the acidic washing step is that the requirements for the material of the washing device are significantly lower. The presence of acidic solutions at high temperatures often requires the use of special materials or coatings, which would lead to a significant increase in costs. In a preferred embodiment, the scrubbing of the purified synthetic crude oil stream with the acidic wash solution therefore takes place at a lower temperature than the contacting of the synthetic crude oil stream with the carbonyl stream.

In a preferred embodiment, the aqueous wash solution contains sulfuric acid. The concentration of sulfuric acid is preferably between 0.5 and 10 % (w/w), in particular between 1 and 5 % (w/w).

It has also proven advantageous if the volumetric mixing ratio between the purified synthetic crude oil stream and the aqueous wash solution is from 10:1 to 1:5, preferably from 5:1 to 1:2.5, even more preferably from 2.5:1 to 1:1.5. Such a mixing ratio enables particularly efficient removal of basic impurities.

The method according to the invention may also contain further washing steps. For example, it is possible for the purified synthetic crude oil stream to undergo further washing or purification steps before washing with the aqueous wash solution takes place. However, it is preferred if no further purification step, in particular no washing step, no filtration step and/or no hydrotreating step, takes place between the separation of the condensation products in order to obtain the purified synthetic crude oil stream and the washing of the purified synthetic crude oil stream with the aqueous wash solution. This has the advantage, among other things, that basic products formed from neutral compounds by basic hydrolysis can be removed in the preferably acidic washing step immediately following the basic washing step.

In a further preferred embodiment of the method according to the invention, the second purified synthetic crude oil stream is washed with a further aqueous wash solution in order to obtain a third purified synthetic crude oil stream. The provision of such a further washing step enables a particularly thorough removal of impurities, which may still be present after the acidic washing step.

In this context, it is particularly preferred if the pH of the further aqueous wash solution is in the range from 3 to 13, preferably from 4 to 12, more preferably from 5 to 11, even more preferably from 6 to 10, even more preferably from 6.5 to 9, most preferably from 7 to 8. A pH in this range is particularly effective for removing small polar neutral molecules as well as inorganic and organic salts. It is particularly advantageous if

the further aqueous wash solution is basic or substantially neutral, in particular substantially neutral.

In connection with the invention, it is preferred if the method for purifying a synthetic crude oil stream is a continuous method. Compared to a batch process, this has the advantage that higher productivity and shorter downtimes are achieved.

Washing the respective crude oil streams with the respective wash solutions as described herein may include mixing the crude oil stream with the wash solution followed by separating the purified crude oil stream from the aqueous wash solution. Preferably, the washing steps of the method according to the invention are 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 steps are each carried out in a mixer-settler, as described above for the treatment with the carbonyl stream.

In connection with the present invention, it has been found that synthetic crude oils have an increased tendency to form gum, in particular when they have a high content of diene compounds in addition to the aromatic compounds described above. Reactive dienes can therefore also act as gum formers and lead to harmful deposits in refinery systems. For example, dienes can sometimes undergo Diels-Alder reactions and thus lead to cross-linking between molecules and ultimately to deposits. In addition, dienes can form stable complexes with catalysts in hydrotreating units. It has therefore been found to be advantageous within the scope of the invention to reduce the diene content of synthetic crude oils in addition to reducing the content of the aromatic compounds described above.

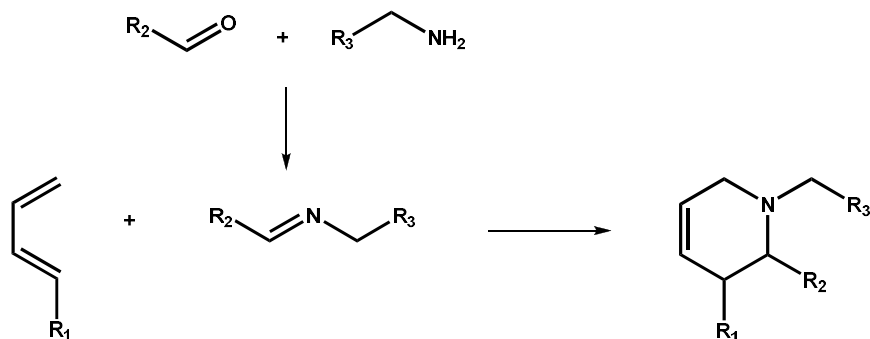
It has been shown that the carbonyl compounds contained in the carbonyl stream can also react with diene compounds. Carbonyl compounds can undergo oxo-Diels-Alder reactions with diene compounds, whereby the diene compounds are converted into diene-free products. However, oxo-Diels-Alder reactions are energetically unfavourable and therefore take place only to a small extent.

In connection with the invention, it has surprisingly been found that the removal of diene compounds can be significantly

avored if the contacting of the synthetic crude oil stream with the carbonyl stream takes place in the presence of a nitrogen compound and/or if a composition containing a nitrogen compound is added to the mixture of the synthetic crude oil stream and the carbonyl stream.

In experiments, the inventors have surprisingly found that the addition of nitrogen compounds, such as amines, can lead to a distinctive orange-red coloration. A closer examination has shown that tetrahydropyridines can be formed, to which this staining is attributable in the opinion of the inventors. At the same time, a sharp reduction in the diene number, i.e. removal of diene compounds, was found. This is also shown, among other things, in Example 2.

According to the inventors, the reason for the more efficient removal of diene compounds in the presence of amines is that the amines can react with the carbonyl compounds to form imines. These imines are significantly more nucleophilic than the starting carbonyl compounds, therefore they also undergo hetero-Diels-Alder reactions with dienes much more readily. Instead of an oxo-Diels-Alder reaction, a much easier Aza-Diels-Alder reaction takes place. This is shown by way of example in the following diagram:



In this scheme, a primary amine is shown as an example. The reaction can proceed in the same manner with NH₃ or other compounds. In principle, open systems can also arise from the various reactions occurring in the mixture, but these can also be separated and thus removed in the same manner.

In a preferred embodiment, the method according to the invention for purifying the synthetic crude oil stream comprises the following steps:

- providing the synthetic crude oil stream, wherein the synthetic crude oil stream contains aromatic compounds and diene compounds and preferably has a diene number of at least 0.1 g/100 g;
- contacting the synthetic crude oil stream with a carbonyl stream containing at least one carbonyl compound selected from an aldehyde and a ketone to form a mixture, whereby at least a portion of the aromatic compounds are cross-linked to condensation products; wherein the contacting of the synthetic crude oil stream with the carbonyl stream takes place in the presence of a nitrogen compound and/or wherein a composition containing a nitrogen compound is added to the mixture of the synthetic crude oil stream and the carbonyl stream, whereby at least a portion of the diene compounds are converted into diene-free products; and
- separating the condensation products and the diene-free products from the mixture in order to obtain a purified synthetic crude oil stream.

The diene compounds contained in the synthetic crude oil stream are preferably compounds containing conjugated or cumulative carbon-carbon double bonds, in particular conjugated carbon-carbon double bonds. Such compounds tend in particular to form gum, for example by Diels-Alder reactions, and can be removed particularly well by the method according to the invention.

The person skilled in the art is familiar with methods for determining the diene number. Preferably, the diene number is determined according to the ASTM UOP326-07 standard.

The synthetic crude oil stream preferably has a diene number of at least 0.1 g/100 g, preferably at least 0.2 g/100 g, more preferably at least 0.3 g/100 g, more preferably at least 0.4 g/100 g, more preferably at least 0.5 g/100 g, more preferably at least 0.6 g/100 g, more preferably at least 0.7 g/100 g, more preferably at least 0.8 g/100 g, more preferably at least 0.9 g/100 g, more preferably at least 1.0 g/100 g, more preferably at least 1.1 g/100 g, more preferably at least 1.2 g/100 g, more preferably at least 1.3 g/100 g, more preferably at least 1.4 g/100 g, more preferably at least 1.5 g/100 g, more preferably

at least 1.6 g/100 g, more preferably at least 1.7 g/100 g, more preferably at least 1.8 g/100 g, more preferably at least 1.9 g/100 g, more preferably at least 2.0 g/100 g. The synthetic crude oil stream preferably has a diene number in the range from 0.1 g/100 g to 15 g/100 g, more preferably from 1.0 g/100 g to 12 g/100 g, in particular from 1.5 g/100 g to 10 g/100 g.

The purified synthetic crude oil stream preferably has a lower diene number than the synthetic crude oil stream. The purified synthetic crude oil stream preferably has a diene number of less than 5 g/100 g, more preferably less than 4 g/100 g, more preferably less than 3 g/100 g, more preferably less than 2 g/100 g, more preferably less than 1.5 g/100 g, more preferably less than 1 g/100 g, more preferably less than 0.9 g/100 g, more preferably less than 0.8 g/100 g, more preferably less than 0.7 g/100 g, more preferably less than 0.6 g/100 g, more preferably less than 0.5 g/100 g. The purified synthetic crude oil stream preferably has a diene number in the range from 0.01 g/100 g to 5 g/100 g, more preferably from 0.1 g/100 g to 2 g/100 g, in particular from 0.2 g/100 g to 1 g/100 g.

Preferably, the at least one nitrogen compound is selected from ammonia, a primary amine, and/or a secondary amine. These nitrogen compounds have been shown to be well suited for the removal of diene compounds. It has been shown that the reactions proceed more readily, with smaller nitrogen compounds. Primary amines and ammonia, in particular ammonia, have proven to be particularly favorable.

Preferably, the at least one nitrogen compound is selected from ammonia, methylamine, dimethylamine, ethylamine, diethylamine, ethanolamine, diethanolamine, 3-methoxypropylamine, dibutylamine, morpholine, and/or triethylamine.

It has been shown that the removal of diene compounds can be additionally promoted if a high concentration of nitrogen compounds is used. It is therefore preferred if the concentration of the nitrogen compounds, based on the total mass of the synthetic crude oil stream and the carbonyl stream is at least 0.01 % (w/w), more preferably at least 0.02 % (w/w), more preferably at least 0.05 % (w/w), more preferably at least 0.1 % (w/w), more preferably at least 0.2 % (w/w). The concentration of the

nitrogen compounds, based on the total mass of the synthetic crude oil stream and the carbonyl stream, is preferably from 0.01 % (w/w) to 5 % (w/w), preferably from 0.02 % (w/w) to 2 % (w/w), more preferably from 0.05 % (w/w) to 0.5 % (w/w).

It has also proven advantageous if the carbonyl compounds and the nitrogen compounds are present in a similar concentration. According to the inventors, this is because one molecule of the carbonyl compound can react with one molecule of the nitrogen compound to form an imine. In a preferred embodiment, the molar ratio of the carbonyl compounds to the nitrogen compounds in the mixture of the synthetic crude oil stream and the carbonyl stream is therefore between 1:5 and 5:1, preferably between 1:2 and 2:1.

The separation of the diene-free products may be performed in the same manner as described above for the condensation products; in particular, the diene-free products and the condensation products can be separated together. The condensation products and the diene-free products are preferably jointly separated via a polar phase, preferably an aqueous phase, in particular in a mixer settler. Preferably, the diene-free products are present in the polar phase at least partially dissolved and/or at least partially as particles.

In a preferred embodiment of the method according to the invention, the purified synthetic crude oil stream, the second purified synthetic crude oil stream or the third purified synthetic crude oil stream is fed into a hydrotreating unit. It has been found that the reduction of the diene content in the synthetic crude oil stream is particularly advantageous, especially in the course of hydrogenation in a hydrotreating unit, since dienes in such systems can form stable complexes with catalysts. The use of the method according to the invention in combination with a hydrogenation can thus considerably improve the service life of the hydrotreating units and in particular of the catalysts used.

In connection with the invention, a "synthetic crude oil stream" is preferably understood to mean a material stream 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. 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 generated 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.

In a preferred embodiment, 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). The method according to the invention has proven to be particularly suitable for purifying pyrolysis oils from the plastic materials mentioned.

Surprisingly, it has been found that the effects according to the invention can also be achieved, at least to a certain extent, by the plastic material containing a carbonyl source from which at least one carbonyl compound selected from an aldehyde and a ketone is released in the course of the pyrolysis. It is particularly preferred if the carbonyl source is an aldehyde source, wherein aldehydes are released from the aldehyde source during the pyrolysis, and wherein the aldehydes crosslink at least a portion of the aromatic compounds to form condensation products. In this case, similar effects can be achieved as when

the carbonyl compound is supplied externally through a carbonyl stream. Instead of the external addition of the carbonyl compounds, these are formed internally during the method, which simplifies the method. Preferably, the carbonyl source (or the aldehyde source) is at least partially decomposed during the pyrolysis, whereby the at least one carbonyl compound (or the aldehydes) is formed.

Even if the plastic material contains a carbonyl source, it may still be advantageous to additionally add a carbonyl stream containing at least one carbonyl compound to further increase the amount of carbonyl compound available for the desired cross-linking reactions.

Surprisingly, it has been found that cellulose and/or starch are particularly suitable carbonyl sources. It has been shown that these materials decompose at the high temperatures during pyrolysis, forming aldehydes that can subsequently undergo the desired reactions. Cellulose and/or starch may therefore also be referred to as aldehyde sources. This has proven to be particularly beneficial, as cellulose and starch are found in different wastes, such as waste paper or biomass. Advantageously, with the method according to the invention, certain proportions of paper waste and/or biomass may thus also be co-processed with a plastic waste, which leads to a synergistic effect for the removal of undesired aromatic compounds and/or diene compounds in the pyrolysis oil. Mixed waste may also be used which, in addition to plastic, also contains certain amounts of paper and/or biomass.

The carbonyl source preferably comprises cellulose and/or starch, and preferably consists thereof. The cellulose and/or starch may be modified cellulose and/or starch, in particular HES, cellulose acetate, HMC, and/or HMS. However, it may also be unmodified cellulose and/or starch.

In a preferred embodiment, the carbonyl source comprises paper, and preferably consists of it.

The concentration of the carbonyl source in the plastic material is preferably at least 0.1 % (w/w), more preferably at least 0.2 % (w/w), more preferably at least 0.5 % (w/w), more preferably at least 1 % (w/w), more preferably at least 2 %

(w/w), more preferably at least 5 % (w/w). It has been shown that a higher concentration leads to the formation of larger amounts of aldehydes and can therefore lead to an even better removal of aromatics and/or diene compounds. The concentration is preferably between 0.1 % (w/w) and 15 % (w/w), more preferably between 0.2 % (w/w) and 12 % (w/w), more preferably between 0.5 % (w/w) and 10 % (w/w), more preferably between 1 % (w/w) and 5 % (w/w).

In a preferred embodiment, the plastic material contains nitrogen-containing polymers, wherein during pyrolysis of the plastic material, the nitrogen-containing polymers are at least partially decomposed and at least one nitrogen compound selected from ammonia, a primary amine, and/or a secondary amine is formed.

It has been shown that the preferred presence of a nitrogen compound in connection with the method according to the invention when contacting the synthetic crude oil stream with the carbonyl stream can also be achieved at least in part by the plastic material having a nitrogen source in the form of nitrogen-containing polymers. As a result, the above-described advantages can be achieved, in particular the improved removal of diene compounds. These advantages can also occur if the carbonyl compound is not supplied in the form of the carbonyl stream, but is formed from the carbonyl source during pyrolysis as described above.

Preferably, the nitrogen-containing polymers comprise polyamides, preferably they consist of them. Particularly preferred are aliphatic polyamides, in particular PA6, PA6.6, PA6.4 and/or PA11.

In a preferred embodiment, the nitrogen-containing polymers comprise nitrogen-containing biopolymers, and preferably consist thereof.

The concentration of the nitrogen-containing polymers in the plastic material is preferably at least 0.1 % (w/w), more preferably at least 0.2 % (w/w), more preferably at least 0.5 % (w/w), more preferably at least 1 % (w/w), more preferably at least 2 % (w/w), more preferably at least 5 % (w/w). It has been shown that a higher concentration can lead to the formation of

larger amounts of the at least one nitrogen compound and therefore an even better removal of diene compounds can be achieved. The concentration is preferably between 0.1 % (w/w) and 30 % (w/w), more preferably between 0.2 % (w/w) and 20 % (w/w), more preferably between 0.5 % (w/w) and 12 % (w/w), more preferably between 1 % (w/w) and 5 % (w/w).

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.

Unless otherwise indicated, all mixing ratios specified herein relate to volumetric mixing ratios, i.e. to volume ratios (volume:volume).

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, the synthetic crude oil stream 1 is obtained by depolymerization of plastic material. The plastic material is compacted, degassed and melted in an extruder 12. The plastic melt emerging from the extruder 12 is mixed in a static mixer 13 with an external solvent 14, preferably heavy oil, and/or with already cracked plastic material, which is recycled as recycling stream 15, in order to reduce the viscosity of the plastic melt. The resulting mixture is introduced into a depolymerization reactor 16, in which the plastic material is depolymerized, preferably at a temperature between 400 °C and 440 °C. Cracked plastic material is obtained as the top product of a column 17. In the embodiment shown, the top product is subsequently contacted with a composition 4 containing a nitrogen compound, preferably NH_3 . A gas stream 18 is separated from the resulting mixture in a further column 19 and the synthetic crude oil stream 1 is thus obtained. The synthetic crude oil stream contains aromatic compounds as well as diene compounds and preferably has a diene number of at least 0.1

g/100 g.

In the embodiment shown, the synthetic crude oil stream 1 is mixed with a carbonyl stream 2 in a mixing zone of a first mixer-settler 8, preferably in a volumetric mixing ratio of 1:1. The carbonyl stream 2 is preferably a basic aqueous solution containing formaldehyde. The mixture of the synthetic crude oil stream 1 and the carbonyl stream 2 preferably has a temperature of at least 50 °C. The aromatic compounds contained in the synthetic crude oil stream 1 undergo at least partial condensation reactions with the formaldehyde and precipitate as insoluble condensation products. In addition, the formaldehyde forms imine compounds with the NH₃ originating from composition 4, which enter into Aza-Diels-Alder reactions with the diene compounds and convert them into diene-free products. As a result, the oil phase is separated from the water phase in a settling zone of the mixer-settler 8. The condensation products and the diene-free products are separated with the water phase. The average residence time in the first mixer-settler 8 is preferably between 5 and 30 minutes. The water phase is removed as part of the wastewater stream 11 and the oil phase is separated as a purified synthetic crude oil stream 3.

Example 1: Reduction of the aromatics content of pyrolysis oils with carbonyl compounds

In order to investigate the removal of undesirable aromatic compounds by means of carbonyl compounds, laboratory tests were carried out with pyrolysis oils. For experiments, different pyrolysis oils were mixed with carbonyl compounds as well as nitrogen compounds, acid and/or base and heated to 50 to 160 °C for 1 to 30 minutes.

The aqueous phase was then removed and the reaction solution was examined directly by means of GC analyses, in accordance with ASTM D 6591-19 and ASTM D5134-21.

Experiment 1:

A light product (boiling range IBP-175 °C) from a pyrolysis of waste plastic was used as pyrolysis oil. The carbonyl compounds used, the reaction conditions and the proportion of

aromatics measured in the product are shown in the following table (percentages refer to percentages by weight):

Carbonyl compound	Other reagents	Conditions	Aromatics [%]
–	–	–	20.21
Formaldehyde (37 %)	H ₂ SO ₄ (5 %)	130 °C, 30 min	17.66
Formaldehyde (37 %)	NaOH (5 %)	130 °C, 30 min	17.55
Formaldehyde (37 %)	Monoethanolamine (95 %)	130 °C, 30 min	17.48
Formaldehyde (37 %)	H ₂ SO ₄ (5 %)	130 °C, 5 min	17.63
Formaldehyde (37 %)	NaOH (5 %)	130 °C, 5 min	17.57
Formaldehyde (37 %)	Monoethanolamine (95 %)	130 °C, 5 min	17.51
Acetone (99 %)	H ₂ SO ₄ (5 %)	130 °C, 30 min	18.3
Acetone (99 %)	NaOH (5 %)	130 °C, 30 min	18.5
Acetone (99 %)	Ammonia (15 %)	130 °C, 30 min	18.9
Formaldehyde (37 %)	Diethanolamine (97 %)	130 °C, 30 min	17.3

Thus, both the treatment with formaldehyde (an aldehyde) and with acetone (a ketone) shows a significant reduction in the aromatics content in the pyrolysis oil. The effect occurred regardless of which other reagents were present. An even greater reduction was observed with aldehyde than with ketone.

Experiment 2:

A heavy product (boiling range IBP 175–410 °C) from a pyrolysis of waste plastic was used as pyrolysis oil. In addition to the total aromatics content, the proportion of 4-core aromatics was also determined in this experiment. This determination was carried out via ASTM D 6591-19 and ASTM D5134-21. The carbonyl compounds used, the reaction conditions and the proportion of

aromatics measured in the product are shown in the following table (percentages refer to percentages by weight):

Carbonyl compound	Other reagents	Condi- tions	Aromatics [%]	4-core aromatics [%]
–	–	–	22.1	1.6
Formaldehyde (37 %)	H ₂ SO ₄ (5 %)	170 °C, 30 min	19.4	1.1
Formaldehyde (37 %)	NaOH (5 %)	170 °C, 30 min	17.8	0.8
Formaldehyde (37 %)	Monoethanolamine (95 %)	170 °C, 30 min	19.0	0.6
Formaldehyde (37 %)	H ₂ SO ₄ (5 %)	120 °C, 30 min	19.1	1.1
Formaldehyde (37 %)	NaOH (5 %)	120 °C, 30 min	17.2	0.8
Formaldehyde (37 %)	Monoethanolamine (95 %)	120 °C, 30 min	19.2	0.6

The treatment with carbonyl compounds thus also led to a significant reduction in the content of 4-ring aromatics, this removal being further facilitated by the presence of a base compared to the presence of an acid.

Experiment 3:

A light gas oil from a pyrolysis of waste plastic was used as the pyrolysis oil. The carbonyl compounds used, the reaction conditions and the proportion of aromatics measured in the product are shown in the following table (percentages refer to percentages by weight):

Carbonyl compound	Other reagents	Conditions	Aromatics [%]
–	–	–	24.5
–	H ₂ SO ₄ (5 %)	120 °C, 30 min	24.5
Formaldehyde (37 %)	H ₂ SO ₄ (5 %)	120 °C,	22.2

		30 min	
Formaldehyde (37 %)	H ₂ SO ₄ (0.1 %)	120 °C, 30 min	22.2
Acetone (99 %)	NaOH (5 %)	120 °C, 30 min	24.0
Formaldehyde (37 %)	NaOH (5 %)	120 °C, 30 min	21.9
Formaldehyde (37 %)	NaOH (0.1 %)	120 °C, 30 min	22.0

Example 2: Reduction of the diene number of pyrolysis oils with carbonyl and nitrogen compounds

Laboratory tests were carried out to investigate the reduction in the diene number of pyrolysis oils. A light product (boiling range IBP-175 °C) from a pyrolysis of waste plastic was used as pyrolysis oil. To carry out the tests, all components were heated together in the closed vessel. The aqueous phase was then removed and the reaction solution was examined directly by means of GC analyses (according to ASTM D 6591-19 and ASTM D5134-21).

The carbonyl compounds used, the reaction conditions and the diene numbers obtained are shown in the following table (percentages refer to percentages by weight):

Carbonyl compound	Other reagents	Condi- tions	Diene num- ber [g/100 g]
-	-	-	2.4
Formaldehyde (37 %)	-	120 °C, 30 min	1.5
Acetone (99 %)	-	120 °C, 30 min	2.1
Formaldehyde (37 %)	Monoethanolamine (95 %)	120 °C, 30 min	<1.2
Formaldehyde (37 %)	Monoethanolamine (95 %)	120 °C, 10 min	1.3
Formaldehyde (37 %)	Monoethanolamine (95 %)	160 °C, 30 min	<1.2

Formaldehyde (37 %)	NH ₃ (15 %)	120 °C, 30 min	<1.2
Acetone (99 %)	Monoethanolamine (95 %)	120 °C, 30 min	1.5

It is apparent from the results that a carbonyl compound alone led to a certain reduction in the diene number, with the aldehyde (formaldehyde) in turn leading to a stronger effect than the ketone (acetone). The reduction in the diene number could be significantly increased by the addition of a nitrogen compound, whereby NH₃ proved to be even more suitable than monoethanolamine.

Example 3: Reduction of the diene number of pyrolysis oils by a carbonyl source in the feedstock

In order to investigate the reduction of the diene number of pyrolysis oils by a carbonyl source in the feedstock, test runs for the production of synthetic crude oil were carried out essentially as described in Figure 1. The starting material used was a plastic mixture to which different amounts of paper were added as a carbonyl source, or more specifically as an aldehyde source.

The starting material with or without added paper was cracked at a temperature between 400 °C and 480 °C and separated as shown in Figure 1. In some test runs, a nitrogen compound was also added to the obtained synthetic crude oil stream in an amount of 0.5-2 kg/h. The nitrogen compound was added at a temperature of 300-400 °C. The condensation products and diene-free products were separated via a polar phase as described above.

The diene numbers for the individual test runs were measured and compared with each other.

Paper in feedstock (% w/w)	Nitrogen compound	Diene number [g/100 g]
–	–	2.8
2 %	–	1.46
2 %	Monoethanolamine (95 %)	<1.2
2 %	NH ₃ (15 %)	<1.2

From these results it can be seen that the addition of paper to the feedstock can lead to a significant reduction in the diene number. This effect is further enhanced by the presence of an amine.

Claims:

1. A method of purifying a synthetic crude oil stream (1), the method comprising the following steps:
 - providing the synthetic crude oil stream (1), wherein the synthetic crude oil stream (1) contains aromatic compounds;
 - contacting the synthetic crude oil stream (1) with a carbonyl stream (2) containing at least one carbonyl compound selected from an aldehyde and a ketone in order to form a mixture, thereby crosslinking at least a portion of the aromatic compounds to condensation products; and
 - separating the condensation products from the mixture in order to obtain a purified synthetic crude oil stream (3).
2. The method according to claim 1, wherein the synthetic crude oil stream (1) has an aromatics content of at least 10 % (w/w).
3. The method according to any one of the preceding claims, wherein contacting the synthetic crude oil stream (1) with the carbonyl stream (2) takes place at a temperature of at least 50 °C.
4. The method according to any one of the preceding claims, wherein the carbonyl stream (2) is an aqueous solution.
5. The method according to any one of the preceding claims, wherein the contacting of the synthetic crude oil stream (1) with the carbonyl stream (2) takes place in the presence of an acid or a base and/or wherein an acid or a base is added to the mixture of the synthetic crude oil stream (1) and the carbonyl stream (2).
6. The method according to any one of the preceding claims, wherein the at least one carbonyl compound is formaldehyde.
7. The method according to any one of the preceding claims, wherein the concentration of the carbonyl compounds, based on the total mass of the synthetic crude oil stream (1) and the carbonyl stream (2), is at least 0.01 % (w/w).

8. The method according to any one of the preceding claims, wherein the mixture formed from the synthetic crude oil stream (1) and the carbonyl stream (2) has a polar phase and a non-polar phase, wherein the condensation products are predominantly present in the polar phase, and wherein the separation of the condensation products from the mixture is achieved by separating the polar phase.

9. The method according to any one of the preceding claims, wherein the contacting of the synthetic crude oil stream (1) with the carbonyl stream (2) takes place in the presence of a nitrogen compound and/or wherein a composition (4) containing a nitrogen compound is added to the mixture of the synthetic crude oil stream (1) and the carbonyl stream (2).

10. The method according to any one of the preceding claims, wherein at least one nitrogen compound is selected from ammonia, a primary amine, and/or a secondary amine; preferably from ammonia, methylamine, dimethylamine, ethylamine, diethylamine, ethanolamine, diethanolamine, 3-methoxypropylamine, dibutylamine, morpholine, and/or triethylamine.

11. The method according to any one of the preceding claims, wherein the concentration of the nitrogen compounds, based on the total mass of the synthetic crude oil stream (1) and the carbonyl stream (2), is at least 0.01 % (w/w).

12. The method according to any one of the preceding claims, wherein the synthetic crude oil stream (1) is generated by depolymerization of plastic material, in particular plastic waste.

13. A method for producing a purified synthetic crude oil stream (3) from a plastic material, comprising the following steps:

- providing the plastic material, wherein the plastic material contains a carbonyl source;
- pyrolyzing the plastic material to obtain a synthetic crude oil stream (1) containing aromatic compounds, wherein at least one carbonyl compound selected from an aldehyde and a ketone is released from the carbonyl source, and wherein the at least one carbonyl compound crosslinks at least a portion of the aromatic

compounds to condensation products; and

- separating the condensation products in order to obtain a purified synthetic crude oil stream (3).

14. The method of claim 13, wherein the carbonyl source comprises cellulose and/or starch.

15. The method according to claim 13 or 14, wherein the plastic material contains nitrogen-containing polymers, preferably polyamides, wherein during pyrolysis of the plastic material, the nitrogen-containing polymers are at least partially decomposed and at least one nitrogen compound selected from ammonia, a primary amine, and/or a secondary amine is formed.