Title: PRODUCTION OF HYDROCARBON FUELS FROM WASTE PLASTIC

Abstract: The present invention relates to a method for producing fuel and additional hydrocarbons from waste plastic comprising the steps of providing at least one plastic material; exposing said at least one plastic material to a primary cracking to obtain a first hydrocarbon fluid; said first hydrocarbon fluid being a gas; exposing said first hydrocarbon gas to a catalytic hydrogenation to obtain a second hydrocarbon fluid; fractional separation of said second hydrocarbon fluid to obtain at least one final product. The present invention further relates to a waste recycling system for recycling waste plastic into fluid hydrocarbon compounds.

Published:
— with international search report (Art. 21(3))
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(b))
PRODUCTION OF HYDROCARBON FUELS FROM WASTE PLASTIC

Field of the invention
This disclosure relates to the recycling of waste plastic and its transformation into hydrocarbon fuels and other hydrocarbon compounds by means of primary cracking and gas-phase catalytic hydrogenation, before fractional separation.

Background of the invention
Huge amounts of plastics end up in nature every year. The environmental consequences hereof have recently been realised. Not only does it destroy the esthetics of nature but it is realised that huge amount of microparticles are formed in particular in the oceans. These microparticles are taken up by fish and other organisms living in the ocean severely affecting their health.

At the same time, it is well known that the release of CO₂ to the atmosphere could beneficially be reduced as CO₂ is acknowledged to be a major factor in global heating. Advantageously, the extraction of petroleum products could be reduced in order to lower the CO₂ outlet. One way of limiting this extraction could be by re-using and/or recirculating material made from petroleum products.

Thus, it would be beneficial for the environment if plastic materials were to be recycled and the release of additional CO₂ into the atmosphere would be limited by lowering the extraction of petroleum products. This could be done for example by re-circulating the plastic material for producing hydrocarbon fuels from waste plastic.

Attempts have been made to re-cycle waste plastic materials in different processes to obtain different hydrocarbon fluids. However, an efficient process, preferably self-sufficient in terms of energy and directed for an optimal production of specific hydrocarbon fuels is still needed.

Brief summary of the invention
An object of the present invention relates to a method and a system for re-using waste plastic to produce liquid fuel, gas and hydrocarbon compounds.
It is a further object of the present invention to re-use the energy obtained in the method for the method to be self-sufficient in terms of energy, for the method only to use a limited amount of extracted petroleum products thereby reducing potential human-produced CO₂ emissions.

These objects are achieved according to the aspects and embodiments of the present invention as described herein.

In one aspect of the invention, a method for producing fuel and additional hydrocarbons from waste plastic is provided, comprising the steps of
- providing at least one plastic material;
- exposing said at least one plastic material to a primary cracking to obtain a first hydrocarbon fluid; said first hydrocarbon fluid being a gas;
- exposing said first hydrocarbon gas to a catalytic hydrogenation to obtain a second hydrocarbon fluid;
- fractional separation of said second hydrocarbon fluid to obtain at least one final product.

In one embodiment, the method further comprises a step of condensation after said step of catalytic hydrogenation, wherein said second hydrocarbon fluid is obtained via at least said steps of catalytic hydrogenation and condensation and wherein said second hydrocarbon fluid is a multi-phase hydrocarbon fluid.

In a further embodiment, the method further comprises a step of separation after said step of condensation, wherein said second hydrocarbon fluid is obtained at least via said steps of catalytic hydrogenation, condensation and separation and wherein said second hydrocarbon fluid is a first hydrocarbon liquid obtained from said multi-phase hydrocarbon fluid during separation.

In a still further embodiment, the method according to any of the preceding items further comprising a step of pre-hydrogenation catalytic cracking performed prior to the step of catalytic hydrogenation, and wherein said first hydrocarbon fluid is obtained at least via said steps of primary cracking and pre-hydrogenation catalytic cracking.
In a still further embodiment, the method further comprises a step of post-hydrogenation catalytic cracking performed after the step of catalytic hydrogenation and wherein said second hydrocarbon fluid is obtained at least via said steps of catalytic hydrogenation and post-hydrogenation catalytic cracking.

In a still further embodiment, primary cracking of the method is performed by an anaerobic thermal cracking reactor.

In a still further embodiment, the method does not include any of the following steps neither alone nor in combination: hydrocracking, hydroconversion, and hydrodealkylation. In an even further embodiment, the method includes a step of catalytic hydrogenation with the proviso that the catalytic hydrogenation is not hydrocracking, hydroconversion, and/or hydrodealkylation.

In a still further embodiment, the catalytic hydrogenation is performed at a pressure range of 0.1 to 10 bar, preferably in the range of 0.7 to 2 bar, such as around 1 bar.

In a still further embodiment, the catalytic hydrogenation is performed at a temperature range of 300°C to 550°C, preferably between 380°C and 460°C, such as around 420°C.

In a still further embodiment, the method further comprises a step of circulating of said second hydrocarbon fluid to a holding tank prior to fractional separation.

In a still further embodiment, the heavy fraction is recycled to the step of primary cracking, catalytic cracking and/or catalytic hydrogenation or to said holding tank.

In a still further embodiment, the heavy fraction is exposed to a step of heavy fraction cracking before being recycled to the step of primary cracking, catalytic cracking and/or catalytic hydrogenation or to said holding tank.

In a further aspect according to the invention, a waste recycling system for recycling waste plastic into fluid hydrocarbon compounds is provided, comprising
- a primary cracking reactor capable of receiving at least one plastic material and producing a first hydrocarbon fluid from said at least one plastic material by a primary cracking, said first hydrocarbon fluid being a gas;
- a catalytic hydrogenation reactor capable of receiving said first hydrocarbon fluid and producing a second hydrocarbon fluid by catalytic hydrogenation,
- and a fractional separator capable of fractional separation of said second hydrocarbon fluid to obtain at least one final product,

where said primary cracking reactor is in fluid connection with said catalytic hydrogenation reactor and said catalytic hydrogenation reactor is in fluid connection with said fractional separator.

In one embodiment, the system further comprises a condenser for producing said second hydrocarbon fluid together with said catalytic hydrogenation reactor and resulting in said second hydrocarbon fluid being a multi-phase hydrocarbon fluid, and wherein said catalytic hydrogenation reactor is further fluidly connected with said fractional separator through said condenser.

In a further embodiment, the system further comprises a post-condensation separator for separating said multi-phase hydrocarbon fluid to provide a first hydrocarbon liquid and a first non-condensable hydrocarbon gas, and wherein said condenser is further fluidly connected with said fractional separator through said post-condensation separator.

In a still further embodiment, the system further comprises a pre-hydrogenation catalytic cracking reactor, wherein said primary cracking reactor is further fluidly connected with said catalytic hydrogenation reactor through said pre-hydrogenation catalytic cracking reactor.

In a still further embodiment, the system further comprises a post-hydrogenation catalytic cracking reactor, wherein said catalytic hydrogenation reactor is further fluidly connected with said fractional separator through said post-hydrogenation catalytic cracking reactor.
In a still further embodiment, the system further comprises a holding tank for storing the second hydrocarbon fluid prior to fractional separation, where said catalytic hydrogenation reactor is fluidly connected with the fractional separator at least via said holding tank.

In a still further embodiment, the system further comprises a gas burner for providing heat to said primary cracking reactor, said gas burner is fluidly connected with said post-condensation separator.

In a still further embodiment, the system further comprises a heavy fraction cracking reactor, said heavy fraction cracking reactor being in fluidly connection with said fractional separator for receiving a heavy fraction obtained from the fractional separation process and wherein said heavy fraction cracking reactor is further fluidly connected with said primary cracking reactor, said pre-hydrogenation catalytic cracking reactor, said post-hydrogenation catalytic cracking reactor and/or said catalytic hydrogenation reactor.

In a still further embodiment, the system further comprises a post-fractional separation condenser, a non-condensable gas separator and a gas burner, said post-fractional separation condenser being in fluidly connection with said fractional separator for receiving a light fraction obtained from the fractional separation process and wherein said post-fractional separation condenser is further fluidly connected with said non-condensable gas separator for separating a light non-condensable hydrocarbon gas; said non-condensable gas separator being further fluidly connected with said gas burner.

In a further aspect of the invention, the use of a system as described herein or a method as described herein for producing fuel and additional hydrocarbons from waste plastic is provided.

In a further use, the fuel is diesel.
Brief description of the figures

The method and system for production of fuel and additional hydrocarbons from waste plastic according to the invention will now be described in more detail and with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the invention.

Fig.1 shows a first embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation and fractional separation;

Fig.2 shows a second embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation, condensation and separation;

Fig.3 shows a third embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation and a pre-hydrogenation catalytic cracking;

Fig. 4 shows a fourth embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation and a post-hydrogenation catalytic cracking;

Fig.5 shows a fifth embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation and heavy fraction cracking, the product of which can be reinjected;

Fig.6 shows a sixth embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation and several paths for reinjection of the heavy fraction;

Fig. 7 shows a seventh embodiment of the invention presented as a process diagram comprising primary cracking, catalytic hydrogenation, fractional separation and re-circulation of a non-condensable gas isolated after fractional separation;
Fig. 8 shows an eight embodiment of the invention presented as a process diagram being a detailed embodiment according to the invention;

Fig. 9A shows a further embodiment of the invention presented as a process diagram comprising primary cracking, fractional separation and catalytic hydrogenation;

Fig. 9B shows an even further embodiment of the invention presented as a process diagram comprising primary cracking, fractional separation and catalytic hydrogenation as fig. 9A but including additional components.

Fig. 10 shows an overview of an experimental set-up as used in experiment 1;

Fig. 11 shows the conversion results obtained in experiment 1 when initially screening alumina supported catalysts at 20 000 h⁻¹ and 300°C;

Fig. 12 shows the carbon number distribution of the product obtained in experiment 2.

**Detailed description of the invention**

By “waste plastic” is to be understood waste, which is made entirely or primarily of plastic materials i.e. the level of non-plastic material in the waste should preferably be no more than 10 wt%.

By “plastic material” is to be understood a wide range of synthetic or semi-synthetic organic polymers of high molecular mass such as polyolefins, acrylcs, polyesters, silicones and polyurethanes. Examples of plastic materials are HDPE, LDPE, PP, PS, PET, ABS and PVC.

By “primary cracking” is to be understood a process where the molecules of the plastic materials are broken down to minor molecules. In one embodiment, the minor molecules are hydrocarbons primarily having a length of C1-C40, such as C1-C30. Primary cracking includes pyrolysis as well as other cracking types such
as all types of anaerobic thermal cracking. Primary cracking is performed in a primary cracking reactor.

By "catalytic hydrogenation" is to be understood a process where hydrogen is used to saturate unsaturated hydrocarbons. Although a limited cracking action cannot be excluded, the main action of the catalytic hydrogenation is saturation. It thus differentiates itself from the processes of hydrocracking, hydroconversion, and hydrodealkylation. Hydrocracking, hydroconversion, and hydrodealkylation are cracking processes which aim is to reduce the length of the hydrocarbons, and thus obtain more of the light fraction, typically C_{6}-C_{10}, at the expense of longer chains of the medium fraction, C_{11}-C_{20}, typical for diesel, which the present invention aims at maximising. With limited cracking action, is to be understood as less than 10 % wt of the incoming hydrocarbons are cracked, preferably less than 5 % wt, such as preferably less than 3 % wt.

The catalytic hydrogenation may or may not involve the action of catalysts. Catalytic hydrogenation is performed in a catalytic hydrogenation reactor.

By "catalytic cracking" is to be understood a process that cracks linear molecules to linear shorter molecules. It will normally have limited effect on aromatic compounds, and lighter molecules with carbon number lower than C7 are rarely cracked. The preferred embodiment for the so called "catalytic cracking" is with a catalyst. However, it covers the alternative use of a cracker without catalyst i.e. a non-catalysed cracking such as steam-cracking or delayed coking. Catalytic cracking is performed in a catalytic cracking reactor.

By "heavy fraction cracking" is to be understood a cracking process i.e. where linear molecules are cracked to linear shorter molecules on the heavy fraction from the fractional separation. This process can be performed with or without the addition of catalysts. Preferably, the process is performed without catalysts. Heavy fraction cracking is performed in a heavy fraction cracking reactor.

By "residence time" is to be understood the time in which a particular molecule is present in the reactor i.e. from entering the reactor to exiting the reactor.
By “fractional separation” is to be understood a process for obtaining several fractions with a good degree of separation i.e. only having a minimal overlap of hydrocarbon chains having similar length in the fractions i.e. if a separated fraction comprises C6 to C10, the following fraction produced by the fractional separator will comprise at the most 50 wt% C6 to C10, preferably at the most 25 wt% C6 to C10, such as at the most 20 wt% C6 to C10, like the most 15 wt% C6 to C10, more preferred at the most 10 wt% C6 to C10, like at the most 5 wt% C6 to C10. The fractional separation may be a distillation or a number of condensation steps. Fractional separation is performed in a fractional separator.

By “catalyst” is to be understood a substance that causes or accelerates a chemical reaction without itself being chemically affected or being consumed in the process. A catalyst may however show reduced capacity as a result of impurities, and need regeneration.

By “first hydrocarbon fluid” is to be understood a fluid i.e. a liquid and/or a gas entering the catalytic hydrogenation step in the catalytic hydrogenation reactor or entering the fractional separation step in the fractional separator as described in the additional method and system without having been submitted to a catalytic hydrogenation. The first hydrocarbon fluid may comprise a water content of 50 wt% or less, like 45 wt% or less, such as 40 wt% or less, like 35 wt% or less, such as 30 wt% or less, like 25 wt% or less, such as 20 wt% or less, like 15 wt% or less, such as 10 wt% or less, like 5 wt% or less, such as 1 wt% or less. In one embodiment, the first hydrocarbon fluid is a gas. In another embodiment, the first hydrocarbon fluid is multi-phase hydrocarbon fluid.

By “second hydrocarbon fluid” is to be understood a fluid i.e. a liquid and/or a gas entering the fractional separation step in the fractional separator after being submitted to catalytic hydrogenation. The second hydrocarbon fluid may comprise a water content of 50 wt% or less, like 45 wt% or less, such as 40 wt% or less, like 35 wt% or less, such as 30 wt% or less, like 25 wt% or less, such as 20 wt% or less, like 15 wt% or less, such as 10 wt% or less, like 5 wt% or less, such as 1 wt% or less. The second hydrocarbon fluid will preferably be a liquid. In one embodiment, the second hydrocarbon fluid is a multi-phase hydrocarbon fluid.
By "multi-phase hydrocarbon fluid" is to be understood a fluid having at least two phases such as for example a liquid phase and a gas phase, two liquid phases, two liquid phases and two gas phases, two liquid phases and one gas phase and two gas phases and one liquid phase.

The fluid may comprise a water content of 50 wt% or less, like 45 wt% or less, such as 40 wt% or less, like 35 wt% or less, such as 30 wt% or less, like 25 wt% or less, such as 20 wt% or less, like 15 wt% or less, such as 10 wt% or less, like 5 wt% or less, such as 1 wt% or less.

By "non-condensable gas" is to be understood a gas, which is not condensed given the particular setting (pressure and temperature) of the condensation and thus remains as a gas after the condensation process.

By "light fraction" is to be understood a fraction obtained from the fractional separation process, where the fraction includes the shortest hydrocarbon chains of the separation. This would often be hydrocarbon chains as present in gasoline. In one embodiment, the light fraction comprises mainly C6-C10 hydrocarbons. In a further embodiment, the light fraction comprises at least 99 wt% C6-C10 hydrocarbons, such as at least 98 wt% C6-C10 hydrocarbons, like 95 wt% C6-C10 hydrocarbons, such as at least 90 wt% C6-C10 hydrocarbons, like 85 wt% C6-C10 hydrocarbons, such as at least 80 wt% C6-C10 hydrocarbons, like 75 wt% C6-C10 hydrocarbons, such as at least 70 wt% C6-C10 hydrocarbons, like 65 wt% C6-C10 hydrocarbons, such as at least 60 wt% C6-C10 hydrocarbons, like 50 wt% C6-C10 hydrocarbons.

By "medium fraction" is to be understood a fraction obtained from the fractional separation process, where the fraction includes hydrocarbon chains of medium length when separated. This would often be hydrocarbon chains as present in diesel. In one embodiment, the medium fraction comprises mainly C11-C20 hydrocarbons, which is the standard length used in diesel. In a further embodiment, the medium fraction comprises at least 99 wt% C11-C20 hydrocarbons, such as at least 98 wt% C11-C20 hydrocarbons, like 95 wt% C11-C20 hydrocarbons, such as at least 90 wt% C11-C20 hydrocarbons, like 85 wt% C11-C20 hydrocarbons, such as at least 80 wt% C11-C20 hydrocarbons, like 75 wt% C11-C20 hydrocarbons, such as at least 70 wt% C11-C20 hydrocarbons, like
65 wt% C11-C20 hydrocarbons, such as at least 60 wt% C11-C20 hydrocarbons, like 50 wt% C11-C20 hydrocarbons.

By “heavy fraction” is to be understood a fraction obtained from the fractional separation process, where the fraction includes hydrocarbon chains of long length when separated. This fraction may also be mentioned as heavy oil. In one embodiment, the heavy fraction comprises mainly C21 and above hydrocarbons. In a further embodiment, the heavy fraction comprises at least 99 wt% C21 and above hydrocarbons, such as at least 98 wt% C21 and above hydrocarbons, like 95 wt% C21 and above hydrocarbons, such as at least 90 wt% C21 and above hydrocarbons, like 85 wt% C21 and above hydrocarbons, such as at least 80 wt% C21 and above hydrocarbons, like 75 wt% C21 and above hydrocarbons, such as at least 70 wt% C21 and above hydrocarbons, like 65 wt% C21 and above hydrocarbons, such as at least 60 wt% C21 and above hydrocarbons, like 50 wt% C21 and above hydrocarbons.

By “A and B being fluidly connected through C” or “A and B being fluidly connected via C”, which is used interchangeably herein, is to be understood that fluid is able to flow from A to C and further from C to B. A, B and C are to be understood as components of the system as described herein.

**Feed material specifications, sorting and pre-treatment**

In one embodiment, said at least one plastic material is pre-treated prior to said primary cracking. In a further embodiment, the system further comprises means for pre-treating said at least one plastic material prior to being received by said primary cracking reactor such as means for shredding and/or means for drying.

The desired plastic material is cleaned if it is contaminated in such grade that the intermediary or final products or by-products specifications do not respect requirements, and dried if necessary according to same principle criteria.

Contamination may be in the form of organic matter, glass, sand, earth particles or any other form of contamination found in e.g. household or industrial waste, or added to the material during collection, transport or handling and storage phases.
The level of contamination should be as low as possible, and preferably no more than 10 wt%, even preferably less than 5 %, or even better less than 1 or 2 %.

The water content, mostly in the form of water on the surface of the plastic material, should be as low as possible and preferably not higher than 5 wt%, preferably less than 3 %, or even better less than 1 %. Should water content be too high, for example higher than 5 wt%, drying may be required. A high water content in the feedstock material such as 10 wt%, 15 wt%, 20 wt% or 25 wt% water would be possible, but the production capacity may end up to be lower due to a lower throughput of the plant.

Water entering the primary cracking reactor may be separated and extracted from the produced oil and gas further down in the process by means of a non-condensable gas separator or a Holding Tank.

In a still further embodiment, the at least one plastic material is HDPE, LDPE, PP and/or PS.

The plastic compositions desirable in the process are HDPE, LDPE, PP and PS. Plastics of the respective types PET, PVC and ABS are less desirable and preferably kept under 1 wt% fraction each in a standard plant, but may be higher if the plant is equipped with process units or chemical additives removing the additional unwanted chemical elements which the treatment of these plastic types may generate:

- PET contains oxygen that may lead to the formation of alcohols, acids, ketones, aldehydes, esters and other oxygenated compounds in the oil products.
- ABS, in addition to cyanides, amines and amides in the oil products, may produce dioxins when chlorine is present, and mercaptans (thiols) when Sulphur is present. It may also lead to an increase of NOx during combustion of non-condensible gases.
- PVC contains more than 50 wt% chlorine and may contribute to the formation of some of the molecules described above, plus HCl and Chlorine.
• In addition to generating unwanted molecules, PET, PVC and ABS will also reduce the capacity of the process by forming fewer alkanes.

In a still further embodiment, the at least one plastic material is pre-treated by shredding and/or sorting said at least one plastic material.

In one embodiment, the material may be shredded into manageable pieces, preferably in the size range of 5-500 mm, more preferably 10-250 mm, even more preferably 10-100 mm.

In a preferred embodiment, the plastic material is not melted before introduction to the primary cracking.

In a further embodiment, the material may be stored in a buffer hopper, or filled in a hopper feeding for example a conveyor to the primary cracking reactor.

In one embodiment, the plastic material is fed after selection and optional pre-treatment to a primary cracking reactor via a feeding system. The feeding system may comprise a dosing bin and the screw conveyer. Other feeding systems as known in the art may also be used.

In one embodiment, the screw conveyer may include, at one or several stage(s), compression of the plastic feed in order to reduce the amount of air fed into the primary cracking reactor.

**Primary cracking**

The step of primary cracking is performed in a primary cracking reactor. Primary cracking is to be understood as pyrolysis as well as other cracking types such as all types of anaerobic thermal cracking. In a preferred embodiment, primary cracking is pyrolysis. In a more preferred embodiment, the primary cracking is an anaerobic thermal cracking. In a further embodiment, the primary cracking reactor is a pyrolysis reactor. In still a further embodiment, the primary cracking reactor is an anaerobic thermal cracking reactor.
The term pyrolysis is used interchangeably with the terms primary cracking and anaerobic thermal cracking throughout the description.

The main primary cracking reaction that provides a carbon distribution of alkanes and olefins primarily from C1-C40, such as C1-C30 is:

\[
\text{Polyethylene} \xrightarrow{\text{Pyrolysis}} \text{Olefin} \xrightarrow{\text{Alkane}} \text{C} + \text{H}_2 \tag{1}
\]

There is a primary cracking reaction side-reaction that produces carbon and hydrogen:

\[
\text{Polyethylene} \xrightarrow{\text{Pyrolysis}} \text{Alkane} \xrightarrow{\text{Carbon Hydrogen}} \text{C} + \text{H}_2 \tag{2}
\]

There will also be reactions that produce naphthenes (cyclic alkanes), but also aromatic and poly-aromatic hydrocarbons that are not listed here, as known in the art.

In the primary cracking process of cracking plastic, some by-products are formed in the shape of solid carbon particles, or char, as described in Reaction (2). The solid particles are preferably removed from the reactor and optionally cooled, to avoid self-ignition, before further handling. One of such handling may be combustion in order to generate heat for the primary cracking reactor.

Hydrogen is formed in parallel with carbon, and is consumed in the following process steps of the invention, mainly in the catalytic hydrogenation step.

The residence time in the primary cracking reactor may typically vary between 0.1 to 10 hours, preferably between 20 and 90 minutes, even more preferably 30 to 60 minutes.

The primary cracking reactor may also receive a complementary feed of a part or whole of a heavy fraction from the fractional separation.

The primary cracking may be performed with or without catalysts.
In one embodiment, the primary cracking is performed without catalysts.

In one embodiment, the primary cracking reactor does not contain catalysts (thermal cracking mode) modifying the composition of the hydrocarbons exiting the primary cracking reactor. The absence of catalysts will reduce the operating costs (opex) of the primary cracking as well as simplifying the design of the reactor (capex).

In another embodiment, the primary cracker contains catalysts, such as known zeolites or based on active metals, such as Ni, Cd, Mo etc.

In one embodiment, the reactor may contain silico-aluminates to reduce the optimal temperature of reaction. These are consumed and discharged with the solid char fraction. The reactor may also contain minerals such as CaO to capture Cl and S according to techniques known in the art. The resulting fraction is solid and will also be discharged with the char fraction. Silico-aluminates and calcium minerals mentioned above are not considered catalysts, as they are consumed in the process.

In one embodiment, the primary cracking reactor is operated at about 420°C, i.e. the temperature of produced hydrocarbons as measured at the terminal outlet of the reactor is about 420°C. More generally, the primary cracking reactor will be operated at temperatures from between 300°C to 550°C, preferably between 380°C and 460°C.

Throughout this description, the operating temperature of the primary cracking reactor is defined by the temperature at the terminal outlet, i.e. the outlet of the last zone of the reactor, before extraction to next process step.

Depending on the reactor design and operating parameters, different zones in the primary cracking reactor may have different temperatures. For example, some primary cracking reactors show an increasing gradient of temperature from the inlet where the at least one plastic material is received, to the outlet of the primary cracking reactor where the product formed, i.e. the first hydrocarbon fluid, exits the primary cracking reactor.
In one embodiment, plastic fed into the primary cracker is vapourised upon entry into the reactor. In another embodiment, the primary cracker comprises a first melting chamber with moderate temperature to produce an intermediary molten plastic product.

Some reactors may have several outlets, and several inlets, enabling for process optimisation extraction and/or injection/reinjection of the first hydrocarbon fluid or other gasses - such as the combustion gasses of the burner heating the primary cracker - in different zones of the reactor.

In one embodiment, the operating pressure will be kept around 1 bar. In another embodiment, the operating pressure is within a range of 0.1 and 10 bar, such as in the range from 0.5 to 5 bar, like in the range from 0.7 to 2 bar, such as in the range from 0.9 til 1.1 bar.

In one embodiment, the primary cracking reactor is operated in at a pressure range of 0.7 to 2 bar, preferably 0.9 til 1.1 bar 1ba and at a temperature between 300°C to 550°C, preferably between 380°C and 460°C, such as around 420°C.

In one embodiment, the primary cracking reactor is operated in a range of 0.9 to 1.1 bar and at a temperature between 380°C and 460°C.

The optimal temperature and pressure of the product at the outlet will vary. It will depend i.e. on the nature of the feed and on the design of the primary cracker reactor.

The primary cracking will i.a. produce non-condensable gases – mainly alkanes with carbon length of 1 to 6. The non-condensable gas may be burned in a gas burner using air for combustion, thus providing heat to the primary cracking reactor. The production of non-condensable gas will depend on the nature of the feed such as type of plastic as well as the operations parameters of the primary cracking reactor such as temperature and pressure. The amount of non-condensable gases is preferably adjusted to be sufficient to heat the primary cracking reactor during running operation. If for any reason there is a shortage of non-condensable gas, increasing the temperature of the primary cracking reactor
or the residence time of the plastic material in primary cracking reactor will increase the production of non-condensable gas, thus correcting the shortage.

Additionally and/or complementarily, additional fuel for combustion may be supplied from a commercial fuel source. The commercial fuel source is also designed for start-up of the primary cracking process: before reaching a stable running operation upon start, the primary cracking reactor will need to be heated up with readily burnable commercial fuels. This often needs to be performed for several hours. Examples of possible fuels are carbon, gasoline, diesel, any type of heavy oil, Liquefied Petroleum Gas (LPG), natural gas (NG), non-condensable gas etc.

Combustion gas from the gas burner (high temperature) will be mixed with returning exhaust gas (lower temperature after heat transfer to the primary cracking reactor) and recycled from the outlet of the primary cracking reactor to reduce the temperature and ensure a gas velocity enabling good heat transfer to the plastic inside the reactor.

In one embodiment, the recycling rate may tentatively vary from 10 to 70% of produced exhaust gas.

In a further embodiment, the temperature of the exhaust gas may vary from 400 to 800°C, preferably 500 to 600°C, more preferred about 550 °C. These temperatures will depend on a number of parameters, of which the plastic feed and the type of reactor.

In one preferred embodiment, the primary cracking reactor is of an indirect heating type, i.e. the main source of heat is not mixed with the waste plastic feed in the reactor.

**Filtration and cooling after primary cracking**

In a still further embodiment, the method further comprises filtering and optionally cooling after the step of primary cracking.
In one embodiment, the first hydrocarbon fluid leaving the primary cracking reactor after e.g. pyrolysis is filtered to remove carbon particles formed in the primary cracker and not discharged as solids e.g. char.

In order to protect the process units downstream, contaminants such as sand, glass, and unreacted plastic will also need to be either collected with char and solids at the bottom/end-part of the primary cracking reactor, or filtered when transported by the fluid exiting the primary cracker.

The particles borne by the first hydrocarbon fluid being a first hydrocarbon gas are expected to have sizes of one to several hundred μm. The amount of the particles are expected to vary with inlet water content, plastic type, contamination and the performance of the pyrolysis reactor.

Filtration methods known in the art may be used to this purpose. In one embodiment, filters will be designed to remove up to at least 95 % of particles larger than 5 microns. In a further embodiment, the filtration will be performed using a cyclone filter.

In a further embodiment, the gas temperature is adjusted to the temperature expected downstream, by means of heat exchangers. The temperature is preferably adjusted after filtering.

In a further embodiment, the gas pressure is adjusted to the pressure expected downstream by means of pressure reducing devices, such as a pressure control valve or other pressure control devices.

Hydrogenation Reactor

After the primary cracking and optional filtration, temperature and pressure adjustments, the first hydrocarbon fluid will undergo a catalytic hydrogenation in a catalytic hydrogenation reactor. Alternatively, the catalytic hydrogenation may be performed on at least one product from the fractional separation process as described for the additional method and system as disclosed herein.
In principle, all unsaturated hydrocarbon molecules such as alkenes, alkynes, aromatics etc. containing a double or triple bond may react in the catalytic hydrogenation process, resulting in the molecules becoming saturated. An example of hydrogenation is shown below:

\[-\text{CH}=\text{CH}- + \text{H}_2 \rightarrow -\text{CH}_2-\text{CH}_2-\]  
(3)

Olefin  Hydrogen  Alkane

The catalytic hydrogenation is run in gas phase. In one preferred embodiment, the process is run at conditions such as pressure and temperature above the Dew Point of the gas feed entering the catalytic hydrogenation reactor.

In a further embodiment, potential condensates in the gas are drained before entering the catalytic hydrogenation reactor i.e. upstream of the catalytic hydrogenation reactor.

In one embodiment, the operating pressure will be kept around 1 bar. In another embodiment, the operating pressure is within a range of 0.1 and 10 bar, such as in the range from 0.5 to 5 bar, like in the range from 0.7 to 2 bar, such as in the range from 0.9 til 1.1 bar.

The operating temperature at one bar will typically be between 150-280°C, preferably between 190-270°C. In one embodiment, the operating temperature will be around 190-200°C. In another embodiment, the operating temperature will be about 270°C.

In a still further embodiment, the catalytic hydrogenation is performed at an operating pressure of 1 bar and by temperatures between 150-280°C, preferably between 190-230°C, such as around 200°C.

In one embodiment, the catalytic hydrogenation is improved by adding hydrogen at several different locations along the catalytic hydrogenation reactor. Hereby, the concentration profile of the hydrogen through the catalyst is improved.
Hydrogen is often provided by the primary cracking reaction resulting from the decomposition as detailed in reaction (2). Thus, the first hydrocarbon fluid would be expected to hold some hydrogen. However, in some embodiments, addition of external hydrogen may be necessary.

Many types of reactors may be used for catalytic hydrogenation. In one embodiment, a packed-bed reactor is used. In another embodiment, a fixed-bed reactor is used, for example filled with a honeycomb structure. In a further embodiment, a fluidised-bed reactor is used.

In one embodiment, the Space Velocity (SV) of the reactor is in a range of from 50 000 to 200 h⁻¹. The SV is calculated as the flow of the fluid to be processed divided by the bed volume of the reactor.

For a packed-bed reactor, the range is preferably from 50 000 to 10 000 h⁻¹, such as from 50 000 to 30 000 h⁻¹, like from 30 000 to 20 000 h⁻¹, such as from 20 000 to 15 000 h⁻¹, like from 15 000 to 10 000 h⁻¹.

For a fixed-bed reactor, an expected range will be 10 000 to 200 h⁻¹, such as from 10 000 to 5 000 h⁻¹, like from 5 000 to 2 000 h⁻¹, such as from 2 000 to 1 000 h⁻¹, like from 1000 to 500 h⁻¹, such as from 500 to 200 h⁻¹.

The catalytic hydrogenation reactor may have an open structure. In one embodiment, flow openings will be of 0.1 to 10 mm, such as 0.5-8 mm, like 1-6 mm, such as 1.5-5 mm, preferably 2-4 mm.

Many catalysts are known to function well for hydrogenation and can be used in this application. For example a catalyst such as Cu-Mn/Al₂O₃ can be used for the catalytic hydrogenation. Other hydrogenation catalysts with good performances may also be used such as Ru/C, Pt/ASA or PtPd/ASA (where ASA is Amorphous Silica-Alumina) and CoMo/γ-Al₂O₃.

In one embodiment, the catalytic hydrogenation reactor receives a complementary feed of a heavy fraction from the fractional separator either
directly from the fractional separator or after the heavy fraction has been exposed to a heavy fraction cracking.

The formation of coke or other impurities on the catalyst surface may deactivate the catalyst. Therefore, regeneration of the catalyst may be required.
In one embodiment, the catalytic hydrogenation reactor is equipped with an in-situ cleaning/regenerating system, as known in the art.
In another embodiment, regeneration may be performed in a plant or in dedicated facilities after extraction of the catalyst from the reactor.

In one embodiment, the catalytic hydrogenation follows primary cracking and optionally filtration and cooling of the gas before entering the catalytic hydrogenation. In this embodiment, a heat exchanger cools the gas coming from primary cracking (indicative preferred temperature of 420°C) before entering the catalytic hydrogenation (indicative preferred temperature below 270°C).

In one embodiment, the required specification for the final product is EN590, and in some cases, the combination of the primary cracking and catalytic hydrogenation without further processing such as for example an additional catalytic cracking would not produce expected yield and quality.

*Catalytic cracking*
In a further embodiment, the gas may undergo an additional cracking step after primary cracking and optionally filtration and cooling,. This additional step may be selected in order to improve productivity, and in particular in order to break long chain molecules such as C21 and above, like C21-C40, such as C21-C30 in the final product. The additional catalytic cracking step may take place before the catalytic hydrogenation (pre-hydrogenation catalytic cracking) or after (post-hydrogenation catalytic cracking).

Throughout the description catalytic cracking and catalytic cracking reactor will refer to both pre-hydrogenation catalytic cracking and post-hydrogenation catalytic cracking as well as pre-hydrogenation catalytic cracking reactor and post-hydrogenation catalytic cracking reactor.
The catalytic cracking reactor will mainly crack linear molecules to linear shorter molecules. It will normally have limited effect on aromatic compounds, and lighter molecules with carbon number lower than C7 are rarely cracked. The catalyst will crack C-C bonds but may also give rise to isomerization of molecules.

In one embodiment, the temperature as measured in the catalytic cracking reactor is kept around 420°C, but the catalytic cracking reactor may also be operated at temperatures from between 350°C to 550°C, and preferably between 380 and 460°C.

In one embodiment, the operating pressure is around 1 bar. In a further embodiment, the operating pressure is in a range between 0.1 and 10 bar, such as in the range from 0.5 to 5 bar, like in the range from 0.7 to 2 bar, such as in the range from 0.9 til 1.1 bar.

In a further embodiment, catalytic cracking is performed at an operating pressure of 1 bar and at temperatures between 350°C and 550°C, and preferably between 380°C and 460°C, such as around 420°C.

Multiple types of reactor may be used. In one embodiment, a packed-bed reactor is used. In another embodiment, a fixed-bed reactor is used, for example filled with a honeycomb structure. In a further embodiment, a fluidised-bed reactor is used.

In one embodiment, the Space Velocity (SV) of the reactor may typically be within a range from 50 000 to 200 h⁻¹.

For a packed-bed reactor, a typical range will be 50 000 to 10 000 h⁻¹, such as from 50 000 to 30 000 h⁻¹, like from 30 000 to 20 000 h⁻¹, such as from 20 000 to 15 000 h⁻¹, like from 15 000 to 10 000 h⁻¹.

For a fixed-bed reactor, a typical range will be 10 000 to 200 h⁻¹, such as from 10 000 to 5 000 h⁻¹, like from 5 000 to 2 000 h⁻¹, such as from 2 000 to 1 000 h⁻¹, like from 1000 to 500 h⁻¹, such as from 500 to 200 h⁻¹.
The catalytic reactor may have an open structure. In one embodiment, flow openings will be of 0.1 to 10 mm, such as 0.5-8 mm, like 1-6 mm, such as 1.5-5 mm, preferably 2-4 mm.

Many catalysts are known to function well for catalytic cracking and can be used according to the invention for example ultrastable Y zeolite (USY) for catalytic cracking. Other catalytic cracking catalysts with good performances may also be used such as acid zeolite catalysts, where USY in an example. Mixed metal sulphides or noble metal catalysts are also used.

The formation of coke or other impurities on the catalyst surface will deactivate the catalyst. Because of this, regeneration of the catalyst is advantageously performed. In one embodiment, the reactor is equipped with an in-situ cleaning/regenerating system, as known in the art for example a system using air, water or inert gas mixture to regenerate the catalyst.

In another embodiment, regeneration may be performed in the plant or in dedicated facilities after extraction of the catalyst from the catalytic cracking reactor.

The pre- or post-hydrogenation catalytic cracker reactor may also receive a complementary feed of a part or whole of the heavy fraction from the fractional separator either directly i.e. without being further processed, from the fractional separator or after the heavy fraction has been exposed to a heavy fraction cracking.

In a further embodiment, a heavy fraction cracker may process the heavy fraction obtained from the fractional separator before re-injecting it upstream in the process. Hereby, the production of light and medium fractions obtained from fractional separation can be increased.

In one embodiment, the catalytic cracker is preferably run at higher temperature than the hydrogenation reactor, in particular in a range of temperature close to the one of the primary cracking reactor such as preferably at a temperature around 420 °C. Thus, from a point of view of the plant energy efficiency the
catalytic cracking is preferably a pre-hydrogenation catalytic cracking. The gas flowing out of the primary cracking reactor will thus need no cooling – nor any pressure reduction - before entering the pre-hydrogenation catalytic cracking reactor. After pre-hydrogenation catalytic cracking, cooling may be required before entering the catalytic hydrogenation reactor, in order to bring the temperature of the first hydrocarbon fluid at the outlet of the pre-hydrogenation catalytic cracker from an operation temperature of for example 420°C, down to below 270°C.

In another embodiment, the catalytic cracking may be a post-hydrogenation catalytic cracking. This is advantageous for optimisation of hydrogen consumption. Catalytic hydrogenation consumes a high amount of hydrogen compared with catalytic cracking, and hydrogen is to come primarily from the primary cracking. In case the amount of hydrogen from the primary cracking reaction is limited, the catalytic cracking after hydrogenation can be a mean to reduce the consumption of the additional hydrogen to be purchased from an industrial gas supplier.

Using post-hydrogenation catalytic cracking may however result in re-creation of unsaturated molecules and the necessity of heating up the gas obtained from the catalytic hydrogenation to a temperature required for catalytic cracking, which is energy consuming.

Condensation and separation

In one embodiment, a condenser is arranged after catalytic hydrogenation and/or post-hydrogenation catalytic cracking for the produced hydrocarbon fluid to flow into the condenser. Alternatively, the condenser may be arranged prior to the fractional separator and/or after the primary cracking.

In the condenser, the temperature is reduced to achieve condensation. From temperatures of for example 270°C or 200°C (outlet of the catalytic hydrogenation reactor) or 420°C, (outlet of the catalytic cracking reactor or the primary cracking reactor), the gas is cooled to preferably 100-130°C, more preferred 110°C, at a pressure in the range of 0.5-1 bar, most preferred 0.7-0.9 bar. In another embodiment, from temperatures of for example 380°C to 460°C (primary cracking reactor), the gas is cooled to 60°C to 180°C. Hereby, most of
the gas is condensed and forms a multi-phase hydrocarbon fluid comprising at least a first non-condensable gas and a first hydrocarbon liquid.

In a further embodiment, the exit temperature of the condenser is 110°C, to keep water in vapour phase and facilitate water separation from hydrocarbon liquid (oil). Preferably, the temperature is kept above 60°C as at lower temperatures, for example below 60 °C, there is a risk of undesirable wax deposition.

In a further embodiment, the fluid after condensation i.e. the multi-phase hydrocarbon fluid passes through a post-condensation separator, where the hydrocarbon liquid fraction (with a possible limited water fraction, of preferably max 0.2 %) is separated from the non-condensable gas fraction (which may contain a small fraction of water vapour).

In a further embodiment, the second hydrocarbon fluid, after optional cooling, and with optional purification (see below), is transferred to a Holding Tank. In one embodiment, the temperature of the Holding Tank is in a range of 60 to 80°C, preferably around 60°C.

In a further embodiment, the second hydrocarbon fluid is further purified before entering the Holding Tank.

In a still further embodiment, the separation further results in the formation of a first non-condensable hydrocarbon gas and wherein at least a part of said first non-condensable hydrocarbon gas is recirculated to and burnt in a gas burner to provide heat to said primary cracking.

In a still further embodiment, the at least a part of said first non-condensable hydrocarbon gas is exposed to further processing before being burnt such as further condensation and separation.

*Purification of the hydrocarbon liquid*

In a further embodiment, impurities are removed after catalytic hydrogenation and/or catalytic cracking. Alternatively, impurities are removed after primary cracking. The impurities may be removed by means of one or more filters.
Impurities may be acids, alcohols, other oxygenated organic compounds, HCl and H₂S to mention the most common ones. For the hydrocarbon liquid, such purification will take place at any location between the post-condensation separator and the Holding Tank. In one embodiment, purification of the second hydrocarbon fluid will take place in the Holding Tank.

In one embodiment, small amounts of water/NaOH solution, alternatively any substance that neutralize acids such as CaO or Ca(OH)₂ are added to the hydrocarbon liquid.

Some of the purification reactions that take place are listed below:

*Alcohol:*
\[
R-OH + NaOH = R-ONa + H₂O \quad (4)
\]

*Acid:*
\[
R-COOH + NaOH = R-COONa + H₂O \quad (5)
\]

*Hydrogen sulfide:*
\[
H₂S + 2NaOH = Na₂S + 2H₂O \quad (6)
\]

*Hydrochloric acid:*
\[
HCl + NaOH = NaCl + H₂O \quad (7)
\]

The formed sodium salts dissolve in water, which may be separated from hydrocarbon fluid in the Holding Tank.

*Fractional separation*

After catalytic hydrogenation optionally followed by further processing as described above, the second hydrocarbon fluid is fractional separated for segregation of different mixes of hydrocarbons. Alternatively, the fractional separation may be performed on the first hydrocarbon fluid as described for the additional method and system as disclosed herein.

The fractional separation process can be distillation or a number of condensation steps in order to obtain several fractions having a good degree of separation.
In one preferred embodiment, the second hydrocarbon fluid is fractional separated by distillation. In another embodiment, the fractional separation step is performed as a distillation.

In a further embodiment, the second hydrocarbon fluid such as the first hydrocarbon liquid in the Holding Tank, being for example 60°C, is heated to for example 160°C before entering a fractional separator. This allows controlling of the final product fractions, based on their respective physical and chemical properties for example the boiling point. The previous primary cracking is expected to produce excess energy, a fraction of which may be available for fractional separation.

In a still further embodiment, the first hydrocarbon liquid is heated before fractional separation.

The fractional separator may use packed beds, sieve trays, clock bottoms, packing material or other material that ensure good gas/liquid contact. The quality of the contact is important to get good separation of the components in the tower. In one embodiment, packed beds may be used.

In one embodiment, it is envisaged to collect three fractions from the fractional separator, a light fraction, a medium fraction, and a heavy fraction. In a still further embodiment, three final products are obtained from said fractional separation step being a light fraction such as mainly C6 to C10; a medium fraction such as mainly C11 to C20 and a heavy fraction such as mainly C21 and above.

Typically, the light fraction is collected at the top of the column after being condensed. The medium fraction, typically a diesel product, is collected between the bottom and the top of the column where the quality is according to specifications. The heavy fraction is collected at a low point of the column.

The definitions of the fractions vary in literature and the industry, depending on the focus, but also because chemistry involved is not strictly segmented by the number of carbons. According to this invention, the fractions are to be understood as and defined by:
light fraction: mainly C6 to C10
Diesel (medium fraction): mainly C11 to C20.
Heavy fraction: mainly C21 and higher.

In a still further embodiment, the light fraction is condensed and optionally separated resulting in at least a light non-condensable hydrocarbon gas, and wherein at least a part of said light non-condensable hydrocarbon gas is recirculated to and burnt in a gas burner to provide heat to said primary cracking.

In still further embodiments, the number of products ("fractions") obtained from the fractional separator may be less or more than tree i.e. two, four, five or six. In a still further embodiment, the ranges of carbon atoms may be different than as described above. For example C6 to C11, C12-C21 and C22 and higher.

The reboiler is located at the bottom of the tower. The reboiler supplies the necessary heat to the fractional separator, in particular consumed for evaporation.

In one embodiment, the fractional separator operates at vacuum, but may also be designed to operate at any pressure, typically up to 50 bar.

In a further embodiment, the fractional separator is designed to operate at vacuum, with the feed pre-heated to approximately 160 °C in a pre-heater before entering the fractional separator. At this temperature, the feed will be approximately 50/50 wt% split of vapour and liquid. Due to the mixed feed stream after heating, a flash vessel is introduced before the fractional separator to ensure adequate liquid-vapour separation so that the vapour does not create turbulence and disturb the equilibrium of the fractional separator.

In a further embodiment, the diameter of the column is 1 000 mm and the height 15 000 mm.

In one embodiment, the top operating pressure of the column is 100 mbar to maintain bottom temperature at 290°C.
To provide some process flexibility to the fractional separator, the feed can be introduced to the fractional separator at different feed locations and also side draw locations can be adjusted. Such fractional separator will not be detailed further, as it is known to a person skilled in the art.

As previously described, the heavy fraction can be in part or in whole recirculated into the process. It can be fed into the primary cracking reactor, the pre-hydrogenation catalytic cracking reactor or as an alternative to the post-hydrogenation catalytic cracking reactor without any significant treatment, or in several of these reactors at the same time when they are present in the process.

In one embodiment, the heavy fraction is recirculated into the reactors without specific chemical treatment. The fraction will though preferably be heated to vaporisation so as to obtain a hydrocarbon gas fraction. The heavy fraction may be returned in whole or in part to the primary cracking reactor in which case vaporisation may not be necessary. As an alternative, the heavy fraction may be returned in whole or in part to the catalytic cracker. These recirculation loops are typically designed and activated on the basis of modelled or observed process operation parameters. Recirculation may in turn require process adjustments as the load may vary to the different reactors, as is known in the process industry.

As an alternative, it can be fed to a dedicated heavy fraction catalytic cracker, as will be described below.

*Heavy fraction cracking*

In a further embodiment, the method comprises a step of heavy fraction cracking performed in a heavy fraction cracking reactor, which solely runs on the heavy fraction from the fractional separation. In doing so, the general process yield of lighter fractions i.e. the fractions with shorter carbon chains than the heavy fraction, such as diesel, is increased as the longer hydrocarbon chains in the heavy fraction are cracked to shorter chains, for example within the diesel range.

In one embodiment, this alternative is preferred to catalytic cracking of the whole hydrocarbon gas (pre- or post-hydrogenation) as undesired cracking of the
potential “diesel fraction” of the gas into a lighter fraction are prevented when the gas is light.

In a further embodiment, the liquid heavy fraction is heated and vaporized to a temperature of close to 420°C before entering the heavy fraction catalytic cracker. The heavy fraction catalytic cracker may be operated at temperatures between 350°C and 550°C, and preferably between 380 and 460°C, where the temperature ranges are defined for operation at 1 bar.

In one embodiment, the operating pressure is kept around 1 bar, but operation is considered at pressure range between 0.1 and 10 bar, such as in the range from 0.5 to 5 bar, like in the range from 0.7 to 2 bar, such as in the range from 0.9 til 1.1 bar.

In one embodiment, the heavy fraction catalytic cracker is operated at temperatures between 350°C and 550°C, and preferably between 380 and 460°C, such as around 420°C.

In a still further embodiment, the heavy fraction catalytic cracking is performed at an operating pressure within a range of 0.1 to 10 bar, preferably 1 bar and by temperatures between 350-550°C, preferably between 380-460°C.

The resultant stream from heavy fraction cracking is in one embodiment a gas phase, and may be introduced upstream the catalytic hydrogenation reactor, the fractional separator, or the catalytic cracking reactors, pre- or post-hydrogenation.

When the stream resulting from the heavy fraction cracking is fed to the catalytic hydrogenation, it should be cooled to the temperature of the catalytic hydrogenation reactor, for example at below 270°C at 1 bar as described above.

If the resultant stream is introduced after the catalytic hydrogenation directly to fractional separator or into the Holding Tank, the stream will be cooled to the temperature of the Holding Tank, for example around 60 °C.
Furthermore, when performing a heavy fraction cracking, it is important to ensure there is sufficient hydrogen to ensure double bonds are not present after cracking, as heavy fraction cracking of the heavy fraction may else form double bonds during the reaction. Thus, in one embodiment, an additional source of industrial hydrogen gas may be added.

**Non-Condensable Gas**

During primary cracking and the additional treatments, non-condensable gas may be formed. The non-condensable gas fraction after primary cracking will contain alkanes, alkenes, alkynes and cyclic hydrocarbons with a carbon number mainly less or equal to 6. After separation following catalytic hydrogenation or catalytic cracking, it will mainly consist of alkanes with a carbon number from 1 to 6.

In the present context, “a carbon number mainly less or equal to 6” is to be understood as preferably at least 50 wt% has a carbon number below 6, such as at least 55 wt% has a carbon number below 6, like at least 60 wt% has a carbon number below 6, more preferred at least 65 wt% has a carbon number below 6, such as at least 70 wt% has a carbon number below 6, like at least 75 wt% has a carbon number below 6, for example at least 80 wt% has a carbon number below 6, most preferred at least 85 wt% has a carbon number below 6, such as at least 90 wt% has a carbon number below 6, like at least 95 wt% has a carbon number below 6, such as at least 97 wt% has a carbon number below 6, like at least 99 wt% has a carbon number below 6.

In one embodiment, the first non-condensable gas after separation is further cooled to partial condensation, generally producing a 3-phase fluid comprising gas, oil, and water. In one embodiment, the gas is cooled down to around 35°C. The fluid is then separated. An embodiment for the non-condensable gas separator is a modified cyclone within a tank, achieving a 3-phase separation, gas, oil and water.

In a further embodiment, the gas is transferred to a gas scrubber/filter as known in the art to ensure that the gas is clean and without contaminants like S and Cl, and running at about the same temperature (for example 35°C). The cleaned
non-condensable gas will then be combusted in the gas burner to heat the primary cracking reactor during continuous and steady state operation.

*Non-condensable gas separation after fractional separation*

In a further embodiment, the multi-phase hydrocarbon composition obtained after condensation is fed directly to fractional separation without prior separation. In such case, condensation may be milder, designed to bring the multi-phase composition to the pressure and temperature conditions required at the inlet of the fractional separator. In such case, the light fraction from the fractional separation is fed to a post-fractional separation condenser and then separated in the non-condensable gas separator.

In still another embodiment, it is the the multi-phase hydrocarbon fluid composition exiting the catalytic hydrogenation or the post-hydrogenation catalytic cracking which is fed to fractional separation, optionally after some cooling in a condenser.

*Services and by-products*

*Heat management of the plant*

Heat management is an important part of the process and operations management. Heat consumption will be optimized, according to good process engineering principles, making use of heat exchangers.

In an embodiment, thermal oil is used to carry and exchange heat in a higher temperature range, while water is used for heat exchange in a lower temperature range.

*Gas loops in the plant*

The cleaned non-condensable gas is mixed with air and burnt to produce the necessary energy to operate the primary cracking reactor as described earlier. Non-condensable gas burnt in the gas burner, together with a recycled part of the primary cracking exhaust gas will provide the flue gas with levels of NOx to be below the local emission limits. The flue gas, will preferably be cooled before emission.
Waste water and Waste solids
There may be waste water from the optional inlet plastic drying plant, from the non-condensable gas separator, from the Holding Tank, and from plant operation. Waste water may also come from the non-condensable gas scrubber. There may also be water coming from the process of collection, transport and separation of carbon particles coming out of the primary cracker, of the particle cleaning filter after primary cracking, of the catalysis regeneration units etc.

Waste water will generally be treated using techniques as known in the art for such type of waste water.

Handling of solids
Produced solids, essentially char from primary cracking but also contaminant particles, rests of plastic, solid residues from cyclone-type and other filters etc. are collected, and further processed. This will preferably be transported to a specialised processing plant, outside of the scope of this description.

Material balance
The primary end product from the waste plastic method as described herein is diesel comprised in the medium fraction, with tentative conversion ratio of 20 to 80 wt% (weight %) such as 25-35%, 35-45%, 45-55%, 55-65% or 65-75%. Additionally, 5-70 wt% light fraction is tentatively produced such as 10-20%, 20-30%, 30-40%, 40-50% or 50-60% light fraction. Furthermore, 3-25 wt% heavy fraction is tentatively produced.

During primary cracking some ash/carbon and non-condensable gases may be formed. Ash production may typically vary between 1 to 30 wt%, non-condensable gases may typically vary from 1 to 30 wt%. Permanent/non-condensable gases and ash/carbon may be re-used for energy production to heat the primary cracking reactors.

Feeding waste plastic after shredding to a continuously running process comprising primary cracking, catalytic hydrogenation in gas phase and fractional separation, provides high efficiency, high throughput, and a stable and predictable quality for the fuel. Furthermore when the light fraction of gas produced is used to
heat the continuous primary cracking process, it results in an almost energy neutral method.

*Additional method and system for producing hydrocarbons from waste plastic*

In an additional method, fuel and additional hydrocarbons from waste plastic are produced by a method comprising the steps of
- providing at least one plastic material;
- exposing said at least one plastic material to a primary cracking to obtain a first hydrocarbon fluid;
- fractional separation of said first hydrocarbon fluid to obtain at least one product,
- exposing at least one of said at least one products to a catalytic hydrogenation to obtain a final product.

In one embodiment, the catalytic hydrogenation is performed on a gas. In a further embodiment, at least one of the products obtained by fractional separation is heated to produce said gas. Thus, the catalytic hydrogenation is in gas phase, and the product may be heated up to a gas phase before entering catalytic hydrogenation.

In a further embodiment, the method comprises a step of condensation prior to said step of fractional separation, wherein said first hydrocarbon fluid is obtained via at least said steps of primary cracking and condensation.

In a further embodiment, the method comprises a step of prehydrogenation catalytic cracking prior to said step of fractional separation and optionally prior to said step of condensation, wherein said first hydrocarbon fluid is obtained via at least said steps of primary cracking and pre-hydrogenation catalytic cracking and optionally condensation.

In a further embodiment, at least three products are obtained from said fractional separation step, being a light fraction such as mainly C6 to C10; a medium fraction such as mainly C11 to C20 and a heavy fraction such as mainly C21 and above.
In a further embodiment, said light fraction is condensed and optionally separated resulting in at least a light non-condensable hydrocarbon gas, and wherein at least a part of said light non-condensable hydrocarbon gas is recirculated to and burnt in a gas burner to provide heat to said primary cracking.

Thus, the fractional separation light fraction may be further processed by a post-fractional separation condenser and a non-condensable gas separator optionally after cooling in order to separate the non-condensable gas from the light fraction. The light non-condensable gas can be used to heat the primary cracking reactor as described above and will result in amount of non-condensable gas for burning similar to other embodiments. The only difference is that in this embodiment, compared to other embodiments as described above, is that the light non-condensable gas will not be saturated/hydrogenated and will thus contain olefins. The difference in heating value between light alkanes and olefins is negligible and thus, it is expected that a similar amount of heat will be provided to the primary cracking reactor.

In a further embodiment, a liquid light fraction is obtained from the non-condensable gas separator. The liquid light fraction is used as such as gasoline or further processed.

In a still further embodiment, said at least a part of said light non-condensable hydrocarbon gas is exposed to further processing in a hydrogen separator prior to being burnt in said gas burner to separate hydrogen from the non-condensable hydrocarbon gas. In an even further embodiment, the hydrogen is recirculated for use in the step of catalytic hydrogenation.

In a further embodiment, the at least one product being exposed to catalytic hydrogenation is said medium fraction.

The main benefit of this configuration is that hydrogen is not consumed in hydrogenating of light and heavy fractions before fractional separation. This reduces the amount of external hydrogen required and specific fractions obtained from the fractional separation such as the medium fraction comprising diesel can be selectively hydrogenated.
In a still further embodiment, said heavy fraction is recycled to one or more of the steps of primary cracking, catalytic cracking or condensing upstream of the fractional separator. In an even further embodiment, said heavy fraction is exposed to a step of heavy fraction cracking before being recycled to one or more of the steps of primary cracking, catalytic cracking or condensing upstream of the fractional separator. In an even further embodiment, said heavy fraction is evaporated prior to being exposed to a step of heavy fraction cracking, the heavy fraction cracker operating in gas phase.

Thus, in one embodiment, the heavy fraction can be cracked in a heavy fraction cracking reactor as described above after fractional separation and the cracked heavy fraction product being recycled to the fractional separator to increase the yield in lighter fractions, for example of the medium fraction comprising diesel.

Such alternative configuration will increase the yield, but the diesel quality/composition will remain the same as the fractional separator can be expected to split the resultant fractions in about the same manner whether it is downstream or upstream of the hydrogenation reactor which should not crack molecules significantly. Hydrogenation of this fraction will occur regardless of the configuration.

In a further aspect, a waste recycling system for recycling waste plastic into fluid hydrocarbon compounds comprising

- a primary cracking reactor capable of receiving at least one plastic material and producing a first hydrocarbon fluid from said at least one plastic material;
- a fractional separator for fractional separation of said first hydrocarbon fluid to obtain at least one product, and
- a catalytic hydrogenation reactor capable of receiving at least one of said at least one products and producing a final product,

where said primary cracking reactor is in fluid connection with said fractional separator and said fractional separator is in fluid connection with said catalytic hydrogenation reactor is described.

In one embodiment, said first hydrocarbon fluid is a gas.
In one embodiment, the system further comprises a heater for gaseifying at least one of said at least one products obtained from said fractional separator and wherein said fractional separator is fluidly connected with said catalytic hydrogenation reactor via said heater.

The catalytic hydrogenation reactor is designed for gas phase, and a heater for gaseifying the product issued from the fractional separator before entering the catalytic hydrogenation reactor may be added.

In a further embodiment, said system further comprises a condenser condensing said first hydrocarbon fluid prior to fractional separation and wherein said primary cracking reactor and fractional separator is fluidly connected via said condenser.

In a still further embodiment, said system further comprises a heavy fraction cracking reactor, said heavy fraction cracking reactor being in fluidly connection with said fractional separator for receiving a heavy fraction obtained from said fractional separation process and wherein said heavy fraction cracking reactor is further fluidly connected with said primary cracking reactor and/or said first hydrocarbon fluid.

In an even further embodiment, the system further comprises a post-fractional separation condenser, a non-condensable gas separator and a gas burner, said post-fractional separation condenser being in fluidly connection with said fractional separator for receiving a light fraction obtained from the fractional separation process and wherein said post-fractional separation condenser is further fluidly connected with said non-condensable gas separator for separating a non-condensable hydrocarbon gas; said non-condensable gas separator being further fluidly connected with said gas burner.

In a further embodiment, the system further comprises a hydrogen separator for separating hydrogen from said non-condensable gas; said hydrogen separator being fluidly connected with said gas burner and said catalytic hydrogenation reactor.
However, the hydrogen produced during primary cracking will not necessarily be accompanying the fractionally separated product to the catalytic hydrogenation. H₂ will be found in the light fraction of the fractional separator. If, as considered in one embodiment, it is not the light fraction which will constitute the product, H₂ may be extracted from this light fraction to be reintroduced in the process at the catalytic hydrogenation reactor. For example, H₂ may be extracted from non-condensable gas returning to the burner.

**Detailed description of the figures**

Fig. 1 illustrates a first embodiment of the invention comprising a primary cracking reactor (20) capable of transforming at least one plastic material into a first hydrocarbon fluid being a gas by primary cracking. The first hydrocarbon fluid is directed via the fluid connection to a catalytic hydrogenation reactor (40) capable of transforming the first hydrocarbon fluid to a second hydrocarbon fluid by catalytic hydrogenation. The second hydrocarbon fluid is directed via the fluid connection to a fractional separator (80) for fractional separation of the second hydrocarbon fluid into three products being a light fraction (81), a medium fraction (82) and a heavy fraction (83).

Fig. 2 illustrates a second embodiment of the invention comprising a primary cracking reactor (20) followed by a catalytic hydrogenation reactor (40). The waste plastic is fed to the primary cracking reactor (20) producing a first hydrocarbon fluid being a gas. The first hydrocarbon fluid is then exposed to catalytic hydrogenation (40) forming a second hydrocarbon fluid. In an alternative embodiment, a filter such as illustrated in fig. 8 (27) at an outlet of the primary cracking reactor (20) is present (not shown in fig. 2). After catalytic hydrogenation (40), the hydrocarbon fluid is exposed to condensation in a condenser (60) and separation in a post-condensation separator (65) resulting in a first non-condensable gas and a first hydrocarbon liquid as the second hydrocarbon fluid to enter the fractional separator. The first hydrocarbon liquid is fed to a fractional separator (80) and being separated into a light fraction (81), a medium fraction (82) and a heavy fraction (83).
In an alternative embodiment (not shown) the second embodiment further includes feeding the first hydrocarbon liquid to a Holding Tank and preheat it before entering the fractional separator (80).

The first non-condensable hydrocarbon gas obtained from the post-condensation separator (65) is fed to a gas burner (19) in connection with the primary cracking reactor (20). Also, the first non-condensable hydrocarbon gas is preferably cooled in a second cooler (not shown) before entering a non-condensable gas separator (not shown) and being scrubbed in a scrubber before being sent to the gas burner (19). This is further elaborated upon in relation to fig. 8.

Variations familiar to the person skilled in the art of process engineering may also be part of these schematic process diagrams.

Fig. 3 illustrates a third embodiment of the invention, where waste plastic is fed into a primary cracking reactor (20). The hydrocarbon fluid exiting the primary cracking reactor (20), being a gas, is then exposed to a catalytic cracking in a pre-hydrogenation catalytic cracking reactor (30) before the first hydrocarbon fluid is catalytic hydrogenated in a catalytic hydrogenation reactor (40). The resulting hydrocarbon fluid is then condensed in a condenser (60) and separated in a post-condensation separator (65) a first non-condensable hydrocarbon gas and a first hydrocarbon liquid. The first hydrocarbon liquid is fed to a fractional separator (80) for fractional separation of the second hydrocarbon fluid into three products being a light fraction (81), a medium fraction (82) and a heavy fraction (83). The first non-condensable hydrocarbon gas is re-circulated to a gas burner (19) heating up the primary cracking reactor (20).

Plastic is fed to the primary cracking reactor (20) producing a hydrocarbon fluid, which is fed to a pre-hydrogenation catalytic cracker (30). Alternatively (not shown), a particle filter at the outlet of the primary cracking reactor (20) as described in fig. 8 may also be included. After catalytic cracking (30), the first hydrocarbon fluid/gas is fed to the catalytic hydrogenation reactor (40). Alternatively (not shown), a cooler at the outlet of the pre-hydrogenation catalytic cracking reactor (30) as described in fig. 8 may be included. After catalytic
hydrogenation, the second hydrocarbon fluid is condensed in a condenser (60) and separated in a post-condensation separator (65).

Variations familiar to the person skilled in the art of process engineering may also be part of this schematic process diagram. In particular, the comparison of fig.8 and fig.3 process diagrams can give an indication of a number of units (in fig.8), which could be included in other embodiments based on the process diagrams shown in the figs. 1-7 and 9.

Fig.4 illustrates a fourth embodiment of the invention where post-hydrogenation catalytic cracking is performed. Plastic is fed to the primary cracking reactor (20) producing a first hydrocarbon fluid. The first hydrocarbon fluid, being a gas, is then fed to a catalytic hydrogenation reactor (40). Alternatively (not shown), a filter at the outlet of the primary cracking reactor (20) as described in fig. 8 may be included. After catalytic hydrogenation (40), the resulting hydrocarbon fluid is cracked in the post-hydrogenation catalytic cracker (50) before being fed to the condenser (60) and the post-condensation separator (65) producing a first non-condensable hydrocarbon gas and a first hydrocarbon liquid. The first hydrocarbon liquid is fed to a fractional separator (80) for fractional separation into three products being a light fraction (81), a medium fraction (82) and a heavy fraction (83). The first non-condensable hydrocarbon gas is re-circulated to a gas burner (19) heating up the primary cracking reactor (20).

Variations familiar to the person skilled in the art of process engineering may also be part of this schematic process diagram.

Fig. 5 illustrates a fifth embodiment of the invention where the catalytic hydrogenation reactor (40) may receive a complementary feed of the heavy fraction (83) after dedicated heavy fraction catalytic cracking in a heavy fraction cracking reactor (35).

A heavy fraction cracking reactor (35) may process the heavy fraction (83) before re-injecting it upstream in the process, with the advantage of increasing the production of light and medium fractions.
The resultant stream from heavy fraction cracking is in gas phase, and may be introduced upstream the catalytic hydrogenation reactor (40) or upstream the fractional separator (80).

This process is similar to the one in fig.2, but for the heavy fraction (83). Instead of being removed from the plant, or returned after optional heating to one or several of the reactors, a part of it is fed after optional heating to a heavy fraction cracking reactor (35), the outlet of which is then reintroduced into the main process flow, either upstream or downstream of the catalytic hydrogenation (40), or both. Recirculation may in turn require process adjustments as the load may vary to the different reactors, as is known in the process industry. Complementary process items (such as those represented in the detailed diagram of fig. 8) and variations familiar to the person skilled in the art are also part of the invention.

Fig. 6 illustrates a sixth embodiment according to the invention where the primary cracking reactor (20) receives a complementary feed of a part or whole of the heavy fraction (83) without significant treatment between the fractional separator (80) and the primary cracking reactor (20). This process is similar to the one in fig.3 but for the heavy fraction (83).

The catalytic hydrogenation reactor (40) may also receive a complementary feed of the heavy fraction (83) without any significant treatment.

The catalytic cracking reactor pre- or post- the catalytic hydrogenation reactor may also receive a complementary feed of a part or whole of the heavy fraction, with or without intermediary heavy fraction cracking.

This embodiment represents alternative recirculation of the heavy fraction (83) into the process without additional treatment. The heavy fraction (83) will though preferably be heated to vaporisation so as to obtain a hydrocarbon gas fraction. The heavy fraction (83) might be returned in whole or in part to the primary cracking reaction (20) in which case vaporisation may not be necessary. As an alternative, the heavy fraction (83) might be returned in whole or in part to the pre-hydrogenation catalytic cracking reactor (30). These recirculation loops are typically designed and activated on the basis of modelled or observed process
operation parameters. Recirculation may in turn require process adjustments as the load may vary to the different reactors, as is known in the process industry.

Complementary process items (such as those represented in the detailed diagram of fig.8) and variations familiar to the person skilled in the art of process engineering may also be part of this schematic process diagram.

Fig. 7 illustrates a seventh embodiment of the invention where the multi-phase hydrocarbon composition obtained after condensation (60) from the condenser is fed directly to the fractional separator (80). In such case, condensation may be milder, designed to bring the multi-phase composition to the pressure and temperature conditions required at the inlet of fractional separation. The light fraction (81) is fed to a post-fractional separation condenser (85) before being separated in a non-condensable gas separator (95).

It is further illustrated that the waste plastic feed is processed and fed to the primary cracking reactor (20) where after the process is similar to the one described for fig.3 until the hydrocarbon fluid reaches the Condenser (60). The product of condensation (60) in this case is fed directly to the fractional separator (80) without separation. The light fraction (81) is condensed, and non-condensable gas is separated at the non-condensable gas separator (95), and then fed to the gas burner (19). Alternatively, a scrubber cleans the Non-Condensable Gas on its way to the gas burner (19), as also described in fig.8. Complementary process items (such as those represented in the detailed diagram of fig.8) and variations familiar to the person skilled in the art of process engineering are also part of the invention.

Fig. 8 shows an eighth embodiment of the invention illustrating a detailed diagram. In the eight embodiment, the waste plastic feed (10) is loaded in a hopper (11), emptied by a conveyor (12) feeding it to a primary cracking reactor (20). The heat will generally be generated via combustion of side products of the process, preferably non-condensable gas or char. During transition periods such as when starting the reactor, other commercial fuels can be burnt to generate heat. The non-condensable gas or any injected fuel is burnt in the combustion chamber. The resulting exhaust gas can be extracted (22) from one or several
zones of the primary cracking reactor (20) and partly recirculated (23), the rest being rejected in the atmosphere as flue gas (24). Recirculation of exhaust gas enables fine tuning of heat transfer in the different areas of the primary cracking reactor (20). Note that in this embodiment, the primary cracking reactor (20) is of indirect heating type, this exhaust gas (22, 23, 24) is at no time in contact with the hydrocarbon phase exposed to cracking in the primary cracking reactor (20).

After primary cracking, the generated hydrocarbon gas is cleaned for particles in a filter (27) before flowing to a pre-hydrogenation catalytic cracker reactor (30), shortening the hydrocarbon molecules. The resulting hydrocarbon gas flows to a cooler (37) then enters the catalytic hydrogenation reactor (40). After hydrogenation, the hydrocarbon gas is condensed in a condenser (60) to produce at least a first non-condensable hydrocarbon gas (vapour phase) and a first hydrocarbon liquid (liquid oil phase), which are then separated in a post-condensation separator (65).

The first hydrocarbon liquid (66) is pumped to the Holding Tank (70). The first hydrocarbon liquid may be the subject of purification with Ca or Na hydroxydes as known in the art. Oil (first hydrocarbon liquid) from the Holding Tank (70) is warmed up at the heat exchanger (77) before entering the fractional separator (80). The fractional separator (80) separates the first hydrocarbon liquid in three fractions of hydrocarbons: a light fraction (81), a medium fraction (82) and a heavy fraction (83).

The first non-condensable hydrocarbon gas (91) from the post-condensation separator (65) comprises a mix of light “non-condensable” gases primarily from C1 to C6, steam, and a heavier hydrocarbon gas fraction. The first non-condensable hydrocarbon gas (91) is cooled in a second cooler (92), then fed to a non-condensable gas separator (95). In the second cooler (92), steam and the heavier hydrocarbon fraction condense into a water and a second hydrocarbon liquid (liquid oil fraction), respectively. The second hydrocarbon liquid (96) is then extracted in the non-condensable gas separator (95), and sent to the fractional separator (80) via the Holding Tank (70). Alternatively, the second hydrocarbon liquid is sent directly to the fractional separator (not shown). The water is extracted (195), and a refined first non-condensable hydrocarbon gas phase (97)
is first fed to the scrubber (99), then to a gas burner (19) arranged in connection with the primary cracking reactor (20).

When starting the primary cracking reactor (20), or in case of too low non-condensable gas production, a complementary supply (18) of commercial fuel can be supplied to the gas burner (19).

In the primary cracking process (20) of cracking plastic, some by-products are formed in the shape of solid carbon particles (120), or char. The solid particles (120) are removed from the reactor and preferably cooled before further handling to avoid self-ignition. These solids (120) may be used in a combustion process in order to generate heat for the primary cracking reactor (20).

In one embodiment, the primary cracking reactor (20) may contain silico-aluminates to reduce the optimal temperature of reaction. They are consumed and discharged with the solid fraction (120). The reactor (20) may also contain minerals such as CaO to capture Cl and S according to techniques known in the art. The resulting fraction is solid, and will also be discharged with the solid fraction (120). Silico-aluminates and calcium minerals mentioned above are not considered catalysts, as they are consumed in the process.

Produced solids, essentially solids such as char from the primary cracking reactor (120), but also contaminant particles, rests of plastic, solid residues from cyclone-type (127) and other filters etc. are collected, and further processed. This will preferably be transported to a specialised processing plant, outside of the scope of this description.

The waste plastic material feeding plant has been schematically represented in fig. 8, by a hopper (11) and a conveyor (12). Although it has not been detailed in the figs. 1-7, it may also, in some embodiments, be part of the method as represented in these figures.

Filtration has been schematically represented in fig. 8. Although it has not been represented in the figs. 1-7, it may also, in some embodiments, be part of the method as represented in these figures.
Fig. 9A shows a further embodiment of the method of producing fuel and additional hydrocarbons from waste plastic. The waste plastic is exposed to primary cracking such as pyrolysis (20) resulting in a first hydrocarbon fluid. The first hydrocarbon fluid is fed to a fractional separator (80p) separating the fluid in three different fractions – a light fraction (81p), a medium fraction (82p) and a heavy fraction (83p). The fractional separator is designed to receive fluid not treated by catalytic hydrogenation. The light fraction (81p) is recirculated, in part or in whole, to a post-fractional separation condenser (85) and a non-condensable gas separator (95) for extracting water (195), a liquid light fraction (81pl) and non-condensable gas (91l), which is used in a gas burner (19) for heating said primary cracking reactor (20). The liquid light fraction (81pl) can be extracted and sold as such, or be transformed further.

The medium fraction (82p) - comprising diesel carbon chains but likely having too high a rate of olefins to be considered as diesel – is exposed to catalytic hydrogenation (40) to reduce the quantity of unsaturated bonds resulting in a useable diesel product (82ph). The heavy fraction (83p) can be utilized as such, or sent back into the process upstream the fractional separator (80) after heavy fraction cracking (35) as described elsewhere in the application.

In this embodiment, water is not removed from the first hydrocarbon fluid before fractional separation, which is why a large quantity of steam will have to be taken into account in the design of the fractional separator.

Fig.9B shows, a more detailed and preferred embodiment of the embodiment in Fig.9A.

The waste plastic is exposed to primary cracking such as pyrolysis (20) resulting in a first hydrocarbon fluid being a gas. The first hydrocarbon fluid is filtered and cleaned by a filter (27) before entering fractional separation (80p). Solids (127) are extracted from filtration. Furthermore, the first hydrocarbon fluid is cooled and at least partially condensed in a condensor (60), before entering fractional separation (80p).
The fractional separator (80ₚ) separates the fluid in three different fractions – a light fraction (81ₚ), a medium fraction (82ₚ) and a heavy fraction (83ₚ). The fractional separator is designed to receive fluid not treated by catalytic hydrogenation. The light fraction (81ₚ) is recirculated, in part or in whole, to a post-fractional separation condenser (85) and a non-condensable gas separator (95) for extracting water (195), a liquid light fraction (81ₚ) and non-condensable gas (91ₐ), which is used in a gas burner (19) for heating said primary cracking reactor (20). The liquid light fraction (81ₚ) can be extracted and sold as such, or be transformed further.

The medium fraction (82ₚ) – comprising diesel carbon chains but likely having too high a rate of olefins to be considered as diesel – is exposed to catalytic hydrogenation (40) to reduce the quantity of unsaturated bonds resulting in a useable diesel product (82ₚₐ). As the catalytic hydrogenation reactor (40) is in gas phase, and the medium fraction (82ₚ) will preferably be in liquid phase, the medium fraction (82ₚ) is heated by a heat exchanger (78) to a gas before entering catalytic hydrogenation (40). The heavy fraction (83ₚ) can be utilized as such, or sent back into the process upstream the fractional separator (80ₚ) after heavy fraction cracking (35) as described elsewhere in the application (illustrated by the dotted lines). Heavy fraction is first heated in the heater/evaporator (34), before entering the heavy fraction cracking reactor (35).

In this embodiment, water is not removed from the first hydrocarbon fluid before fractional separation, which is why a large quantity of steam will have to be taken into account in the design of the fractional separator.

In this configuration, the hydrogen produced during primary cracking may still be used for catalytic hydrogenation, as will be explained now. Hydrogen from primary cracking (20) will be collected with the light fraction (81ₚ) of the fractional separator (80ₚ). It may be separated from the non-condensable light fraction (91ₐ) in a hydrogen separator (100), preferably after scrubbing (99) if scrubbing is available. Hydrogen is then recirculated (101) upstream the catalytic hydrogenation reactor (40). This hydrogen separator (100) may for example be a membrane separator. As an alternative, hydrogen gas may be supplied directly to the reactor, when starting up the process, or any time as a complement.
It is to be understood that even though the same numbering is retained throughout the description of the figures, the design of the components in the different embodiments may be different as long as the described process occurs.

5 Experiments
The processes as described above have been the object of experiments.

Experiment 1: Catalytic hydrogenation of a model gas mixture
In a first experiment, catalytic hydrogenation feasibility and various catalysts were tested in a lab on a model gas mixture.

10 In this experiment, catalytic hydrogenation of a (diluted) model gas was tested on different catalysts. The model gas was chosen to be an olefin mixture containing ethylene and propylene in order to measure the catalysts activity. Conversion rates were measured for these two olefins.

15 In the experimental set-up as illustrated in fig. 10, the gas mix from the gas vessel (1) is mixed with water from the liquid vessel (2) and passed through a pre-heater (3). Thereafter, the gas/steam mixture is passed through the catalytic hydrogenation reactor (packed-bed reactor)(4) and then onto a steam condensation (5) and gas separation unit (6) before the gas is analysed in a Micro-GC (9) and the water is collected in a collection vessel (13).

The gas from the gas vessel (1) is entered into the hot-zone of the pre-heater (3), in which it is mixed with the water from the liquid vessel (2), which is evaporated to steam almost instantaneously. The flow of the gas is controlled by a MFC (Mass Flow Controller) (7) and the water flow by an HPLC-pump (8). The water that is used is de-ionized using a Millipore Milli-DI system and fed from a vessel. The pre-heater (3) and the reactor (4) are situated in a vertically divisible, two-zone tube furnace.

30 The two temperature-zones in the furnace are controlled independently of each other and the temperatures are set such that the inlet temperature of the catalyst bed is as close as possible to the desired temperature. The temperatures are monitored by four thermocouples, two in the preheater (3) and two in the reactor
(4). The inlet temperature is measured where the catalyst bed starts and the outlet temperature is measured where the bed ends.

The experiments were performed at the temperatures 150°C, 200°C, 250°C and 300°C and at ambient pressure; in some instances, also 350°C was investigated.

Table I: Model gas composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Gas mixture (Volume%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>43.60</td>
</tr>
<tr>
<td>Methane</td>
<td>13.36</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.56</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.30</td>
</tr>
<tr>
<td>Propane</td>
<td>0.20</td>
</tr>
<tr>
<td>Propylene</td>
<td>0.20</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.20</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>5.87</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>24.84</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>9.87</td>
</tr>
</tbody>
</table>

The catalysts investigated were tested at a space velocity of 20 000 h⁻¹. To avoid gradients in the bed, the catalyst bed was diluted 6 times using sintered α-alumina. When steady-state operation was reached and verified at each test point a minimum of three gas-samples were extracted. If the three consecutive gas chromatograph analyses were found to be identical (with a minimum time interval of 10 minutes in-between), the conditions were considered to be stable and the experimental conditions were changed to a new test point. The gas analysis was performed using a Varian CP-4900 2-Channel Micro Gas Chromatograph (one molecular-sieve 5A PLOT column and one PoraPlot column, with double TCD detectors).

The catalysts were prepared by incipient wetness method known in the art.

A series of supported metals on δ-alumina was prepared and tested for the hydrogenation of ethylene and propylene in a gas mixture mimicking an envisioned feed representing the plastics pyrolysis reactor.
Conclusion: Good conversion rates were observed, especially for the Cu-Mn/Al₂O₃ catalyst as illustrated in fig. 11.

**Exp 2: catalytic hydrogenation of a pyrolysis reactor hydrocarbon gas**

In this experiment, we tested hydrogenation on a fraction of a pyrolysis product (hydrocarbon fluid) produced from a demo plant with 5 tonnes plastic per day capacity. The hydrocarbon gas obtained from the pyrolysis reaction was then fractional separated in a demo batch distillation column with focus on the temperature range typical for a diesel fuel i.e. 140-380°C in order to provide a hydrocarbon composition made mostly of diesel C10-C20, as illustrated in fig.12.

One part of the distillate was hydrogenated in gas phase in the experimental set-up similar to the set-up as illustrated in fig. 10 using catalysts as in Experiment 1, The remaining part of the distillate was left untreated. Referring to the experimental set up, the gas in the gas vessel (1) is hydrogen, whereas the liquid in the liquid vessel (2) is the distillate.

The two hydrocarbon samples – one hydrogenated, the other one untreated (non-hydrogenated), were analysed for hydrocarbon types by fluorescent indicator adsorption as indicated in Table II. The results are presented in the table II.

**Table II**

<table>
<thead>
<tr>
<th>Test</th>
<th>Unit</th>
<th>Non-hydrogenated</th>
<th>Hydrogenated</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>% v/v</td>
<td>35,2</td>
<td>56,1</td>
<td>ASTM D1319</td>
</tr>
<tr>
<td>Aromatics</td>
<td>% v/v</td>
<td>9,8</td>
<td>7,5</td>
<td>ASTM D1319</td>
</tr>
<tr>
<td>Olefins</td>
<td>% v/v</td>
<td>55,0</td>
<td>36,4</td>
<td>ASTM D1319</td>
</tr>
</tbody>
</table>

Conclusion: From Table II, it can be seen that the olefin level is strongly reduced in the hydrogenated product. Thus, hydrogenation contributed to increase significantly the saturated fraction of the hydrocarbons.
Reference numbers
1: gas vessel
2: liquid vessel
3: pre-heater
4: catalytic hydrogenation reactor
5: condenser
6: separator
7: MFC
8: HPLC-pump
9: micro-GC
10: waste plastic feed
11: hopper
12: conveyor
13: collection vessel
18: complementary supply
19: gas burner
20: primary cracking reactor
22: primary cracking reactor gas extractions
23: primary cracking reactor extracted gas for recirculation
25: rejected flue gas
27: filter
30: pre-hydrogenation catalytic cracking reactor
34: heater/evaporator
35: heavy fraction cracking reactor
37: cooler
40: catalytic hydrogenation reactor
50: post-hydrogenation catalytic cracking reactor
60: condenser
65: post-condensation separator
66: first hydrocarbon liquid
70: holding Tank
77: heat exchanger before fractional separation
78: heat exchanger before catalytic hydrogenation
80: fractional separator
80: fractional separator designed to receive fluid not treated by catalytic hydrogenation
81: light fraction
81: liquid light fraction resulting from separation of 81
82: medium fraction (diesel)
82: medium fraction with a higher a rate of olefins
82: medium fraction after hydrogenation of 82
83: heavy fraction
83: heavy fraction with a higher rate of olefins
85: post-fractional separation condenser
91: first non-condensable hydrocarbon gas
91: light non-condensable hydrocarbon gas, produced from 81
92: second cooler
95: non-condensable gas separator
96: second hydrocarbon liquid
97: refined first non-condensable hydrocarbon gas
99: scrubber
100: hydrogen separator
101: hydrogen
120: solids from the primary cracking reactor (char)
127: solids from filtration
170: water and purification fluids extracted from Holding Tank
195: water extracted from non-condensable gas separator
Claims

1. A method for producing fuel and additional hydrocarbons from waste plastic comprising the steps of
   - providing at least one plastic material;
   - exposing said at least one plastic material to a primary cracking to obtain a first hydrocarbon fluid; said first hydrocarbon fluid being a gas;
   - exposing said first hydrocarbon gas to a catalytic hydrogenation to obtain a second hydrocarbon fluid;
   - fractional separation of said second hydrocarbon fluid to obtain at least one final product.

2. The method according to claim 1 further comprising a step of condensation after said step of catalytic hydrogenation, wherein said second hydrocarbon fluid is obtained via at least said steps of catalytic hydrogenation and condensation and wherein said second hydrocarbon fluid is a multi-phase hydrocarbon fluid.

3. The method according to claim 2 further comprising a step of separation after said step of condensation, wherein said second hydrocarbon fluid is obtained at least via said steps of catalytic hydrogenation, condensation and separation and wherein said second hydrocarbon fluid is a first hydrocarbon liquid obtained from said multi-phase hydrocarbon fluid during separation.

4. The method according to any of the preceding claims further comprising a step of pre-hydrogenation catalytic cracking performed prior to the step of catalytic hydrogenation, and wherein said first hydrocarbon fluid is obtained at least via said steps of primary cracking and pre-hydrogenation catalytic cracking.

5. The method according to any of the preceding claims further comprising a step of post-hydrogenation catalytic cracking performed after the step of catalytic hydrogenation and wherein said second hydrocarbon fluid is obtained at least via said steps of catalytic hydrogenation and post-hydrogenation catalytic cracking.

6. The method according to claim 3 wherein said separation further results in the formation of a first non-condensable hydrocarbon gas and wherein at least a part
of said first non-condensable hydrocarbon gas is recirculated to and burnt in a gas burner to provide heat to said primary cracking.

7. The method according to claim 6, wherein said at least a part of said first non-condensable hydrocarbon gas is exposed to further processing before being burnt such as further condensation and separation.

8. The method according to any of the preceding claims, wherein three final products are obtained from said fractional separation step, these products being a light fraction such as mainly C6 to C10; a medium fraction such as mainly C11 to C20 and a heavy fraction such as mainly C21 and above.

9. The method according to claim 8, wherein said light fraction is condensed and optionally separated resulting in at least a light non-condensable hydrocarbon gas, and wherein at least a part of said light non-condensable hydrocarbon gas is recirculated to and burnt in a gas burner to provide heat to said primary cracking.

10. The method according to any of the preceding claims wherein said at least one plastic material is HDPE, LDPE, PP and/or PS.

11. The method according to any of the preceding claims wherein said primary cracking is performed by anaerobic thermal cracking.

12. The method according to any of the preceding claims wherein said primary cracking is performed at a temperature between 300°C to 550°C, preferably between 380°C and 460°C, such as around 420°C.

13. The method according to any of the preceding claims, wherein said primary cracking is performed at a pressure range of 0.1 to 10 bar, preferably in the range of 0.7 to 2 bar, such as around 1 bar.

14. The method according to any of the preceding claims, wherein said primary cracking is performed without catalysts.
15. The method according to any of the preceding claims, wherein said primary cracking comprises minerals to reduce the reaction temperature and/or capture elements such as Cl or S.

16. The method according to any of the preceding claims further comprising filtering and optionally cooling after the step of primary cracking.

17. The method according to any of the preceding claims, wherein said catalytic hydrogenation is performed at operating temperatures between 150-280°C, preferably between 190-230°C, such as around 200°C.

18. The method according to any of the preceding claims, wherein said catalytic hydrogenation is performed at a pressure range of 0.1 to 10 bar, preferably a range of 0.5 to 5 bar, like in the range of 0.7 to 2 bar, such as in the range of 0.9 to 1.1 bar, preferably around 1 bar.

19. The method according to any of the preceding claims further comprising a step of circulating of said second hydrocarbon fluid to a holding tank prior to fractional separation.

20. The method according to any one of the claims 8-19, wherein said heavy fraction is recycled to the step of primary cracking, catalytic cracking and/or catalytic hydrogenation or to said holding tank.

21. The method according to claim 20, wherein said heavy fraction is exposed to a step of heavy fraction cracking before being recycled to the step of primary cracking, catalytic cracking and/or catalytic hydrogenation or to said holding tank.

22. A waste recycling system for recycling waste plastic into fluid hydrocarbon compounds comprising
   - a primary cracking reactor capable of receiving at least one plastic material and producing a first hydrocarbon fluid from said at least one plastic material by a primary cracking, said first hydrocarbon fluid being a gas;
- a catalytic hydrogenation reactor capable of receiving said first hydrocarbon fluid and producing a second hydrocarbon fluid by catalytic hydrogenation,
- a fractional separator capable of fractional separation of said second hydrocarbon fluid to obtain at least one final product,

where said primary cracking reactor is in fluid connection with said catalytic hydrogenation reactor and said catalytic hydrogenation reactor is in fluid connection with said fractional separator.

23. The system according to claim 22, wherein said system further comprises a condenser for producing said second hydrocarbon fluid together with said catalytic hydrogenation reactor and resulting in said second hydrocarbon fluid being a multi-phase hydrocarbon fluid, and wherein said catalytic hydrogenation reactor is further fluidly connected with said fractional separator through said condenser.

24. The system according to claim 23, wherein said system further comprises a post-condensation separator for separating said multi-phase hydrocarbon fluid to provide a first hydrocarbon liquid and a first non-condensable hydrocarbon gas, and wherein said condenser is further fluidly connected with said fractional separator through said post-condensation separator.

25. The system according to any of the claims 22-24, wherein said system further comprises a pre-hydrogenation catalytic cracking reactor, wherein said primary cracking reactor is further fluidly connected with said catalytic hydrogenation reactor through said pre-hydrogenation catalytic cracking reactor.

26. The system according to any of the claims 22-25, wherein said system further comprises a post-hydrogenation catalytic cracking reactor, wherein said catalytic hydrogenation reactor is further fluidly connected with said fractional separator through said post-hydrogenation catalytic cracking reactor.

27. The system according to any one of the claims 22-26, wherein said primary cracking reactor is an anaerobic thermal cracking reactor.
28. The system according to any one of the claims 22-27, wherein said system further comprises a holding tank for storing the second hydrocarbon fluid prior to fractional separation, where said catalytic hydrogenation reactor is fluidly connected with the fractional separator at least via said holding tank.

29. The system according to any one of the claims 22-28, wherein said system further comprises a gas burner for providing heat to said primary cracking reactor, said gas burner is fluidly connected with said post-condensation separator.

30. The system according to any one of the claims 22-29, wherein the system further comprises a heavy fraction cracking reactor, said heavy fraction cracking reactor being in fluidly connection with said fractional separator for receiving a heavy fraction obtained from the fractional separation process and wherein said heavy fraction cracking reactor is further fluidly connected with said primary cracking reactor, said pre-hydrogenation catalytic cracking reactor, said post-hydrogenation catalytic cracking reactor and/or said catalytic hydrogenation reactor.

31. The system according to any one of the claims 22-30, wherein the system further comprises a post-fractional separation condenser, a non-condensable gas separator and a gas burner, said post-fractional separation condenser being in fluidly connection with said fractional separator for receiving a light fraction obtained from the fractional separation process and wherein said post-fractional separation condenser is further fluidly connected with said non-condensable gas separator for separating a light non-condensable hydrocarbon gas; said non-condensable gas separator being further fluidly connected with said gas burner.

32. Use of a system as described in any of the claims 22-31 or a method as described in any of the claims 1-21 for producing fuel and additional hydrocarbons from waste plastic.

33. Use according to claim 32, wherein said fuel is Diesel.
Fig. 2
Fig. 10
**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C10G1/10 C10G1/00 C10G1/02 C10G11/00 C10G45/00

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2012/149954 A1 (FRACZAK DARIA [PL] ET AL) 14 June 2012 (2012-06-14) paragraphs [0017], [0018], [0022], [0042] claim 1 figures 1-3</td>
<td>1-3, 6-9, 11-14, 22-24, 27-29, 31-33</td>
</tr>
<tr>
<td>X</td>
<td>US 2003/199718 A1 (MILLER STEPHEN J [US]) 23 October 2003 (2003-10-23) figure 2 paragraphs [0023], [0026], [0027], [0032], [0033]</td>
<td>1, 8, 10-14, 22, 27, 32, 33</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  
  **A** document defining the general state of the art which is not considered to be of particular relevance
  
  **E** earlier application or patent but published on or after the international filing date
  
  **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  
  **O** document referring to an oral disclosure, use, exhibition or other means
  
  **P** document published prior to the international filing date but later than the priority date claimed
  
  **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  
  **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  
  **Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  
  **S** document member of the same patent family

**Date of the actual completion of the international search**

5 September 2019

**Date of mailing of the international search report**

06/11/2019

**Name and mailing address of the ISA/ European Patent Office, P.B. 5018 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-3040, Fax: (+31-70) 340-3016**

Pardo Torre, J
### Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ✔ Claims Nos.:  
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ✔ Claims Nos.:  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ✔ Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- see additional sheet

1. ✔ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ✔ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of additional fees.

3. ✔ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ✔ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

    1-3, 6-14, 22-24, 27, 29, 31-33

**Remark on Protest**

- ✔ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ✔ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ✔ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3, 6-14, 22-24, 27, 29, 31-33
   Optimising product recovery and avoiding oxygenate production
   1.1. claims: 1-3, 6-9, 22-24, 29, 31-33
       Optimising product recovery
   1.2. claim: 10
       Maintaining product capacity and alkane production
   1.3. claims: 11, 27
       Avoiding oxygenate production
   1.4. claims: 12, 13
       Optimising cracking conditions
   1.5. claim: 14
       Simplifying the design of the reactor

2. claims: 4, 25
   Improving energy efficiency

3. claims: 5, 26
   Optimising hydrogen consumption

4. claim: 15
   Reducing downstream gas pollution

5. claim: 16
   Preventing the solids from damaging downstream equipment

6. claims: 17, 18
   Optimising hydrogenation conditions

7. claims: 19, 28
Reducing water content

8. claims: 20, 21, 30

Increasing the yield of lighter fractions
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PL 218781 B1</td>
<td>30-01-2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2012149954 A1</td>
<td>14-06-2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2010136850 A1</td>
<td>02-12-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 20032223462 A1</td>
<td>03-11-2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR 0308864 A</td>
<td>22-03-2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 5252766 B2</td>
<td>31-07-2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2005527672 A</td>
<td>15-09-2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2010121140 A</td>
<td>03-06-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL 1023217 C2</td>
<td>22-09-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2003199718 A1</td>
<td>23-10-2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 03089545 A1</td>
<td>30-10-2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA 200303051 B</td>
<td>17-10-2003</td>
</tr>
</tbody>
</table>