

Method for the Conversion of Biomass to Liquid and/or Gaseous Energy Carriers

The present invention relates to a method for the pyrolysis of a hydrocarbon-containing solid biomass for the obtention of liquid and/or gaseous energy carriers in the presence of a heat carrier, in which a mixture of the heat carrier and the hydrocarbon-containing biomass is heated to the pyrolysis of the hydrocarbon-containing biomass.

Methods for the pyrolysis of biomass in the presence of a heat carrier are known.

In doing so, the pyrolysis can be performed with solid heat carriers (e.g., with sand in the form of a flash pyrolysis) or with liquid heat carriers. The latter alternative is referred to as liquid-phase pyrolysis.

An important variant of the liquid-phase pyrolysis consists in using a heavy oil as a heat carrier. In said variant, a thermal cracking of the heavy oil occurs simultaneously during the pyrolysis of the biomass, whereby combustibles and fuels, respectively, are obtained in addition.

WO 2010/031803 A describes a method for the liquid-phase pyrolysis of a hydrocarbon-containing biomass with heavy oil as a heat carrier, wherein a hydrocarbon-containing biomass is to be used the moisture content of which amounts to, at most, 1.0% by weight, based on the biomass. According to WO 2010/31803 as well as WO 2008/034596 A1 and WO 2008/11925 A1, the biomass can be impregnated prior to the pyrolysis with the heat carrier (heavy oil), i.e., with the liquid with which also the pyrolysis is performed.

AT 508469 B1 describes a liquid-phase pyrolysis of a biomass, wherein a biological catalyst, which is a residual plant matter, is added.

DE 10 215679 A1 describes a method of a liquid-phase pyrolysis in a temperature range from 350 to 500°C and under a system pressure of up to 100 bar. Solid zeolites and, in a supporting role, alkaline chemicals are indicated as catalysts.

US 2009/0299112 A1 describes the processing of a biogenic raw material comprising a hydrocarbon via hydrogenation under high-pressure conditions.

Further methods are known, for example, from US 4,266,083, US 4,941,966, US 2007/0261996, US 2012/271074 and EP 0 027 962 A2.

In particular during the liquid-phase pyrolysis of a biomass, i.e., the pyrolysis of biomass in a liquid carrier medium, a conversion of solid biomass to a liquid, a solid and a gaseous phase occurs in the temperature range from 300 to 450°C. If a hydrocarbon – e.g., an intermediate of a refinery such as a vacuum gas oil – is used as a carrier medium, the liquid phase will consist of a hydrophobic hydrocarbon fraction as well as a hydrophilic pyrolysis oil fraction.

In doing so, the objective is to transfer as much energy of the biomass as possible into the liquid and/or gaseous hydrocarbon fraction, for example, through the transfer of biogenic carbon. The transfer rate increases as the pyrolysis temperature rises, but, in general, is below 20-30% by weight, based on the employed biomass. Thus, a further improvement in the conversion of biomass to the desired fraction is desirable.

In the literature, a temperature rise is suggested for this purpose, on the one hand. However, especially in a liquid-phase pyrolysis, the temperature rise is limited physically by the distillation range of the carrier liquid due to the system pressure which is prevailing. At an overpressure of typically <0.5 bar, the process temperature is thus limited physically to a maximum of 450°C. With the temperature rising, the required energy input rises as well and the costs for operating the plant increase.

Alternatively, the use of zeolite-based catalysts, which are supposed to provide a higher selectivity, is reported in the literature. However, in laboratory testing, the use of solid catalysts has failed to produce an appropriate effect. Moreover, the subsequent use of the remaining coal would thereby either deteriorate or else require a costly separation of the coal from the catalyst.

It is the object of the present invention to increase the rate of the transfer of biogenic carbon into the liquid hydrocarbon fraction in a generic method.

Said object is achieved by a method for the pyrolysis of hydrocarbon-containing solid biomass for the obtention of liquid and/or gaseous energy carriers by means of pyrolysis in the presence of a heat carrier, whereby a mixture of the heat carrier and the hydrocarbon-containing biomass is heated to the pyrolysis of the hydrocarbon-containing biomass, which is characterized in that the biomass is impregnated with a volatile, non-aqueous liquid before being mixed with the heat carrier.

Short description of the figures

Fig. 1 shows a process diagram of an embodiment of the method according to the invention.

Figs. 2 and 3 show the results of the implementation of two comparative tests and of the implementation of the method according to the invention in a laboratory system.

Figs. 4 and 5 show the results of the implementation of a comparative test and of the implementation of the method according to the invention in a continuous pilot plant.

Fig. 6 shows a comparison of boiling point curves for the hydrocarbons used in example 2 for impregnating the biomass.

Detailed description of the invention

It has been found that, by impregnating the biomass with a volatile, non-aqueous liquid before being mixed with the heat carrier and thus before the actual pyrolysis, the reaction processes on the particles of the biomass can be influenced positively in such a way that, at a comparable reaction temperature, an improved conversion toward the liquid and/or gaseous hydrocarbon phase will occur.

Undesirable secondary reactions can be suppressed by a shortened dwell time of the reaction products in the hot, reactive phase (= liquid bath). From the literature, it is known that, in the dry flash pyrolysis, shorter dwell times lead to increased conversions toward a liquid product. However, especially in the liquid-phase pyrolysis, the heating duration of the particle is in the range of minutes and cannot be accelerated to any substantial degree, not even by optimal flow conditions.

It has now been found that, via impregnation with a liquid which evaporates rapidly under reaction conditions (unlike the heat carrier which essentially does not evaporate at the reaction temperature), the local flow and mass exchange conditions are significantly improved and the conversion is accelerated. A further positive effect is the entrainment of biogenic components from the surrounding carrier medium, which is improved by the evaporation of the liquid, whereby those components are no longer available for coking reactions, which possibly might take place, and a larger concentration gradient between biomass particles and carrier medium is created. In this way, the mass exchange is again accelerated and the reaction is influenced positively in the desired direction. As a

consequence, less solid residue (coal) of the biomass will remain upon completion of the pyrolysis.

According to the invention, the hydrocarbon-containing biomass is impregnated with the volatile liquid before being mixed with the heat carrier. In doing so, the biomass is preferably soaked continuously with the volatile liquid in a first step, the excess amount is allowed to drip off, and the impregnated biomass is supplied continuously to the pyrolysis step.

In this way, the pores of the biomass are filled with the liquid. The impregnated biomass is mixed with the heat carrier which is essentially resistant against the high pyrolysis temperatures, and, as soon as the pyrolysis temperature is reached, a sudden evaporation of the volatile liquid takes place, resulting in a steam explosion effect within the pores.

The mass ratio of the volatile liquid to the biomass is thereby preferably 1.5 to 1 or less, particularly preferably 1:1 or less, based on the mass of the dry biomass.

The volatile liquid shows a boiling behaviour according to which the final boiling point (95% evaporated) is lower than or, at most, equal to the temperature of the pyrolysis step so that the volatile liquid evaporates essentially completely at the temperature of the pyrolysis step.

Preferably, the volatile liquid has a final boiling point (95%) of 380°C or less (in line with EN590). This applies in particular in case of a liquid-phase pyrolysis, using, for example, heavy oil as a heat carrier.

In case of a solid-phase pyrolysis, e.g., with a sand bed as a heat carrier, wherein pyrolysis temperatures of, e.g., 550°C occur, a liquid with a correspondingly higher final boiling point can also be used as a volatile liquid.

Particularly preferably, the volatile liquid is a hydrocarbon mixture with a content of aromates of 1% or more.

The volatile liquid can be selected in particular from the group consisting of light gas oil (LCO or LGO), diesel, petrol and mixtures thereof. A person skilled in the art understands a light gas oil to be a precursor of middle distillates such as diesel fuel and extra-light heating

oil, which is derived directly from the fractionation of crude oil and the boiling temperature of which is between 190 and 400°C.

Particularly preferably, a refinery intermediate is used as the volatile liquid.

If a volatile intermediate of refinery is used (e.g., LCO, crude diesel (light gas oil LGO), crude petrol), it is possible to deliberately influence the biogenic amount in a desired boiling range, e.g., preferably toward diesel, toward kerosine or toward petrol, simultaneously improving the transfer of biogenic carbon into the liquid phase. Ideally, fractions from the refining area can thus be applied in fields for which they were previously unsuitable (e.g., the use of LCO in the fuel fraction).

The gases formed during the pyrolysis can be removed in a manner known per se and can be condensed for obtaining the liquid energy carriers or, respectively, can be separated further into the desired fractions.

The pyrolysis process can be performed at an overpressure of 0.5 bar or less.

According to a further preferred embodiment of the present invention, the pyrolysis is carried out in the form of a liquid-phase pyrolysis. The problems arising especially in connection with a pyrolysis of biomass in the form of a liquid-phase pyrolysis have already been discussed hereinabove.

In said embodiment, particularly preferably a heavy oil, in particular a vacuum gas oil, is used as a heat carrier, and thus a liquid-phase pyrolysis is performed, with the heavy oil being thermally cracked at the same time.

In said embodiment, the pyrolysis step of the method according to the invention is typically carried out at temperatures of 300-450°C and at an overpressure of, at most, 0,5 bar. The quantitative proportion between the biomass and the heavy oil is typically in the range of 1:2.

In the following, preferred embodiments of the invention are illustrated in further detail on the basis of the figures as well as the exemplary embodiments:

According to Fig. 1, an optionally moist hydrocarbon-containing biomass BM is pretreated (PT) mechanically and/or thermally. For example, moisture (M) present during the pretreatment can be removed.

In the preferred embodiment shown in Fig. 1, an impregnation I of the pretreated biomass with a volatile liquid FL is provided subsequently. Also in this step, moisture M may be removed from the biomass as a result of the impregnation. In a first separator S1, excess liquid FL is removed from the biomass and returned to the impregnation step I.

The impregnated biomass is supplied continuously to a reactor R. A heat carrier HC, in the preferred embodiment of the invention a heavy oil, is also supplied to the reactor. In the reactor R, a pyrolysis is performed in a manner known per se at temperatures typically ranging from 300°C to 550°C and at a slight overpressure (e.g., up to 450°C and at an overpressure of, at most, 0.5 bar), whereby the volatile liquid present in the pores of the biomass escapes abruptly. The vapours of the reactor reach a condenser K. Gaseous components are collected as a gas G. The condensed components reach a second separator S2 and are separated there into oily fractions O and aqueous fractions W.

In a third separator S3, the bottom product of the reactor R is split into solid products (SO) and a heat carrier, with the latter being returned to the reactor R as the heat carrier HC.

Example 1:

A laboratory test was performed at a reaction temperature of 370°C and an overpressure of about 0,05 bar, using spruce wood as a biomass with vacuum gas oil as a carrier medium. As a reactor unit, a stirrer vessel heated from the outside was used on a laboratory scale with an adjacent condenser unit.

For a first comparative test (indicated by „NO“ in Figs. 2 and 3), approx. 100g wood was predried and supplied conventionally without previous impregnation to the laboratory reactor, with vacuum gas oil as the carrier medium (ratio of vacuum gas oil to biomass 5:1). Upon completion, the arising liquid and solid products were separated and weighed. The resulting gases being still condensable were calculated from a mass difference to the biomass employed. As the products of pyrolysis, solid coal, a liquid pyrolysis oil not miscible with water and comprising reaction water as well as a hydrocarbon-soluble liquid product fraction were formed.

As a further comparative test (indicated by „VGO“ in Figs. 2 and 3), dry spruce wood was impregnated with vacuum gas oil at about 60°C at a mass ratio of 1:1 and subsequently supplied to the laboratory reactor. Upon completion, the arising liquid and solid products were separated and weighed. The resulting gases being still condensable were calculated from a mass difference to the biomass employed.

In the test according to the invention (indicated by „LGO“ in Figs. 2 and 3), the biomass was dried, subsequently impregnated with diesel fuel (mass ratio of approx. 1:1) and treated with vacuum gas oil in the liquid-phase reactor, as in the comparative tests.

In the method according to the invention, the result indicates considerably less coal formation (R) and hence more mass transfer of the solid biomass into the desired liquid and gaseous fractions (C).

Looking at the mass transfer of solid biomass into the hydrocarbon fraction, the result is even more distinct. Using a low-boiling hydrocarbon (LGO) according to the invention, the conversion could be increased from about 10% by weight to almost 17% by weight. Using a high-boiling hydrocarbon for the impregnation (VGO), a conversion of only about 14% by weight was achieved. Hence, the use of the low-boiling liquid (LGO) according to the invention resulted in a 16% increase, as compared to the use of the high-boiling liquid (VGO).

Fig. 2 shows the mass conversion of solid biomass to liquid as well as gaseous products (C) and the remaining solid material (R) of example 1. Left-hand side: comparative test without impregnation (NO). Middle: comparative test with a high-boiling vacuum gas oil (VGO). Right-hand side: a test according to the invention with low-boiling gas oil (LGO).

Fig. 3 shows the mass transfer („BtL“) of solid biomass to the hydrocarbon fraction – i.e., the mass fraction of liquefied biomass which is miscible with hydrocarbons – of example 1. Left-hand side: comparative test without impregnation (NO). Middle: comparative test with a high-boiling vacuum gas oil (VGO). Right-hand side: a test according to the invention with low-boiling gas oil (LGO).

Example 2:

In a continuous pilot plant, about 60kg/h of dry spruce wood was subjected to a pyrolysis at approx. 375°C. In doing so, vacuum gas oil was used as a heat carrier medium at a ratio to the biomass of approx. 4:1. The arising liquid and solid pyrolysis products were detected in their mass flow and analysed for their content of biogenic carbon by means of the radiocarbon method (C14).

As a comparative test, the biomass was initially impregnated with vacuum gas oil (VGO) at approx. 150°C (mass ratio of approx. 1:1) and subsequently subjected to a pyrolysis step. The amount of solid residue (R) forming as a coal was determined, and its content of biogenic carbon was detected via C14 measurement. In this way, a conversion of solid biomass to liquid and gaseous products of about 64%, and, respectively, a transfer of biogenic carbon to liquid and gaseous products of 57% could be determined.

In a test according to the invention, the biomass was impregnated with light gas oil (LGO) at about 120°C (mass ratio of approx. 1:1) and subsequently subjected to a pyrolysis step. The amount of solid residue (R) forming as a coal was determined, and its content of biogenic carbon was detected via C14 measurement. In this way, a conversion of solid biomass to liquid and gaseous products of about 67%, and, respectively, a transfer of biogenic carbon to liquid and gaseous products of 61% could be determined. Using a volatile liquid according to the invention, the conversion of the pyrolysis from a solid biomass to the desired products could thus be increased demonstrably also in a continuous pilot operation.

Fig. 4 shows the mass conversion of solid biomass to liquid as well as gaseous products (C) and the remaining solid material (R) of example 2. Left-hand side: comparative test with a high-boiling vacuum gas oil (VGO). Right-hand side: a test according to the invention with low-boiling gas oil (LGO).

Fig. 5 shows the mass transfer (T) of biogenic carbon to liquid as well as gaseous fractions of example 2. Left-hand side: a comparative test with a high-boiling vacuum gas oil (VGO). Right-hand side: a test according to the invention with low-boiling gas oil (LGO).

Fig. 6 shows the boiling point curves of the hydrocarbons used in example 2 for impregnating the biomass: Top part: high-boiling vacuum gas oil (VGO). Bottom part: low-boiling gas oil (LGO).

Claims:

1. A method for the pyrolysis of a hydrocarbon-containing solid biomass for the obtention of liquid and/or gaseous energy carriers in the presence of a heat carrier, whereby a mixture of the heat carrier and the biomass is heated up to pyrolysis of the biomass, characterized in that the biomass is impregnated with a volatile, non-aqueous liquid before being mixed with the heat carrier.
2. A method according to claim 1, characterized in that the volatile liquid exhibits a final boiling point (95%) lower than or, at most, equal to the temperature of the pyrolysis step.
3. A method according to claim 2, characterized in that the volatile liquid exhibits a final boiling point (95%) of 380°C or less.
4. A method according to any of the preceding claims, characterized in that the volatile liquid is a hydrocarbon mixture with a content of aromates of 1% or more.
5. A method according to claim 4, characterized in that the volatile liquid is selected from the group consisting of gas oil (LCO/LGO), diesel, petrol and mixtures thereof.
6. A method according to claim 5, characterized in that a refinery intermediate is used as the volatile liquid.
7. A method according to any of the preceding claims, characterized in that the mass ratio of the volatile liquid to the biomass is 1.5 to 1 or less, preferably 1:1 or less, based on the mass of the dry biomass.
8. A method according to any of the preceding claims, characterized in that the pyrolysis is performed at an overpressure of 0.5 bar or less.
9. A method according to any of the preceding claims, characterized in that the pyrolysis is carried out in the form of a liquid-phase pyrolysis.
10. A method according to claim 9, characterized in that a heavy oil, in particular a vacuum gas oil, is used as the heat carrier of the liquid-phase pyrolysis.