

## **METHOD OF CONDUCTING A HYDROTHERMAL CARBONISATION REACTION**

The present invention relates to a method of conducting a hydrothermal carbonisation reaction, in which biomass is supplied to a reaction tank and the reaction conditions with regard to pressure and temperature required for the course of a hydrothermal carbonisation reaction are created by introduction of steam and are maintained for a reaction period.

Methods of that kind are already known in various forms in the prior art, for example from DE 10 2011 001 954 Al. This specification provides for undertaking thorough mixing of the biomass and of the steam added thereto while the hydrothermal carbonisation is taking place, in order to provide by way of the thorough mixing a large reaction area and thereby a large attack area for pressure and heat. It has proved that a carbonisation reaction that clearly starts faster and proceeds more uniformly takes place as a result.

The basis of the hydrothermal carbonisation reaction is the supplied biomass, which usually contains lignin in which the cellulose intended for carbonisation is bound. At the start of the HTC process (hydrothermal carbonisation process), hydrolysis firstly takes place, in the course of which conversion of the cellulose to glucose occurs. In that case, the glucose is dissolved in the process water. The hydrolysis requires only a short time, for example one to two minutes, within the process. After hydrolysis of the cellulose and conversion thereof to glucose, the actual carbonisation reaction then takes place.

As described in the special case of the above-mentioned specification, the actual carbonisation reaction is accelerated therein due to the fact that thorough mixing of the biomass takes place. As a result it is ensured that the required reaction conditions, namely a pressure of approximately 25 bar and a temperature of about 230° C, are available as uniformly as possible to the entire material to be processed.

After the actual carbonisation, the so-called condensation, in which the water-soluble carbon components are joined together to form larger molecules, takes place as practically the last major step. The HTC coal subsequently forms therefrom. A measure of the solids component in the biomass mixture, the so-called slurry, is the dry

residue. This measure is defined as the proportion of dry mass to the entire mass of a slurry.

In the last step of the method, the biocoal that has formed is separated from the process water that has also formed, so that the dry residue can be removed as biocoal and the process water can be supplied for a different use or re-used for the reaction. In this regard, it normally has to be taken into consideration that a certain proportion of carbon remains in the process water.

It similarly has to be taken into consideration that a relatively long dwell time in the reaction tank, which allows a high yield of biocoal, logically leads to poorer capacity utilization of the reaction tank, so that here, too, the shortest possible dwell time would be helpful in the sense of an economic solution.

It is the object of the present invention, against the background of these considerations, to propose a method for conducting a hydrothermal carbonisation reaction that allows a distinct reduction in the dwell time of the slurry in the reaction tank and at the same time is accompanied by a higher yield of biocoal and thereby greater pollutant elimination from the process water.

This is accomplished by a method in accordance with the features of claim 1. Further practical embodiments of such a method can be inferred from the accompanying subclaims.

According to the invention a hydrothermal carbonisation reaction takes place in a reaction tank, similarly to the procedure in the prior art, in which biomass and steam are brought together. The biomass carbonises under pressure and elevated temperature and in that case forms a dry residue, which can be recovered from the slurry by separation from the process water that arises.

It has proved, however, that the proportion of water-insoluble coal able to be precipitated from the slurry or the process water is not constant and also does not increase uniformly. Instead, in the first instance dry mass from the added biomass is present, but initially this mass is to be split up and carbonised. With the start of the carbonisation reaction, the dry residue clearly decreases, since the original biomass is

split up. As condensation starts, the effect reverses again, however, and the dry residue increases again, in which case now the desired biocoal is contained in the slurry as a load. At this point, however, the biocoal in turn starts to decompose again and the dry residue clearly decreases once more, so as to then remain more or less constant in the case of an appreciable prolonging of the process.

In order to obtain the greatest possible yield of dry residue of biocoal, it is therefore necessary to seek the point in time at which the dry residue reaches its maximum. However, this is problematic, since the dry residue cannot be readily determined as a value during ongoing operation. It is true that an ideal time can be determined for certain materials by a series of tests, but biomaterials that can be supplied vary so greatly that the required series of tests would involve an uneconomic degree of effort. This is especially because even different batches of the same materials can already have completely different values.

It has proved, however, that the progression of the pH value of the slurry in the reaction tank has a maximum at approximately the same time as the course of the dry residue. In contrast to the dry residue, however, the pH value can be measured even while the carbonisation reaction is taking place, so that a break-off signal for the reaction can be generated practically in real time, at an instant when the dry residue in the slurry is the greatest and the yield is therefore the highest. For this reason, according to the invention it is not the progression of the dry residue itself that is monitored, but rather the progression of the pH value. As soon as it is determined during the carbonisation reaction that a maximum of the pH value has been exceeded the reaction is terminated. The slurry to then be removed from the reaction tank has the greatest possible dry residue.

In concrete terms, this can be managed by the progression of the pH value of the slurry being detected at specific points in time and memorised in a database and by the measured values being compared with the preceding values. For this purpose, use can be made of one or more measuring probes which are assigned to the reaction tank directly or in a bypass line. The measurement values of the at least one measuring probe are evaluated by a process controller and a maximum of the pH value is sought by means of reconciliation with preceding values. As soon as this maximum is reached, the reaction is terminated.

The at least one measuring probe can be based on different technical solutions known in the prior art. The two significant solutions relate to potentiometry and measurement by means of ion-sensitive field effect transistors.

Potentiometry makes use of the fact that hydrogen ions accumulate on the surface of a glass vessel, so that a galvanic voltage builds up between the inner side and the outer side of the glass vessel. This voltage is dependent on the difference in the pH values on the two sides of the surface and can be measured with use of reference electrodes.

In the case of measuring by means of field effect transistors the same effect is utilised, with hydrogen ions attaching themselves, similarly to as described above, to an ion-sensitive gate membrane of an ion-sensitive field effect transistor. The potential that occurs in this regard can then in turn be detected by measurement technology.

With some advantage, such measurement probes are mounted close to the bottom of the reaction tank in order to ensure that the probe is always in contact with the slurry and a series of measurements that can be evaluated is formed.

By means of additional mixing the slurry can furthermore be moved in the reaction tank, ideally swirled up, in order to expose the biomass to the pressure and the temperature in the reaction tank as directly as possible from all sides. In this way, a more uniform reaction and therefore a more reliable measurement of the pH value take place. Thorough mixing can be carried out by way of mixing nozzles that swirl up the slurry, or, however, by way of a stirring mechanism.

In order not to falsify the measurements and trigger the termination criteria too soon, measurement can start, in particular, when the reaction conditions of hydrothermal carbonisation, in terms of pressure and temperature, have been reached and when biomass and hot steam have already been introduced into the reaction container. Only when these processes have been concluded - which, however, happens even at the onset of the reaction - is measuring commenced.

If the reaction is terminated when the maximum of the pH value is reached, then this termination can take place, in practical terms, by the slurry present in the reaction tank

being transferred to a cooling tank. The reaction conditions can thereby be continuously maintained in the reaction tank so that the energy loss remains as low as possible. For this purpose, the slurry can, for example, be pumped out of the reaction tank into a cooling tank, or, preferably - because of the significantly greater pressure in the reaction tank - it can be flushed into the cooling tank at a noticeably lower pressure by means of pressure equalisation.

The invention disclosed in the forgoing can be explained in more detail in the following by way of an embodiment. In that case, Figure 1 shows a diagram of an exemplifying progression 1 of the dry residue in % in a solid line and in direct relation thereto the progression 2 of the pH value in a dot-dash line. The lefthand upright axis denoted by pH represents the pH value and the righthand upright axis denoted by TR [%] represents the dry residue in percent. The longitudinal axis is a time axis, wherein the numbers indicated thereat represent information in minutes.

The reaction illustrated here starts at the instant  $t = 0$  min. In the first instance, it can be determined that at the onset of the reaction the pH value strongly decreases and already reaches a minimum at  $t = 15$  min. By contrast, the dry residue decreases more slowly and reaches its minimum only at about  $t = 60$  min. From here on, both the dry residue and the pH value increase uniformly and both reach a maximum at  $t = 180$  min. The diagram also shows the further development of the two values for the case that the reaction is not conducted in accordance with the invention. Then, pH value and dry residue will clearly decrease and assume a more or less constant value at about  $t = 240$  min. Although the dry residue amounts to as much as 17% at its maximum, it lies at 12 to 13% in the case of a longer duration, thus a good quarter below. Terminating the reaction, in accordance with the invention, when the maximum of the progression of the pH value has been reached, however, ensures that the dry residue does not decrease due to a lack of further reaction. At this instant, according to the invention, the slurry is removed from the reaction tank, cooled and subsequently separated from the process water.

Thus, described in the foregoing a method for conducting a hydrothermal carbonisation reaction which allows an appreciable reduction in the dwell time of the slurry in the reaction tank and at the same time brings with it a higher yield of biocoal and thereby greater pollutant elimination from the process water.

## REFERENCE NUMERAL LIST

|         |                                 |
|---------|---------------------------------|
| 1       | progression of dry residue in % |
| 2       | progression of pH value         |
| pH      | scale of first upright axis     |
| TR [%]  | scale of second upright axis    |
| t [min] | scale of longitudinal axis      |

## CLAIMS

1. Method of conducting a hydrothermal carbonisation reaction in which a biomass is supplied to a reaction tank and reaction conditions, with respect to pressure and temperature, required for allowing a hydrothermal carbonisation reaction to take place are created by introduction of steam and are maintained for a reaction time period, characterised in that during the reaction period of time a slurry forms from the introduced steam and biomass and is monitored with respect to progression of its pH value, wherein the reaction is terminated as soon as the exceeding of a maximum of its pH value is ascertained.
2. Method according to claim 1, characterised in that the progression of the pH value (2) of the slurry is determined continuously or at discrete time intervals with the help of at least one measuring probe, which is assigned to the reaction tank, and is recorded in a database, wherein a process controller compares a current pH value with preceding measurement values from the same series of measurements within the reaction time period and triggers a termination signal when there is a decrease in pH value following an increase phase.
3. Method according to claim 1, characterised in that the progression of the slurry (2) is determined continuously or at discrete time intervals with the help of at least one measurement probe, which is assigned to a bypass pipe of the reaction tank, and the pH values are recorded in a database, wherein a process controller compares a current pH value with preceding measurement values from the same series of measurements within the reaction time period and triggers a termination signal when there is a decrease in pH value following an increase phase.
4. Method according to one of claims 2 and 3, characterised in that the at least one measuring probe is arranged in the vicinity of a bottom of the reaction tank.
5. Method according to any one of the preceding claims, characterised in that the slurry is thoroughly mixed in the reaction tank during the reaction time period.
6. Method according to any one of the preceding claims, characterised in that measuring begins when the reaction conditions of hydrothermal carbonisation with

respect to pressure and temperature have been reached and biomass and hot steam have already been introduced into the reaction container.

7. Method according to any one of the preceding claims, characterised in that the hydrothermal carbonisation reaction is terminated by transferring the slurry from the reaction tank to a cooling tank by pumping or on the basis of pressure equalisation.