Nitrogen-Containing Hydrochar: The Influence of Nitrogen-Containing Compounds on the Hydrochar Formation

Muhammad-Jamal Alhnidi,*[a] Paul Körner,[b] Dominik Wüst,[a] Jens Pfersich,[a] and Andrea Kruse[a]

Hydrothermal carbonization (HTC) of fructose and urea containing solutions was conducted at 180 °C to study the influence of nitrogen-containing compounds on the conversion process and HTC products properties. The concentration of fructose was fixed, while the concentration of urea was gradually increased to study its influence on the formation of nitrogen-containing hydrochar (N–HC). The degradation of urea has an important influence on the HTC of fructose. The Maillard reaction (MR) promotes the formation of N–HC in acidic conditions. However, in alkaline conditions, MR promotes the formation of bio-oil at the expense of N–HC. Alkaline conditions reduce N–HC yield by catalyzing fragmentation reactions of fructose and by promoting the isomerization of fructose to glucose. The results showed that adjusting the concentration of nitrogen-containing compounds or the pH value of the reaction environment is important to force the reaction toward the formation of N–HC or N-bio-oil.

1. Introduction

The establishment of a circular bioeconomy requires the use of innovative technologies to convert renewable non-food bio-resources, such as lignocellulosic biomass in a sustainable bio-refinery route to functionalized materials. Hydrothermal carbonization (HTC) is promising green technology to convert biomass in an aqueous medium under self-generated pressure to carbonaceous materials with high carbon content and with a heating value similar to lignite. This carbon-rich material is known as hydrochar (HC).[1] The reaction temperature usually ranges from 180 to 250 °C and is applied up to several hours.[2] The presence of subcritical water conditions is crucial for HTC, as under these conditions water gains unusual properties; with increasing temperature and pressure the dielectric constant of water decreases, and its ionic products increases. Consequently, water behaves as a catalyst for reactions that normally require the presence of acids or bases.[3] Furthermore, water is a cheap and non-toxic solvent, is naturally present in biomass, and promotes fast and complete conversion of biomass. These remarkable features of subcritical water are key to the environmental performance of HTC. During HTC of biomass, many reactions occur, mainly hydrolysis, decarboxylation, dehydration, condensation and polymerization reactions, which are influenced by the properties of water.[3,4,5,6]

Nitrogen exists in almost all types of biomass in different chemical forms and in various concentrations. Therefore, comprehensive knowledge about the reactions of nitrogen-containing compounds and nitrogen distribution between different phases during HTC is necessary to achieve a sustainable conversion of bio-resources, to design sustainable applications of HC, and to recycle unused N-compounds for sustainable applications e.g. as bio-based fertilizer. Additionally, the incorporation of nitrogen atoms in the carbon network during HTC is also important. Nitrogen-containing hydrochar (N-HC) could be used in an abundance of applications depending on its N-functional groups and N-content. For instance, heterocyclic N-containing functionalities in the HC is a beneficial property when using HC in electrical applications e.g. supercapacitors.[7]

Due to the importance of the reactions of N-compounds during HTC, many studies gave special attention to the subject of nitrogen during HTC. Kruse et al., 2016 reported that the distribution of nitrogen between the liquid phase and solid phase depends on the type of nitrogen-containing compounds and showed that around 50% of the initial nitrogen goes to the liquid phase during HTC.[8] Zhuang et al., 2017 studied the transformation pathway of nitrogen compounds during HTC of sewage sludge and showed that reaction time and temperature influence the forms of nitrogen-containing compounds in the liquid phase.[9]

Arauzo et al., 2019 illustrated that the extraction of protein from the biomass before HTC reduced HC yield.[10] Latham et al., 2013 showed that the addition of ammonium sulfate promotes the HTC of sucrose and increases the HC yield in both acidic and basic solutions.[11] Furthermore, Latham et al., 2018 illus-

[a] M.Sc. M.-J. Alhnidi, Dipl.-Ing. D. Wüst, M.Sc. J. Pfersich, Prof. Dr. A. Kruse
Department of Conversion Technologies of Biobased Resources
Institute of Agricultural Engineering
University of Hohenheim
Garbenstrasse 9
70599 Stuttgart (Germany)
E-mail: mjamal.alhnidi@uni-hohenheim.de
jamal_alhnidi@hotmail.com
[b] M.Sc. P. Körner
Deutsches Biomasseforschungszentrum (DBFZ)
Torgauer Strasse 116
04347 Leipzig (Germany)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/open.202000148

trated that the addition of ammonium salts enhances the HTC of saccharides and increases the HC yield via the Maillard reaction (MR).[12] On the contrary, Wang et al., 2018 showed that the use of a high concentration of amino acid (glycine) and ammonium salts (ammonium sulfate and ammonium chloride) during HTC of glucose caused a reduction in HC yield.[13] Fan et al., 2018 studied the hydrothermal treatment of lactose and maltose at 250–350 °C with and without the addition of lysine and showed that the MR inhibits HTC and promotes the production of bio-oil at the expense of solid products.[14]

The promoting or inhibiting influence of nitrogen-containing compounds on the HTC of biomass and on the formation of N–HC needs further investigation. In this work, the influence of nitrogen-containing compounds on the formation pathway of HC will be studied and the following questions will be addressed: How nitrogen-containing compounds promote or inhibit the formation of HC? Which factors may contribute to this influence? Moreover, can we affect or maybe control this influence towards the production of certain reaction products with special properties and avoid others?

To simplify the complex HTC reaction system and to solve a small part of the "puzzle", HTC was conducted using fructose as the main carbon source and urea (Carbamide) as the nitrogen precursor. The main aim of this work is to investigate the influence of the degradation products of urea on the HTC of fructose and on N–HC yield. A comparison between the reaction pathway during HTC of fructose with and without the addition of urea in different concentrations and at different pH values was conducted. The possible influence of MR and pH value of the reaction conditions on the formation of N–HC was also investigated. The results of this study guide future work into the complex reaction mechanisms of carbon-nitrogen HTC.

2. Results

2.1. Hydrochar Yield and the Elementary Composition of Hydrochar

(Figure 1) illustrates the HC yield after HTC of the first group of solutions. The HC yield depends on the amount of urea added. After the addition of urea, two distinct contradictory effects on HC yield can be observed. When comparing the HC yield obtained after 2 h reaction time of SA with the HC yield obtained from urea-containing solutions for the same reaction time, a slight increase in HC yield of 1.5 % was noticed after the addition of 0.05 M urea (SB). A relatively high increase (12 %) in HC yield was noticed after the addition of 0.19 M urea (SC). On the contrary, a significant decline in the HC yield was observed after the addition of 2.92 M urea (SD). Moreover, after the hydrothermal treatment of pure urea solutions (0.19 and 2.92 M urea), no solid yield was detected only gas and liquid products.

Table 2 shows a variation in the elementary composition of HC after 2 h HTC of the first group of solutions (A, B, C, and D). The highest content of N in the HC was found after HTC of SD. The higher the N content in the HC, the fewer C and O content, and the higher H content. Interestingly, the variation in the elemental composition of HC was accompanied by a color variation (Figure 3).

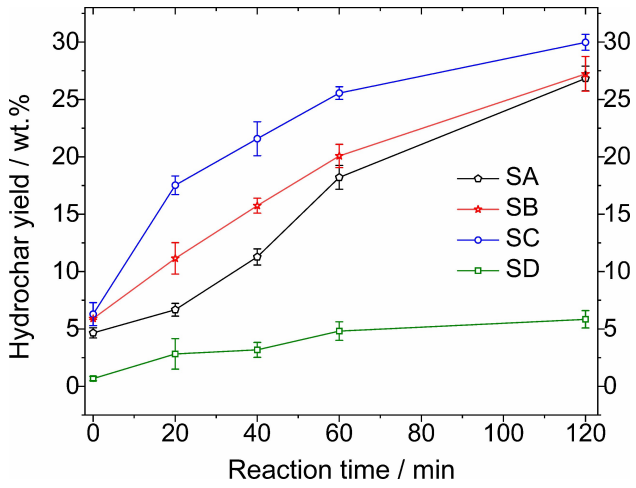

Figure 1. The hydrochar yield (wt.%) during the HTC of the first group of solutions (A, B, C, and D). Experiments were performed in triplicates, and the resulting values show their average and deviation (error bars in figures). The lines between points are used to show the trend during the reaction and are not related to the kinetics of the reaction.

Table 1. The composition of the first, second, and third groups of solutions before HTC.

Name of solution	Composition of solution	Modified pH	Reaction time
The first group of solutions			
SA	0.62 M Fructose	NO	0, 20, 40, 60, and 120 min
SB	0.62 M Fructose +0.05 M Urea	NO	
SC	0.62 M Fructose +0.19 M Urea	NO	
SD	0.62 M Fructose +2.92 M Urea	NO	
The second group of solutions			
SA (pH 9)	0.62 M Fructose	YES	120 min
SC (pH 9)	0.62 M fructose +0.19 M Urea	YES	
SM (pH 1.9)	0.62 M fructose +0.38 M Urea	YES	
The third group of solutions			
Pure urea (0.19)	0.19 M Urea	NO	0, 20, 40, 60, and 120 min
Pure urea (2.92)	2.92 M Urea	NO	

Table 2. The elementary composition of HC after 2 h HTC of the first group of solutions (A, B, C, and D). Experiments were performed in triplicates, the analysis of the samples was performed in triplicates as well, the standard deviation (STD) was less than 5 % for all samples.

Solution	Elemental analysis wt.%				
	N	C	H	O	N/C
SA (Fru + 0 M Urea)	0	65.88	4.32	29.79	–
SB (Fru + 0.05 M Urea)	2.88	63.98	4.72	28.42	0.04
SC (Fru + 0.19 M Urea)	7.21	61.30	5.14	26.35	0.12
SD (Fru + 2.92 M Urea)	17.36	58.58	5.33	19.17	0.30

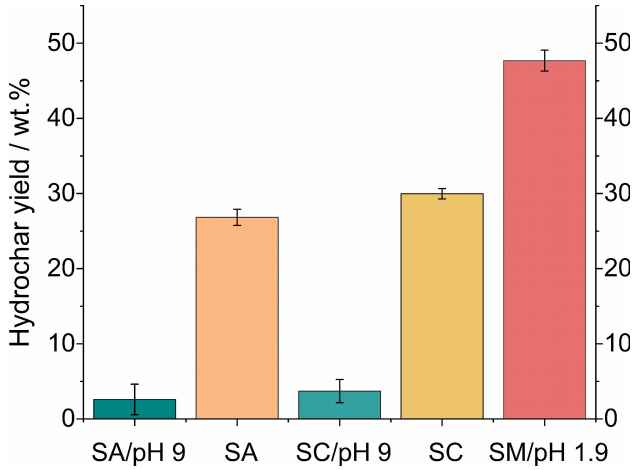

Figure 2. The hydrochar yield (wt.%) after 2 h HTC of the second group of solutions [SA (pH 9), SC (pH 9), and SM (pH 1.9)]. SA and SC were added for comparison. Experiments were performed in triplicates, and the resulting values show their average and deviation (error bars in figures).

(Figure 2) illustrates HC yield after HTC of the second group of solutions (with the use of buffer solution). When comparing HC yield after HTC of SA and SA (pH 9), a major decline was registerd when HTC is conducted in alkaline conditions; with less than 4% HC yield. The same observation was made after HTC of solution SC and SC (pH 9), in which the HC dropped from 30% to 3.7% in alkaline conditions. Moreover, the "char-like" appearance of HC was not noticed after HTC of SC (pH 9), instead, an oily product was obtained (Figures 3 and 4). The highest HC yield in this work (47.7%) was obtained after HTC of SM (pH 1.9) which contains double the amount of urea than SC.

2.2. Analysis of the Liquid Phase

2.2.1. Dissolved Organic Compounds

HPLC measurements were conducted to characterize the liquid phase after HTC of the first group of solutions (Figure 4) and the second group of solutions (see Scheme S3 in the supporting information). As shown in Figure 4, the addition of urea caused significant changes in the type and concentration of fructose degradation products.

Fructose: The degradation rate of fructose strongly depends on the concentration of urea. While small amounts of urea cause a decelerated degradation, higher amounts of urea remarkably accelerate the fructose disappearance. In the case of SD, all the fructose is converted during the heating time.

Glucose: The highest concentration of glucose was obtained during HTC of SB, then in SC in which the glucose formation mainly occurred during the heating time. During the HTC of SA, glucose is formed within the first 20 min of the reaction and

Figure 3. Top left: HC–HTC of SA (0.62 M Fru), 180 °C, 2 h (N/C = 0).Top right: HC–HTC of solution SD (0.62 M Fru + 2.92 M urea), 180 °C, 2 h (N/C = 0.3). Bottom left: HC produced after hydrothermal carbonization of SM (0.62 M Fru + 0.38 M urea) in acidic conditions (pH value of 1.9), 180 °C, 2 h. Bottom right: Bio-oil produced after hydrothermal treatment of SC (0.62 M Fru + 0.19 M urea) in alkaline conditions (pH value of 9), 180 °C, 2 h.

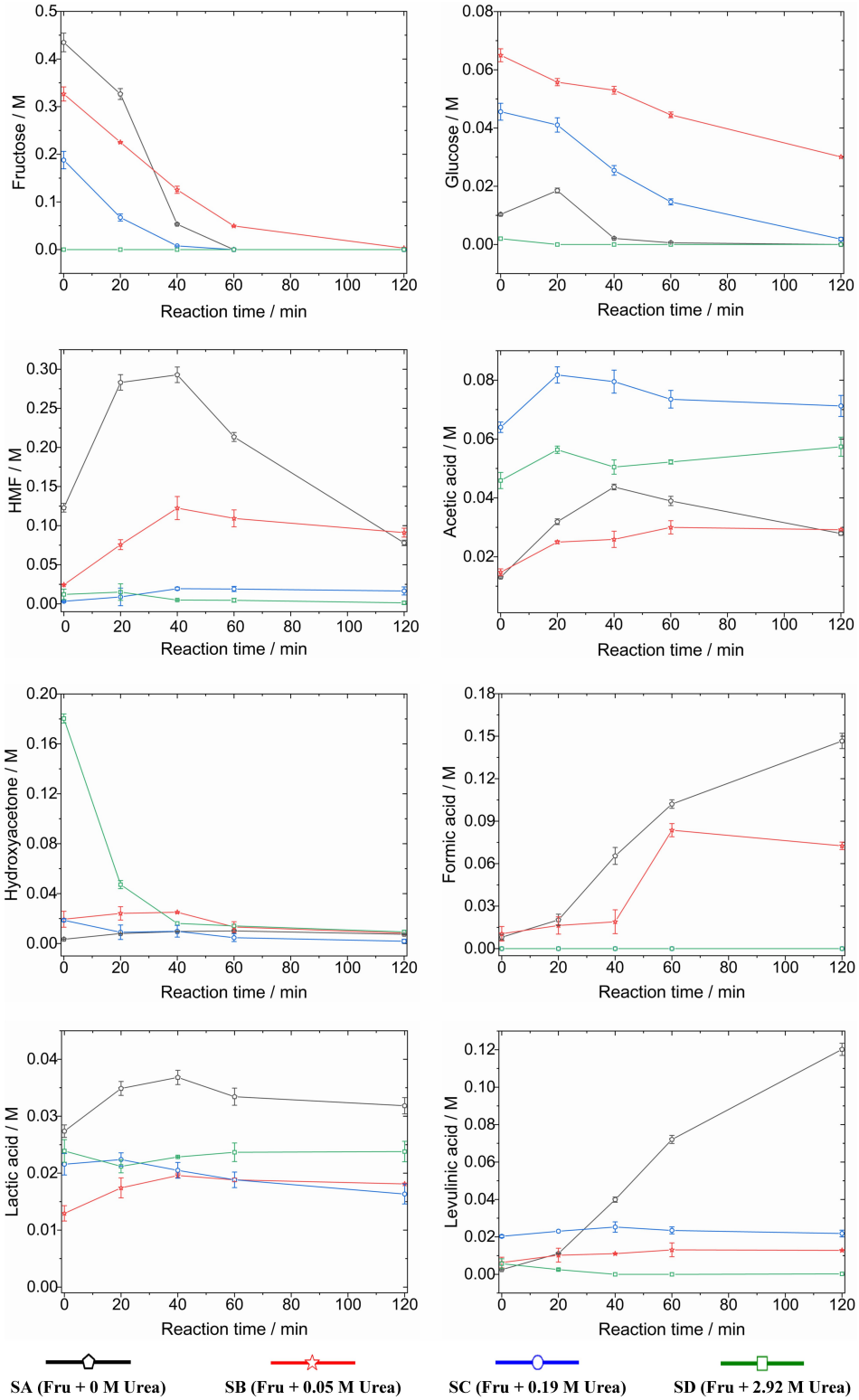

Figure 4. The concentrations of Fructose, Glucose, HMF, Furfural, Lactic Acid, Levulinic Acid, Formic Acid, Acetic Acid, and, Hydroxyacetone in the liquid phase during HTC of the first group of solutions: A (pure fructose), B (Fru + 0.05 M Urea), C (Fru + 0.19 M Urea), and D (Fru + 2.92 M Urea). The lines between points are used to show the trend during the reaction and are not related to the kinetics of the reaction.

subsequently disappears. During the HTC of SD, only traces of glucose were detected shortly after the heating time.

Hydroxymethylfurfural (HMF): During the HTC of SA and SB, HMF is accumulated within the first 40 min of the reaction time. Subsequently, the HMF concentration decreases, whereby in SB,

HMF formation and degradation rate are significantly lower compared to SA. During HTC of SC and SD, only traces of HMF were detected at any time.

Formic acid: The formation of formic acid was noticed during the HTC of SA and SB where its concentration increased gradually during the reaction time. However, no formic acid was detected during the HTC of SC, or SD.

Acetic acid: The formation of acetic acid was detected during the HTC of all solutions (A, B, C, and D). The highest concentration of acetic acid was obtained during the HTC of SC, while SB gave the lowest acetic acid yield.

Levulinic acid: The highest concentration of levulinic acid was obtained during the HTC of SA, in which its concentration gradually increased during the reaction time. Significantly lower concentrations of levulinic acid were obtained during the HTC of SC and only traces of it were detected during the HTC of SB and SD.

Lactic acid: The formation of lactic acid was detected during the HTC of all solutions (A, B, C, and D). The concentrations of lactic acid were relatively stable during the reaction time. The highest concentration of lactic acid was obtained after HTC of SA, while the lowest concentration was gained during the HTC of SB.

Hydroxyacetone: Hydroxyacetone was only found in significant amounts during the HTC of SD, whereby it was formed during the heating time and was subsequently consumed during the first 40 min of the reaction. The presence of hydroxyacetone was confirmed by NMR, as in HPLC, hydroxyacetone co-elutes with propionic acid, which is apparently not present in any samples of this work.

Furfural: In this work, very low concentrations of furfural were detected during HTC (see Scheme S2 in the supporting information) SA resulted in the highest yields, followed by SB and SC, while SD is essentially free of furfural.

The HPLC results after HTC of the second group of solutions (buffered solutions) is available in (see Scheme S3 in the supporting information) It shows that a significant concentration of glucose was produced after HTC of SA (pH 9) and SC (pH 9).

2.2.2. Dissolved Carbon and Nitrogen Compounds in the Liquid Phase

The concentrations of NH_4^+, NO_2^-, TIC, TNb, and TOC were investigated during HTC of fructose-urea solutions (SC) and the hydrothermal treatment of pure urea solutions (0.19 M urea). After hydrothermal treatment of the pure urea solution (0.19 M urea), only NH_4^+ and TIC were detected, TOC was under the detection limit. (Figure 5, left panel) illustrates the concertation of NH_4–N and TIC during the hydrothermal treatment of pure urea solution (0.19 M urea). The concentrations of NH_4–N and TIC were relatively stable during the reaction time.

(Figure 5, right panel) demonstrates the concentrations of TOC and TNb during HTC of SC, the concentrations of TOC and TNb decreased during the reaction time.

3. Discussion

3.1. Degradation Pathway of Fructose and Urea

Investigating the products of the degradation of nitrogen-containing compounds (urea in this article) is important to understand its possible influence on N–HC yield and therefore its influence on the subsequent applications of N–HC and the potentials for nitrogen recovery after HTC.

The hydrothermal treatment of urea was studied before.[15,16,17] These studies suggest that urea decomposes via hydrothermolysis, forming carbon dioxide and ammonia.

This suggestion matches the TIC and NH_4–N results obtained after the HTC of pure urea (0.19 M urea) solution (Figure 5, left panel). The existence of only inorganic carbon after reaching the target temperature indicates that the hydrothermolysis of urea is completed during the heating time. Moreover, the figure demonstrates that nitrogen and carbon content were relatively stable during the reaction time, while no organic carbon was detected. CO_2 can act as an acid during the reaction and buffers the effect of the basic urea or NH_3 as demonstrated in equation (1):[16,17]

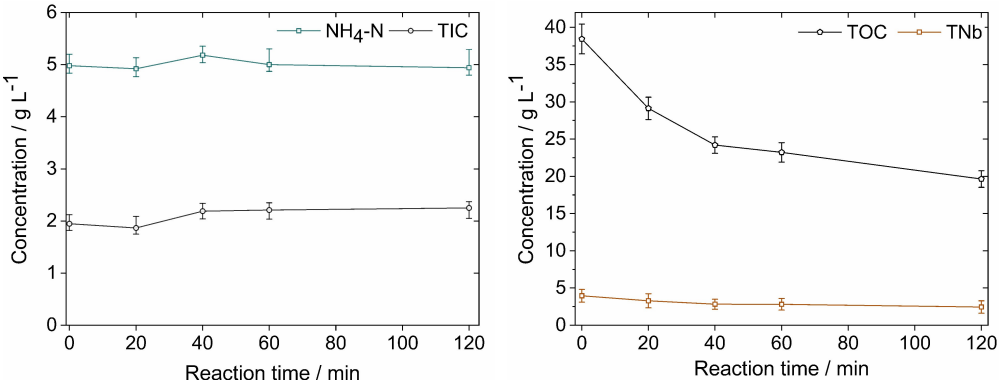

Figure 5. Left panel:The concentration of NH4–N and TIC during the hydrothermal treatment of pure urea solution (0.19 M urea). Right panel: The concentrations of TOC and TNb during HTC of S.C (Fru + 0.19 M Urea). The lines between points are used to show the trend during the reaction and are not related to the kinetics of the reaction. Experiments were performed in triplicates, and the resulting values show their average and deviation (error bars in figures).

$$2NH_3 + CO_2 + H_2O \rightleftharpoons NH_4^+ + HCO_3^- + NH_3 \rightleftharpoons 2\ NH_4^+ + CO_3^{2-} \quad (1)$$

Thus, NH_3/NH_4^+ could be considered as the main nitrogen-containing product of the hydrothermolysis of urea. It is also worth mentioning that NH_3 is one of the main products of hydrothermolysis of many nitrogen-containing compounds such as proteins,[9] amino acids,[18,19] acetamides,[20] and nitriles.[21]

In general, the degradation of protein yields peptides and amino acids, with further degradation ammonia is formed. In the hydrothermal treatment, ammonia plays two roles: it is a reactant forming organic, nitrogen-containing compounds, and it is a base shifting the pH value of the reaction medium upwards and, hence, affecting the reaction pathways of other molecules indirectly.

The decomposition pathways of monosaccharides such as fructose, in particular, has been widely studied.[22,23,24] Based on the literature, two main degradation pathways of fructose can be distinguished: base-catalyzed degradation and acid-catalyzed degradation.[25,26]

In an acidic environment, the main product of the degradation of fructose is 5-hydroxymethylfurfural (HMF). The degradation of fructose to form HMF is an acid-catalyzed dehydration, which includes triple dehydration from fructose with maintaining the ring structure as it dehydrates to form HMF. Subsequent rehydration of HMF leads to the formation of lower molecular weight compounds (levulinic acid and formic acid). While HMF and levulinic acid formation require acidic conditions, it can be auto-catalytic because of the parallel formation of organic acids from fructose e.g. acetic acid and lactic acid.[25]

In an alkaline environment, the degradation of fructose tends more to fragmentation reactions, especially retro-aldol condensation, forming glyceraldehyde, glycolaldehyde, erythrose, dihydroxyacetone and pyruvaldehyde.[25,26,27,28] Glyceraldehyde and dihydroxyacetone have a reversible isomerization state and their dehydration leads to pyruvaldehyde, which yields lactic acid via benzylic acid rearrangement.[25,29] Furthermore, direct production of glycolaldehyde and erythrose via retro-aldol condensation of fructose is not possible, but an isomerization from fructose to glucose is required.[28] In this work, direct retro-aldol condensation products of hexoses were not analyzed. Another degradation product of fructose especially obtained under alkaline conditions is hydroxyacetone (Acetol). During hydrothermal treatment, hydroxyacetone can be formed from glucose or fructose via multiple pathways involving several dehydrations, tautomerisation, hydrogenation and retro-aldol reactions.[30,31,32,33]

Under subcritical conditions, both acid and base-catalyzed degradation pathways of fructose may take place.[23,25,26] In principle, as fructose is degraded into organic acids, the pH value is decreased, and acid-catalyzed reactions are favored. However, the degradation of urea into ammonia is shifting the pH value upwards and alkaline-catalyzed reactions are favored. Therefore, the final pH value depends on the initial concentration of the reactant materials. Moreover, the pH value of the liquid phase was relatively stable during the reaction time, which indicates that the influence of degradation products of the reactant materials on the pH value occured during the heating time (40 min). In this work, both acid and base-catalyzed degradation of fructose are possible during HTC of all fructose-urea solutions (B, C, and D). However, acid-catalyzed dehydration of fructose is assumed to be dominating during HTC of SA, SB, and SC in which high amounts of HMF, levulinic acid, and formic acid are obtained and the lowest pH value of the liquid phase was noticed (2.2–4). Yielding the highest amount of HMF (main products of acid-catalyzed dehydration of fructose) and levulinic acid and formic acid (rehydration products of HMF[25]) support the assumption that acid-catalyzed dehydration of fructose took place during HTC of these solutions. On the other hand, base-catalyzed dehydration of fructose is suggested to be dominating during HTC of SD, in which the highest pH value of the liquid phase was obtained (9–10). Moreover, no formic acid was formed and only traces of HMF and levulinic acid were detected. In turn, the yields of acetic acid and hydroxyacetone tend to be higher, which indicates that the degradation of fructose underwent (mostly) via fragmentation reactions e.g. (reverse aldol condensation) in which HMF was not produced. The results obtained in this work are comparable with a previous publication in which buffered fructose solutions with pH values between 2.2 and 8.0 were hydrothermally treated, it could be demonstrated that at low pH values the formation of HMF, levulinic acid, and formic acid dominates. In turn, at high pH values, the dominating reactions are the formation of acetic acid and lactic acid from reverse aldol products as well as glucose from isomerization, while less HMF and subsequent products are formed.[34] The major reduction in HC yield after HTC of SA (pH 9) in comparison with HC yield from SA also supports the assumed influence of alkaline conditions on the degradation pathway of fructose. The dominating alkaline conditions in SA (pH 9) catalyzes Lobry de Bruyn-van Ekenstein transformation toward the formation of glucose[35] (see Scheme S3 in the supporting information). Higher transformation to glucose means that less fructose will be hydrolyzed to HMF and thus, less HC is formed. The HC formation is also observed from glucose, but is very slow and it is not clear whether this is a direct pathway or via other hexoses.[36]

Nevertheless, the outcome of these base-catalysis products is different in the presence of urea compared with other bases (see Scheme S3 in the supporting information). Esposito and Antonietti, 2013 investigated the formation of lactic acid from glucose under alkaline conditions. Whereas, they achieved good yields, when using various alkali and alkaline earth metal hydroxides as catalysts, no lactic acid was formed in the presence of NH_4^+. Also, the yields of formic and acetic acid, common by-products, were lower.[37]

In this work, the lactic acid yield is also relatively low. Interestingly, it is the highest from a pure fructose solution and the lowest from SB. The yields of acetic acid and glucose first increase with increasing urea concentration and then decrease with the further increase of the urea concentration. Obviously,

the presence of NH_4^+ has an influence on the sugar decomposition, not only by acting as a base increasing the pH value but also by forming nitrogen-containing compounds, such as aminosugars. However, this is discussed in the upcoming section.

3.2. Influence of the Degradation of Urea on the Formation of Nitrogen-Containing Hydrochar

The formation of HC during HTC of biomass is not fully understood. Karayildirim, Sinağ and Kruse, 2008 revealed that HC could be formed via a solid-solid conversion pathway, solved intermediates pathway, or a combination of both pathways.[38] In comparison with biomass, the reaction pathway from monosaccharides, e.g. fructose, is less complex. In general, the formation of HC from carbohydrate includes the following reactions: hydrolysis in the case of oligo- and polysaccharides, dehydration, and aldol condensation.[39,40] HC, at least, if produced from pure hexose, can be considered as polycondensated HMF or derivatives obtained from it.[41]

Evidently, the presence of urea and ammonia, respectively, has a strong impact on the HC formation. Figure 1 shows a significant reduction in the HC yield after HTC of SD. One reason is the degradation of urea, which has already detailed results in the formation of ammonia and, hence, in a high pH value of around 9. Under these conditions, the degradation of fructose underwent a base-catalyzed degradation pathway, in which fragmentation reactions occur and no HMF or other HC precursors are produced, which means that the HC formation via the solved-intermediates pathway is suppressed. However, the pH value of the liquid phase during the heating time is not available, moreover, the degradation of pure fructose or urea solution in subcritical water is relatively rapid.[25,17] Thus, it is unreasonable to claim that the reaction medium was completely alkaline during the heating time or to exclude the possibility of an acid-catalyzed degradation of fructose especially at the beginning of the heating time. Moreover, it has also been found that HC is at least partially soluble in alkaline media,[42] which may have also contributed to the HC yield reduction after HTC of SD.

Here, the following question arises: which factor(s) is/are mainly responsible for the reduction/increase of N–HC? MR or base-catalyzed degradation of fructose or a combination of both? The results obtained after HTC of solution SC (pH 9) in which a bio-oil was produced corresponds to the findings of Fan et al., 2018, which showed that MR is enhancing hydrothermal liquefaction (HTL) at the expense of HTC. However, when the concentration of urea was doubled in SM (pH 2) to enhance the production of bio-oil, contrasting results were obtained with more than 47% HC yield, while the formation of bio-oil was not noticed (Figure 2) Of course, acidic conditions catalyze the following reactions such as condensation and polymerization forming HC, and may have contributed to the increase of HC yield, however, these results indicate that MR (in acidic conditions) neither has an inhibition effect on the formation of N–HC nor provokes the production of oil.

The Maillard reaction (non-enzymatic browning) is an interconnected reaction network that takes place in the presence of reducing sugars and amino acids or amine compounds.[43,44,45] The chemistry underlying the MR is complicated and it includes a complex sequence of several reaction pathways e.g. Hodge pathway,[46] Namiki pathway,[47] and Wolff pathway.[48] Reihl, Oliver. 2004 showed that MR includes three main stages, in the early stage many intermediates are formed e.g Schiff bases, glyoxal, Heyns and Amadori products. The advanced stage includes the formation of more C_3 fragments. The final stage is distinguished by the formation of brown nitrogenous polymers and co-polymers e.g Melanoidins.[49] Many factors including temperature, reaction time, and the pH value of the system have a significant influence on the reaction pathways in MR and therefore on its final products.[50,51,52] In general, a higher pH value enhances Maillard browning.[50,53] The optimum pH for Maillard browning is between pH 6 and 10.[48,54] In turn, lower pH values induce the formation of furfural and HMF via MR.[53,55] The chemistry of MR under subcritical conditions is not clear, however, it is obvious that in this work the pH value of the reaction milieu has a significant influence on MR products during hydrothermal treatment. It seems that under subcritical conditions MR behaves in two contradicting ways depending on the pH value of the reaction milieu; at low pH value only the early stage of MR is taking place and it supports the formation of HMF and therefore increases the HC yield. However, in alkaline conditions, MR provokes the formation of bio-oil at the expense of HC, a possible reaction pathway for the formation of oil via MR in subcritical conditions is available in.[14]

Based on the previous discussion, it seems that a high pH value has a negative influence on the formation of N–HC by inducing base-catalyzed degradation of fructose and by provoking the formation of oil via MR. On the other hand, this result also indicates that hydrothermal liquefication may occur in mild reaction conditions (180 °C) via MR in alkaline conditions. However, more investigation is required regarding this point.

In addition to MR and the pH value of the reaction environment, other factors may contribute to the formation of N–HC yield. Interestingly, when HTC was conducted in acidic conditions the addition of urea increased the N–HC yield (SB, SC, and SC [pH 1.9]). This effect may be ascribed to the influence of ammonia on the cross-linking process between N–HC precursors by lowering their respective energies with hydrogen bonds, forming intermediates, and therefore being incorporated in the HC. Moreover, ammonium salts could catalyze the dehydration of fructose to HMF, which increases the selectivity of HMF formation and consequently leads to a higher HC yield.[56] On the other hand, in the first group of solutions, HTC of SC yielded the highest HC. This may partially be attributed to the higher pH value, which in this case, inhibits the degradation of HMF and other potential HC precursors into dissolved end products, such as levulinic acid.[34] Another possible reason is related to the precipitation of NO_x salts on the HC which increases N–HC yield.[8] Moreover, a recent study demonstrated that HC and levulinic acid formation compete, whereby the latter dominates at low pH values.[57] Another

reason for the gravimetric HC yield variation could be related to the influence of ammonia on the isomerization reactions between the monosaccharides. Yang et al., 2016 showed that alkaline effective amino acids act as a catalyst for the isomerization of glucose to fructose in water. However, the acidic condition may promote the reversibility of the reaction.[58] Although HC formation is also observed from glucose via furfural,[6] however, a higher isomerization rate toward the formation of glucose means that less fructose will be dehydrated to HMF, and as a consequence, less HC will be formed.

4. Conclusions

The concentration of nitrogen-containing compounds and the pH value of the reaction environment have an enhancing or inhibiting influence on the degradation pathway of biomass during HTC and on the formation of N–HC. Under subcritical conditions, the degradation of urea forms ammonia, which influences HTC by shifting the pH value of the reaction milieu upwards, and by acting as a reactant with fructose and other intermediates. Under alkaline conditions, the degradation of fructose undergoes via a base-catalyzed degradation pathway, in which fragmentation reactions occur and much less HMF or other HC precursors are produced and consequently less N–HC is formed. The alkaline conditions catalyze Lobry de Bruyn-van Ekenstein transformation toward the formation of glucose and thus causes a reduction in N–HC yield. Besides, higher pH values enhance Maillard browning and provoke the formation of bio-oil. In contrast, under acidic conditions, MR enhances the formation of HMF and increases N–HC yield. Thus, by adjusting the pH value of the reaction environment, it is possible to control the effect of nitrogen-containing compounds on the initial but also the following reactions of HTC and guide the reaction toward the formation of N–HC or N-bio-oil. Finally, we are coming closer to understand the design of N–HC from biomass.

Experimental Section

Materials

D(−)-Fructose (180.16 g mol^{-1}) urea (60.06 g mol^{-1}), citric acid (192.13 g mol^{-1}), and dipotassium hydrogen phosphate (174.18 g mol^{-1}), supplied by VWR in analytical grade, were used for the production of the model solutions.

Methods

Hydrothermal conversion of three sets of model solutions was conducted (Table 1) to study the influence of urea on the HTC of fructose. The first group included HTC of urea-fructose mixture with deionized water. To investigate the influence of MR and the pH value of the HC formation, the second group included HTC of urea-fructose with buffer solution, in this group, a mixture of 2 M dipotassium phosphate solution and 1 M citric acid was used as a buffer solution to modify the pH value of the solutions before HTC, whereby base and acid are mixed in different ratios to achieve different pH values between 1.9 and 9.0. In the third group, the hydrothermal conversion of pure urea solutions was conducted to study the degradation products of urea. In all fructose-urea solutions, the molarity of fructose was fixed to 0.62 M. However, the molar ratio of urea to fructose was gradually increased.

HTC of the model solutions was conducted in stainless-steel autoclaves with a maximum internal volume of 24.5 ml. 70% of the total volume of the autoclaves was filled with the solution. The autoclaves were heated using a gas chromatography (GC) oven. Six autoclaves were placed inside the GC furnace, of which one was equipped with a thermocouple to measure the temperature. The heating temperature of the GC oven was set to 22 °C for a few minutes to provide the autoclaves with the same temperature before the heating starts. Subsequently, the autoclaves were heated up to 180 °C within approximately 40 min and were left to react at the desired reaction temperature. Reaction time 0 min represents the moment when the autoclave reaches the target temperature (180 °C). When the planned reaction time was over, the reaction was quenched rapidly by cooling down the autoclave to room temperature in cold water. All the HTCs were performed at least in triplicates, and the resulting values show their average and deviation (error bars in figures).

Samples Preparation

After cooling down the autoclave, the suspension of the solid yield (hydrochar) and liquid yield (process water) was filtrated using a vacuum pump and 0.45 μm PTFE filtration membrane filter. Then HC was dried at 105 °C for 24 h. After the drying, the weight of the dry HC was measured with an analytical balance. The liquid phase was collected in HDPE bottles and then was frozen at −24 °C to avoid oxidation and degradation reactions before characterization.

Samples Characterization

Nitrogen and Carbon Profile in the Liquid Phase

The total carbon (TC), total inorganic carbon (TIC), and total nitrogen (TNb) were measured by a DIMATOC 2100 instrument (DIMATEC Analysentechnik GmbH, Essen, Germany). The total organic carbon (TOC) was calculated by a differential method (TOC=TC–TIC). The nitrite content was measured using (LCK 341) colorimetric methods (Dr. Bruno Lange GmbH, Düsseldorf, Germany). The colorimetric method ammonium test (114752) was used to measure NH_4^+/NH_3 provided by Merck (Darmstadt, Germany).

High-Performance Liquid Chromatography (HPLC)

The liquid phase samples after HTC were filtered by a 0.45 μm membrane filter and were analyzed by HPLC (Shimadzu Deutschland GmbH, Duisburg, Germany). Hydroxymethylfurfural (HMF), fructose, glucose, lactic acid, acetic acid, formic acid, levulinic acid, and furfural are separated on a BioRad Aminex column (300 × 7.8 mm I.D.) at 35 °C and detected by a refractive index detector. 4 mM sulfuric acid is used as an eluent with a flow rate of 0.6 ml/min.

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra of the liquid phase sample were recorded on a Bruker Avance III HD NMR 600 MHz spectrometer equipped with a 5 mm BBO Prodigy cryo-probe (Bruker BioSpin GmbH, Ettlingen Germany.

The sample was dissolved in 600 µl of H_2O, containing 10% D_2O. 1D 1H with presaturation and 2D homo- and heteronuclear NMR experiments (COSY, HSQC, HMBC1) were recorded at 300 K. For acquisition, processing, and evaluation of NMR spectra, the software TopSpin 3.5pl7 (Bruker) was used.

The pH Value

The pH value was measured using SI Analytics ™ BlueLine pH Combination Electrode. The pH values of the solutions (before and after HTC) were measured under ambient conditions.

Hydrochar Yield

The mass of the dried hydrochar was measured with an analytical balance (±0.001)

The hydrochar yield was calculated using formula (A):

$$\textit{Hydrochar Yield}\ (\text{wt.\%}) = \frac{\text{Mass of dried hydrochar (g)}}{\text{Mass of initial feedstock (g)}} \times 100 \quad (2)$$

The Elementary Composition

The elementary composition (CHNS) of the hydrochar was determined by Elemental Analyser (Euro EA-CHNSO), 3000 Series (HEKAtech GmbH, Wegberg, Germany according to the DIN standards 51732. The oxygen content was calculated by difference:

$$O\ (\%) = 100\,\% - (C\% + H\% + N\%) \quad (3)$$

Acknowledgement

Special thanks are given to Prof. Dr. Schmidt-Rohr and Prof. Michael T. Timko for their valuable comments. Many thanks to Yujie Fan, Zebin Cao, and Qusay Ibrahim for their constructive suggestions. Sincere thanks to the German Academic Exchange Service (DAAD) for their generous grant to fund the research of Muhammad Jamal Alhnidi. Many thanks to the German Research Foundation (DFG) – 328017493/GRK 2366 for funding the work of Mr. Pfersich. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: hydrothermal carbonization · Maillard reaction · nitrogen · hydrochar formation · bio-oil

[1] A. Kruse, A. Funke, M.-M. Titirici, *Curr. Opin. Chem. Biol.* **2013**, *17*, 515–521.
[2] A. Funke, F. Ziegler, *Biofuels Bioprod. Biorefin.* **2010**, *4*, 160–177.
[3] A. Kruse, N. Dahmen, *J. Supercrit. Fluids* **2015**, *96*, 36–45.
[4] A. Kruse, E. Dinjus, *J. Supercrit. Fluids* **2007**, *41*, 361–379.
[5] J. A. Libra, K. S. Ro, C. Kammann, A. Funke, N. D. Berge, Y. Neubauer, M.-M. Titirici, C. Fühner, O. Bens, J. Kern, et al., *Biofuels* **2011**, *2*, 71–106.
[6] D. Wüst, C. R. Correa, D. Jung, M. Zimmermann, A. Kruse, L. Fiori, *Biomass Convers. Biorefinery* **2019**, DOI 10.1007/s13399-019-00488-0.
[7] Q. Wang, J. Yan, Y. Xiao, T. Wei, Z. Fan, M. Zhang, X. Jing, *Electrochim. Acta* **2013**, *114*, 165–172.
[8] A. Kruse, F. Koch, K. Stelzl, D. Wüst, M. Zeller, *Energy Fuels* **2016**, *30*, 8037–8042.
[9] X. Zhuang, Y. Huang, Y. Song, H. Zhan, X. Yin, C. Wu, *Bioresour. Technol.* **2017**, *245*, 463–470.
[10] P. J. Arauzo, L. Du, M. P. Olszewski, M. F. Meza Zavala, M. J. Alhnidi, A. Kruse, *Bioresour. Technol.* **2019**, *293*, 122117.
[11] K. G. Latham, G. Jambu, S. D. Joseph, S. W. Donne, *ACS Sustainable Chem. Eng.* **2014**, *2*, 755–764.
[12] K. G. Latham, A. Ferguson, S. W. Donne, *SN Appl. Sci.* **2019**, *1*, 54.
[13] T. Wang, Y. Zhai, Y. Zhu, Z. Wang, H. Xiao, C. Peng, B. Wang, C. Li, *Bioresour. Technol.* **2019**, *5*, 343–350.
[14] Y. Fan, U. Hornung, N. Dahmen, A. Kruse, *Biomass Convers. Biorefinery* **2018**, *8*, 909–923.
[15] M. Okazaki, T. Funazukuri, *J. Mater. Sci.* **2008**, *43*, 2316–2322.
[16] M. L. Kieke, J. W. Schoppelrei, T. B. Brill, *J. Phys. Chem.* **1996**, *100*, 7455–7462.
[17] J. W. Schoppelrei, M. L. Kieke, X. Wang, M. T. Klein, T. B. Brill, *J. Phys. Chem.* **1996**, *100*, 14343–14351.
[18] N. Sato, A. T. Quitain, K. Kang, H. Daimon, K. Fujie, *Ind. Eng. Chem. Res.* **2004**, *43*, 3217–3222.
[19] F. Pietrucci, J. C. Aponte, R. Starr, A. Pérez-Villa, J. E. Elsila, J. P. Dworkin, A. M. Saitta, *ACS Earth Sp. Chem.* **2018**, *2*, 588–598.
[20] D. S. Lee, E. F. Gloyna, *Environ. Sci. Technol.* **1992**, *26*, 1587–1593.
[21] A. Krämer, S. Mittelstädt, H. Vogel, *Chem. Eng. Technol.* **1999**, *22*, 494–500.
[22] C. Yao, Y. Shin, L.-Q. Wang, C. F. Windisch, W. D. Samuels, B. W. Arey, C. Wang, W. M. Risen, G. J. Exarhos, *J. Phys. Chem. C* **2007**, *111*, 15141–15145.
[23] B. M. Kabyemela, T. Adschiri, R. M. Malaluan, K. Arai, *Ind. Eng. Chem. Res.* **1999**, *38*, 2888–2895.
[24] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499–1597.
[25] F. Salak Asghari, H. Yoshida, *Ind. Eng. Chem. Res.* **2006**, *45*, 2163–2173.
[26] Z. Srokol, A.-G. Bouche, A. van Estrik, R. C. J. Strik, T. Maschmeyer, J. A. Peters, *Carbohydr. Res.* **2004**, *339*, 1717–1726.
[27] B. M. Kabyemela, T. Adschiri, R. Malaluan, K. Arai, *Ind. Eng. Chem. Res.* **1997**, *36*, 2025–2030.
[28] B. M. Kabyemela, T. Adschiri, R. M. Malaluan, K. Arai, H. Ohzeki, *Ind. Eng. Chem. Res.* **1997**, *36*, 5063–5067.
[29] M. J. Antal, W. S. L. Mok, G. N. Richards, *Carbohydr. Res.* **1990**, *199*, 111–115.
[30] M. J. Antal, W. S. L. Mok, G. N. Richards, *Carbohydr. Res.* **1990**, *199*, 91–109.
[31] M. Möller, F. Harnisch, U. Schröder, *Biomass Bioenergy* **2012**, *39*, 389–398.
[32] T. Deng, H. Liu, *J. Mol. Catal. A* **2014**, *388–389*, 66–73.
[33] F. Yue, C. M. Pedersen, X. Yan, Y. Liu, D. Xiang, C. Ning, Y. Wang, Y. Qiao, *Green Energy Environ.* **2018**, *3*, 163–171.
[34] P. Körner, D. Jung, A. Kruse, *ChemistryOpen* **2019**, *8*, 1121–1132.
[35] Z. Wang, in *Compr. Org. Name React. Reagents*, John Wiley & Sons, Inc., Hoboken, NJ, USA, **2010**.
[36] J. Poerschmann, B. Weiner, R. Koehler, F.-D. Kopinke, *ACS Sustainable Chem. Eng.* **2017**, *5*, 6420–6428.
[37] D. Esposito, M. Antonietti, *ChemSusChem* **2013**, *6*, 989–992.
[38] T. Karayıldırım, A. Sınağ, A. Kruse, *Chem. Eng. Technol.* **2008**, *31*, 1561–1568.
[39] M. Sevilla, A. B. Fuertes, *Carbon N. Y.* **2009**, *47*, 2281–2289.
[40] S. K. R. Patil, C. R. F. Lund, *Energy Fuels* **2011**, *25*, 4745–4755.
[41] D. Jung, M. Zimmermann, A. Kruse, *ACS Sustainable Chem. Eng.* **2018**, *6*, 13877–13887.
[42] I. van Zandvoort, E. J. Koers, M. Weingarth, P. C. A. Bruijnincx, M. Baldus, B. M. Weckhuysen, *Green Chem.* **2015**, *17*, 4383–4392.
[43] M. Titirici, *Sustainable Carbon Materials from Hydrothermal Processes*, John Wiley & Sons, Ltd, Oxford, UK, **2013**.
[44] N. Baccile, G. Laurent, C. Coelho, F. Babonneau, L. Zhao, M. Titirici, *J. Phys. Chem. C* **2011**, *115*, 8976–8982.
[45] A. Kruse, A. Krupka, V. Schwarzkopf, C. Gamard, T. Henningsen, *Ind. Eng. Chem. Res.* **2005**, *44*, 3013–3020.
[46] J. E. Hodge, *J. Agric. Food Chem.* **1953**, *1*, 928–943.

[47] M. Namiki, T. Hayashi, *in Mail. React. Foods Nutr.*, American Chemical Society, **1983**, pp. 21–46..
[48] S. P. Wolff, R. T. Dean, *Biochem. J.* **1987**, *245*, 243–250.
[49] O. Reihl, *Synthesis and Characterization of Maillard Cross Links Their Role in the Reaction Processes*, University of Hohenheim, PhD thesis, **2005**.
[50] J. M. Ames, *Food Chem.* **1998**, *62*, 431–439.
[51] E. H. Ajandouz, A. Puigserver, *J. Agric. Food Chem.* **1999**, *47*, 1786–1793.
[52] K. H. Wong, S. Abdul Aziz, S. Mohamed, *Int. J. Food Sci. Technol.* **2008**, *43*, 1512–1519.
[53] S.-H. Oh, Y.-S. Lee, J.-H. Kim, J.-H. Kim, J.-W. Lee, M. R. Kim, H.-S. Yook, M.-W. Byun, *Food Chem.* **2006**, *94*, 420–427.
[54] S. H. Ashoor, J. B. Zent, *J. Food Sci.* **1984**, *49*, 1206–1207.
[55] H. E. Nursten, in *Conc. Dry. Foods* (Ed.: D. MacCarthy), Elsevier Applied Science, London, **1986**, pp. 53–68.
[56] Q. Cao, X. Guo, J. Guan, X. Mu, D. Zhang, *Appl. Catal. A* **2011**, *403*, 98–103.
[57] D. Jung, P. Körner, A. Kruse, *Biomass Convers. Biorefinery* **2019**, DOI 10.1007/s13399-019-00507-0.
[58] Q. Yang, M. Sherbahn, T. Runge, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3526–3534.

Manuscript received: May 19, 2020
Revised manuscript received: July 5, 2020