Full Length Article

Understanding the fate of nitrogen during catalytic hydrothermal liquefaction of sewage sludge

Yujie Fan [a,b,*], Leif Meyer [c], Miao Gong [d], Bärbel Krause [e], Ursel Hornung [b], Nicolaus Dahmen [b]

[a] Nanyang Institute of Technology, School of Civil Engineering, Nanyang, PR China
[b] Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Karlsruhe, Germany
[c] Hochschule Furtwangen, Faculty of Medical and Life Sciences, Villingen-Schwenningen, Germany
[d] Hefei University of Technology, School of Civil Engineering, Hefei, PR China
[e] Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation, Karlsruhe, Germany

ABSTRACT

In this study, the fate of nitrogen during catalytic hydrothermal liquefaction (HTL) of sewage sludge (SS) is investigated using three different catalysts ($CuNi/SiO_2$, HCOOH, $CuSO_4$) with 5 wt% loading. The bio-crude yields obtained from HTL experiments catalyzed with $CuNi/SiO_2$ are similar to those obtained through non-catalyzed experiments. HCOOH slightly increases the bio-crude yields, while maximum yields of 24.5 wt% is obtained in the presence of $CuSO_4$, which also reduces the nitrogen content by 15 % and enhances the hydro-carbons compared to the non-catalyzed HTL. Mechanistic investigations regarding the interaction of amino acids and carbohydrates by Maillard reactions are carried out using model compounds, namely lysine and lactose. $CuSO_4$ effectively increases the yield with 50 % and reduces the nitrogen content by 24 % in the bio-crude during HTL of lysine alone. In the case of the model mixtures, bio-crude yields, nitrogen content, and Maillard reactions products behaved similarly both for catalytic and non-catalytic HTL, a slight reduction of amines was found in the presence of $CuSO_4$. Hydro-char and some organic compounds are assumed to act highly reductant during catalytic HTL. Coke deposition and adsorbed poisoning by Maillard reaction products are proposed as the main reasons for the deactivation of catalysts.

1. Introduction

With the rapidly rising population and urbanization growth, the increasing volume of sewage sludge (SS) from wastewater treatment plant is becoming an important global concern. Current treatment approaches for sludge include dewatering, anaerobic digestion, incineration and landfills. However, the disposal of sludge is particularly challenging and creates severe environmental hazards owed to the high content of organic, heavy and toxic metals, micro pollutants among its constituents [1,2]. Hydrothermal liquefaction (HTL) of SS into energy and fuel is a promising technology to deal with the expanding global sewage supply by reducing its pollutants in an environmentally benign way [3,4]. Without a pre-drying procedure, this organic matter can be converted to bio-crude, bio-char and nutrient-rich aqueous phases, developing further applications and hence reducing waste.

Previous studies have investigated the application of HTL processing of SS, under different conditions, from batch reactor test to continuous-flow processes [5,6], with controllable product quality remaining hard to achieve. Catalysts play an important role to control reaction pathways and improve the bio-crude yield, either homogeneous or heterogeneous catalysts. the presence of catalysts generally reduces the activation energy and thereby increases overall conversion efficiency. Catalysts can reduce the condensation and/or repolymerization reactions of the intermediate products formed by the decomposition of biomass, leading to higher bio-crude yields. It is still considered a challenge to employ the bio-crude without any type of upgrading, as meeting industrial standards proves difficult, i.e. due to the high nitrogen (N) content [7,8]. Reducing this N content during HTL would decrease the follow-up cost of downstream processing. This does however require a deeper understanding of the fate of N during HTL.

The first studies, which focused on the N content from catalytic hydrothermal treatment of different varieties of SS, were performed by Dote et al. [9]. The results showed promising bio-crude yields of 40 wt%, while high N concentrations around 5.8–6.1 % remained into the bio-

crude. Later, Xu et al. [10] demonstrated the effects of alkaline metal catalysts on direct liquefaction of pulp/paper sludge. The presence of K_2CO_3 unexpectedly suppressed the formation of both heavy oil and water-soluble products. As proven in previous work, the alkali catalyst is not favorable for the conversion of high protein-containing feedstock such as SS. Usually, dehydration might result in unsaturated compounds which further polymerize into char. [11,12]. It was also found that HCOOH can improve the bio-crude yield from 24.9 to 34.4 wt% at 300 °C with an undesirable increase of N content. Publications by Ross et al. [13] and Prestigiacomo et al. [14] also confirmed these trends, and implied that short chain organic acids can improve the bio-crude yield. These findings are associated with alternative chemical pathways such as dehydration reactions, which are enhanced by the acidification of the reaction medium. HCOOH can form carbon monoxide and in-situ hydrogen which further acts as a proton donor to improve the bio-crude production [15]. Besides the common acidic and alkaline catalysts, transition metal catalysts, like $CuSO_4$, $ZnSO_4$, $CoSO_4$, and $FeSO_4$ were applied to catalytic HTL of municipal SS in ethanol and water co-solvent conditions [16,17]. $CuSO_4$ was identified as being the best performing one, regarding the positive impact on the bio-crude yield and its elemental composition. $CuSO_4$ can promote the formation of esters and impede the decarboxylation of fatty acid, leading to a better quality of bio-crude. Optimized operating conditions reduced the N content in bio-crude by 14.6 %, while the N distribution to other phases and detailed catalytic mechanisms were not explored.

Most of these previous studies typically involved homogenous catalysts, research on HTL of biomass with potential heterogeneous catalysts is rare. The latter represent a very interesting option, as they could promote the upgrading of bio-crude *in situ* during its production and are generally separable from the reaction products. In the terms of upgrading, the lifetime of hydro-treating agents was reduced by coking and deactivation. Duan et al. [18] examined the application of common hydrocarbon processing catalysts (Pd/C, Pt/C, Ru/C, $Ni/SiO_2-Al_2O_3$, sulfide $CoMo/\gamma-Al_2O_3$ and zeolite) to HTL of microalgae; all tested catalysts produced higher bio-crude yields than the non-catalyzed experiments. The reported bio-crude quality was largely insensitive to the catalyst used. Wang et al. [19] recently tested HTL of microalgae with various transition metal M/TiO_2 catalysts. The results showed Ni/TiO_2 to be the most effective catalyst to improve the bio-crude yield and quality. There is limited information available on the catalytic liquefaction of SS with heterogeneous catalysts. Wang et al. [20] investigated catalytic HTL of SS over alumina-based and attapulgite-based heterogeneous catalysts (Co, Mo), and it was reported that Co-Mo/ATP catalyst inhibited amides formation enhanced the maximum bio-crude yields with higher hydrocarbons (16.6 %). The employed catalyst can specially promote certain reactions. While, in another case, transition metal based catalysts such as $MoO_3-CoO/\gamma-Al_2O_3$ and Ru/C were found to reduce the bio-crude yields compared to non-catalyzed experiments in HTL of SS. Their effect on the heteroatom content of the bio-crude was not considered, and the unexpected effects were not explored in terms of catalytic mechanism [21].

Different catalysts reported above have shown positive and negative effects on the maximization of bio-crude yields derived from HTL of SS, however, less promising efficiencies on the reduction of N were achieved. For fuel applications the N content is a decisive parameter and thus, the cost of additional post-treatments of the "recalcitrant" N may offset the improved yields efficiency. Therefore, it is essential to investigate the catalytic effects on the behavior of N, specifically, to figure out the influences on *N*-containing compounds in the obtained bio-crude. To the best of our knowledge, no studies were reported regarding the catalytic effects on the fate of N during HTL of SS in particular. With regard to the N content in the bio-crude obtained from HTL of protein-containing biomass, Amidation and Maillard reactions have previously been confirmed as driving factors to impact the N distribution into different product phases when producing bio-crude with HTL of protein-containing biomass [22,23]. The former leads to the production of long chain aliphatic amides, the latter results in more *N*-containing heterocycles which are accepted as the major problematic compounds for fuel application. Accordingly, it is can be assumed that the effects of catalysts on the fate of N largely depend on its role in Maillard reactions. It was also reported that the Maillard reactions were favored with Al_2O_3 and ATP based catalyst, leading to more pyrazine and indole derivatives [20].

In this study, the performance of $CuSO_4$, $CuNi/SiO_2$ and HCOOH, as catalyst and additives on HTL of SS and model mixtures are studied. As mentioned above, $CuSO_4$ and HCOOH have achieved promising results in bio-crude production in terms of yields and compositions. However, the application of these catalysts has been poorly investigated on the fate of N during HTL of SS, and the effects of nitrogen-containing compounds on the catalytic mechanism has not revealed. $CuNi/SiO_2$, as a common heterogeneous hydro-treating catalyst for upgrading, was assumed to promote the *in situ* upgrading of the generated bio-crude during HTL, since the produced hydrogen during HTL may be capable of providing hydrogen donor. While, no reports can be found about the $CuNi/SiO_2$ efficiency for the catalyst application in HTL of SS. Therefore, the objectives of this work are: 1) to examine the catalytic efficiency on the bio-crude yields and quality in the presence of potential catalyst and additives; 2) to investigate the catalytic effects on the fate of N with special focus on the *N*-containing compounds in the bio-crude; 3) to determine the possible catalytic mechanism during HTL of SS combined with HTL of model substances.

2. Materials and methods

2.1. Materials

Digested sewage sludge was obtained from a wastewater treatment plant in Plieningen, Stuttgart, Germany. After collection, the SS sample was stored at −18 °C until used in experiments. Due to the inhomogeneity of the SS, pre-treatment was required to create homogenized sludge slurry. The water content of the raw SS was determined before the samples were dried in a freeze-dryer at −82 °C and 30 mbar for three consecutive days. Subsequently, the sludge was pulverized and then reintroduced to water and stirred to match the original water content. Kjeldahl method was applied for crude protein quantification, photometric estimation by DuBois method was used for carbohydrates analysis, and Soxhlet extraction was carried out for lipids quantification. The basic properties and organic compositions (daf.) of SS are listed in Table 1.

In the current study, lactose (lac) and lysine (lys) were selected as model compounds, not only to keep consistent with our previously published work [24], but also because they are representative for a wide range of substances: lactose is a strongly reducing disaccharide widely occurring in natural products. Lysine is known to be the most reactive amino acid in the Maillard reactions due to the presence of two reactive amino groups. Lactose and lysine were of analytical grade and purchased from Sigma-Aldrich. HPLC grade dichloromethane (DCM) purchased from Sigma-Aldrich was used for the bio-crude recovery from the reaction vessel. $CuSO_4 \cdot 5H_2O$ and formic acid (88 % in water) were analytically pure and purchased from Sigma-Aldrich. The nickel-copper catalyst $NiCu/SiO_2$ was synthesized by wet impregnation. The fraction of Ni and Cu was determined to be 27.9 wt% and 3.2 wt%, respectively. More information regarding the catalyst preparation and characterization can be found in a previous publication [25].

Piperidine, 2,5-dimethylpyrazine and 2,3,5-trimethylpyrazine were purchased from Alfa Aesar, octahydrodipyrido[1,2-*a*:1′,2′-*d*]pyrazine-6,12(2H,6aH)-dione (ODP) was purchased from MolPort, caprolactam was purchased from Sigma-Aldrich.

Table 1
Characterization of the sewage sludge sample used in this study.

Moisture (wt.%)	Ash(wt.%)[a]	Organic compositions (wt.%)[b]			
		Carbohydrates	Proteins	Lipids	Others
78.75	35.61	27.9	34.6	13.9	23.6

Elemental compositions (wt.%)[a]					HHVs(MJ/kg)
C	H	O[c]	N	S	
29.10	5.70	23.19	5.00	0.90	13.84

Inorganic content (wt. %)[a]											
Al	Ca	Fe	Mg	Mn	P	Zn	Ba	Cr	K	Na	Cu
4.26	3.7	1.17	0.03	0.03	3.31	0.14	0.05	0.01	0.57	0.16	0.04

[a] : dry basis.
[b] : dry ash-free basis.
[c] : calculated by difference.

2.2. Experimental setup and procedure

2.2.1. Hydrothermal liquefaction

The HTL experiments were carried out in micro-autoclaves with a volume of 24.5 mL made of stainless-steel alloy 1.4571, which can withstand pressures of up to 40 MPa and a maximum temperature of 400 °C. The reactors were loaded with carefully weighed amounts of homogenized sludge slurry, as well as defined amounts of additives (5 wt% loading, dry basis). For model compounds, each batch was constituted of 10 wt% of organic matter that was dissolved in distilled water and filled into the reactor. For the mixture tests, 50:50 wt% of lactose and lysine were employed. In the case of catalytic HTL, 10 wt% loading was added. The micro-autoclaves were flushed to remove the undesired air and then pressurized to 2 MPa using nitrogen gas. Heating was performed in a gas chromatography furnace (with a heating rate of 40 K/min) and kept at the target temperature (250, 300, or 350 °C) for 20 min, the heating up rate of the claves is around 12 K/min. After the reaction, the autoclaves were taken out of the oven and put in cold water to cool down and to stop the reaction. The micro-autoclaves were opened in a gas-tight containment after flushing air out using nitrogen. To confirm reproducibility and comparability of the results, all experiments were carried out in duplicates. Each measured value reported in the results represents the mean of the independent experiments, with an error corresponding to their standard deviation.

2.2.2. Samples separation and analysis

The gas composition was measured by manually injecting 100 μl of the gas sample into an Agilent 7890A gas chromatograph. The aqueous phase, bio-crude and solid residue were washed with DCM, then the mixed products were vacuum filtered using a Whatman nylon membrane. The solid residue remaining on the filter was placed in an oven and dried overnight at 105 °C to determine its dry weight. The bi-phasic mixture of aqueous phase and bio-crude was separated by centrifugation. The organic solvent was then evaporated by flushing with nitrogen for 24 h. Once a constant weight was achieved, it was recorded and considered as the bio-crude yield.

The C, H, N and S contents of the bio-crude and solid residue were measured by elemental analysis (Vario EL III, Elementar Analysensysteme GmbH, Hanau, Germany), with the O content being calculated by difference. The ash content was determined by weight loss due to calcination in a muffle oven under atmospheric condition at 550 °C for 5 h (ASTM-E1755). Mineral composition in the products was analyzed using an ICP-OES Spectrometer (Agilent Technologies 725, Australia).

Analysis of bio-crude was carried out using an Agilent 6890 N gas chromatograph (GC) with an Agilent 5973 MSD mass spectrometry (MS) detector and a DB-5 capillary column (30 × 0.25 mm × 0.25 μm) The substances were identified using the NIST library, considering only molecules with a match quality above 80 %. The quantitative analysis of

selected chemicals identified by GC–MS was measured by GC-FID with an Agilent a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm).

The total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC) and total nitrogen (TN) content were measured by a Dimatec® 2100 instrument. Ammonium (NH_4^+), and Nitrate (NO_3^-) and nitrite (NO_2^-) were investigated by Metrohm 838 advanced sample processor device.

The crystalline structure of solid residue was investigated by powder X-ray diffraction (XRD) using an X́Pert PRO MPD instrument (PAN-analytical GmbH) equipped with a copper anode (Cu Kα 1.54060 Å). The sample was measured in a 2θ range between 5° and 120° for 2 h. The surfaces of solid residues were analyzed by X-ray photoelectron spectroscopy (XPS). The measurements were performed in an ultra-high vacuum chamber (base pressure 10–8 Pa) equipped with an unmonochromated XR-50 Mg K alpha X-ray source and a Phoibos 150 analyzer (manufacturer SPECS). The data analysis was performed with the software Casa XPS. The energy scale of the spectra was calibrated with the C—C component of the C1s peak at a binding energy of 284.8 eV.

2.3. Data definition

The yields (Y_i) of the different product fractions were calculated as the weight of the recovered mass of organic matter in the product (OM_i) related to the total input mass of organic matter (OM_{input}, dry ash-free) loaded in the reactor, see Eq. (1).

$$ProductYields(wt.\%) = \frac{OM_i}{OM_{input}} \times 100 \qquad (1)$$

The nitrogen distribution (ND) is defined as the amount of nitrogen in the product (m_i) relative to the nitrogen amount in the SS (m_{ss}), see Eq. (2).

$$NitrogenDistribution(wt.\%) = \frac{m_{i-N}}{m_{SS-N}} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Catalytic HTL of sewage sludge

3.1.1. Product yields

The yields of different product phases were calculated on a dry ash-free basis, as the ratio of the weight of organics in the recovered product and the organics of the initial feedstock (Eq (1)). The total mass balance calculated as the mass of obtained products based on the input mass of feedstock with catalysts is illustrated in Fig. S1, and the organic content in the solid residue is listed in Table S1. Fig. 1 shows that around 50 wt% of organic contents is turning into solid residue by HTL of SS at 250 °C with or without catalysts. With raising temperatures, the solid residue yields decrease as the bio-crude yields and aqueous phase increase,
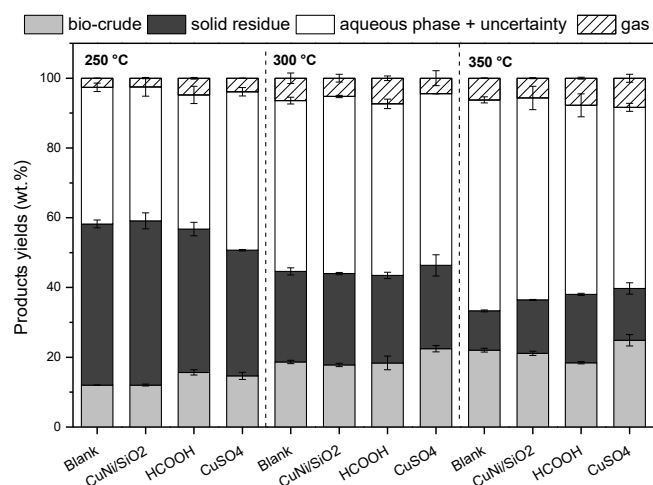
Fig. 1. Yields of different products (ash-free basis) from HTL of SS under different conditions.

indicating that the organic compounds in the solid phase decompose into water soluble chemicals. Oligomers and monomers are produced through condensation, dehydration, and decarboxylation reactions to form bio-crude. A strong temperature dependency is observed with the experiments at 350 °C yielding around 80 % more bio-crude than the experiments conducted at 250 °C. CuNi/SiO$_2$ has no observable impact on the amount of different product phases at all temperatures. HCOOH slightly improves the bio-crude yields at 250 °C, while it inhibits bio-crude formation at 350 °C; accordingly, much more product gas is obtained. In the presence of CuSO$_4$, higher bio-crude yields are found compared to the blank test and the other two catalysts. A slight decrease of solid residue is found at lower temperatures, while at 350 °C, both the solid and bio-crude yields are higher than that of the blank test, suggesting the CuSO$_4$ enhance the water-soluble intermediates covert into bio-crude and further polymerized into solid residue.

3.1.2. N distribution

The nitrogen distribution (ND) in the different phases of the diverse experiments is compared in Fig. 2. The ND is defined as the mass amount of N in the product relative to that in the feedstock. The N balance is determined only for the bio-crude, solid residue and the aqueous phases, ND in the gas phase is negligible due to the small gas yields produced across all the experiments (see Fig. S2). The N balance is not covered to
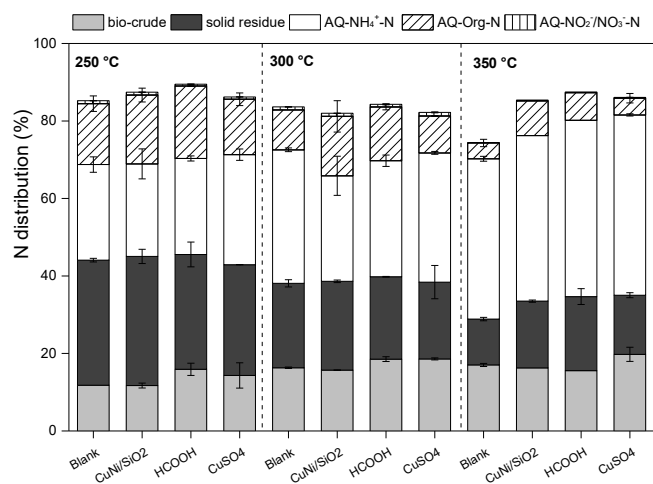

Fig. 2. Nitrogen distribution of HTL products from SS for the catalyst tested at different temperatures (AQ means aqueous phase).

100 % as a result of excluded gas products and the uncertainty. The loss of recovery is caused by some products remaining stuck on the micro-autoclave walls after reaction, the loss of volatile compounds (during extraction solvent removal), and experimental errors. In general, a noticeable, increasing trend of ND in the bio-crude and aqueous phase is correlated with the elevating temperature. Correspondingly, a decrease of the N content is observed in the solid residue. The N found in the aqueous phases can be classified into three fractions: ammonia (NH_4^+-N), nitrite/nitrate (NO_2^-/NO_3^-), and organic nitrogen-containing compounds (Org-N). Organic nitrogen was calculated as the difference between total nitrogen and the sum of nitrogen in the forms of nitrite, nitrate, and ammonium species. Less than 1 % of NO_2^-/NO_3^- is found in the aqueous phase after HTL of SS at all conditions. More than half of N in the aqueous phase is formed by NH_4^+-N, dramatically increasing with rising temperature. Consistently, a decrease of Org-N is detected. Specifically, ammonium increases with the reaction temperature, indicating that high temperature favors the deamination of proteins and amino acids during HTL.

Compared with the un-catalyzed experiments, no impact is detected with the addition of CuNi/SiO$_2$ regarding the overall ND; a very slight decrease of ND in the bio-crude is observed at 350 °C. When HCOOH is present, the ND in the bio-crude is higher than that of the un-catalyzed tests at temperatures below to 300 °C. A slight decrease of ND in the bio-crude along with an increase in the solid residue is found at 350 °C. Generally, the addition of formic acid results in a higher fraction of N accumulating in the aqueous phase. Among these catalysts, CuSO$_4$ leads to more ND convert in the bio-crude phase and aqueous pahse, facilitates a stronger N transformation from organic to inorganic substances, along with a bigger reduction in the solid residue.

3.1.3. Bio-crude composition

The elemental compositions of the bio-crude from catalytic HTL of SS are compiled in Table 2. Compared with the SS feedstock, the recovered bio-crude has significantly higher C, H, and lower N and O contents. The HHVs is increased with rising temperature due to the rising C and H content paired with a dropping O content, as a result of occurring deoxygenation. In the absence of any catalysts, the C content in the bio-

Table 2

Elemental composition and high heating values in the original sludge (based on dry organic matter) and obtained bio-crude.

samples	C (wt. %)[a]	H (wt. %)	N (wt. %)	O[b] (wt. %)	S (wt. %)	HHV(MJ/ kg)
SS	45.2	8.9	7.8	36.0	1.4	21.5
HTL-250 °C						
Blank	66.5	9.9	7.6	14.0	2.0	34.1
CuNi/SiO$_2$	64.3	9.5	7.6	17.3	1.5	32.1
HCOOH	65.6	10.1	7.4	15.5	1.6	33.8
CuSO$_4$	66.6	10.1	6.7	15.6	1.3	34.1
HTL-300 °C						
Blank	69.2	10.0	6.8	12.4	1.7	35.5
CuNi/SiO$_2$	69.4	10.2	6.9	12.2	1.4	35.8
HCOOH	67.1	10.2	6.8	14.5	1.5	34.6
CuSO$_4$	69.5	9.7	6.5	13.3	1.1	35.0
HTL-350 °C						
Blank	72.8	10.0	6.0	9.8	1.5	37.1
CuNi/SiO$_2$	72.5	9.3	6.5	11.1	0.7	35.8
HCOOH	71.6	9.4	6.3	11.8	0.9	35.5
CuSO$_4$	73.4	9.4	6.0	10.6	0.6	36.2

[a]: dry organic basis.
[b]: calculated by difference.

crude is increased from 66.5 to 72.8 wt% with raising temperature, While CuNi/SiO$_2$ and HCOOH decreased the C content, CuSO$_4$ slightly improves it.

There is no big difference regarding the H content in all the bio-crude products, ranging between 9.5 and 10.2 wt%. HCOOH was expected to act as a hydrogenating reagent, but no increase of H content in the bio-crude is observed. Reversely, in agreement with the literature findings reported by Ross et al., there is an increase in O content [26]. The N content is generally lower than in the original SS sample, showing a slight reduction with increasing temperature, no clear catalytic effect is observable. S content is reduced with increasing temperature, as well as with catalysts and additives, even with CuSO$_4$, which in itself adds S to the HTL reactions. However, the S content is mostly higher than in the original SS sample when temperature is under than 300 °C. The heating values of the bio-crude products were almost tripled compared to those of the feedstock (13.8 vs 37.3 MJ/kg).

Another important characteristic of the bio-crude is the *N*-containing component. Qualitative analysis of the bio-crude composition is conducted with GC–MS. The identification of organic compounds was achieved by comparing the spectra of sample components (limited to the top 50 compounds based on the peak-normalized volume) with those in the electronic spectrum library of NIST. The major GC-detectable compounds were categorized into 5 groups according to the functional groups: *N*-containing heterocycles, amines and amides, hydrocarbons, O-containing compounds, and others, which are mainly composed of unknown substances. It should be noted that some low molecular weight components may get lost during the solvent evaporation process for bio-crude oil recovery, while some higher molecular weight compounds might not have eluted from the GC column. Thus, not all components in the bio-crude can be characterized through GC–MS. Fig. 3 shows the relative areas of the classified compositions with typical structures, the detailed chemicals can be found in Table S2 (in SI).

In the absence or presence of catalyst and additives, up to 70 % of detectable components can be identified by GC–MS. Although the chemical components in all the bio-crude from non-catalytic and catalytic HTL were quite similar, some amounts were altered. The *N*-cyclic heterocycles (e.g., pyrazines, pyrrolidinediones, and indole), amines and amides (piperidines, acetamides, and hexadecanamide) are the main compounds, followed by O-containing compounds (phenolic compounds and (3α,5β)-cholestan-3-ol). In general, the addition of catalysts and additives reduce the amount of oxygenates, but different effects on other fractions depend on the catalysts type. For example, both CuNi/SiO$_2$ and HCOOH increase *N*-containing species, while CuSO$_4$ reduces *N*-heterogenic species but increases amines and amides. Hydrocarbons are the desirable compounds in any biofuel, CuNi/SiO$_2$ and CuSO$_4$ improve

the number of hydrocarbons, whereas HCOOH results in similar amount as the blank test.

3.1.4. Evolution of nitrogen functionalities in solid residues

To better understand the transformation of N in the solid residue, except displaying the ND in the different products phases from HTL of SS with or without catalysts, the evolution of nitrogen functionalities was also investigated by N 1 s XPS spectra, as shown in Fig. 4. For all samples, the maximum of the N 1 s spectrum was found at a binding energy of 400 ± 0.2 eV (peak 1). For the peak fit, two additional components at 401.7 ± 0.2 eV (peak 2) and 398 ± 0.2 eV (peak 3) were required to account for the broadening of the N 1 s peak at 350 °C, and the asymmetric peak shape at lower temperatures. Independent of the sample, the full width at half maximum of all components was 1.8–2 eV. Additional minor components, e.g. around 401 eV (usually attributed to pyrrolic-N), are not required for a consistent fit, but cannot be excluded. Peak 1 is usually attributed to amino-N, peak 2 to quaternary-N, and peak 3 to pyridinic-N [27–29]. While the N 1 s spectra at 250 °C and 300 °C are similar, the spectra at 350 °C change significantly. Peak 1 decreases while peak 2 and 3 increase. This indicates that the protein-N (400 eV) was converted into other compounds like pyridine and other heterocyclic-N species. These results may be due to the sequential cyclization and ring condensation of *N*-containing intermediates through Diels − Alder reaction [30]. It seems that this process is enhanced in the presence of CuSO$_4$.

3.2. Catalytic HTL of model substances

According to the reported work, the *N*-containing compounds in the bio-crude are largely produced by Maillard reactions and Amidation. While, Maillard reactions products like *N*-cyclic heterocycles are proven as the most problematic and "recalcitrant" compounds in the bio-crude. To elaborate the effect of Maillard reactions on the catalytic system, HTL of lysine alone and as a mixture with lactose represented for carbohydrate were investigated with and without CuSO$_4$ at a selected temperature of 300 °C. In the current study, lactose was chosen because it is a strongly reducing disaccharide widely occurring in natural products. Lysine is known to be the most reactive amino acid in the Maillard reactions due to the presence of two reactive amino groups. CuSO$_4$ was screened due to the relative positive catalytic effects on the bio-crude yields and nitrogen reduction, as a promising catalyst, it is necessary to explore the catalytic mechanism for further application. 300 °C was selected as the representative temperature due to the relative mild reaction for most HTL biomasses.
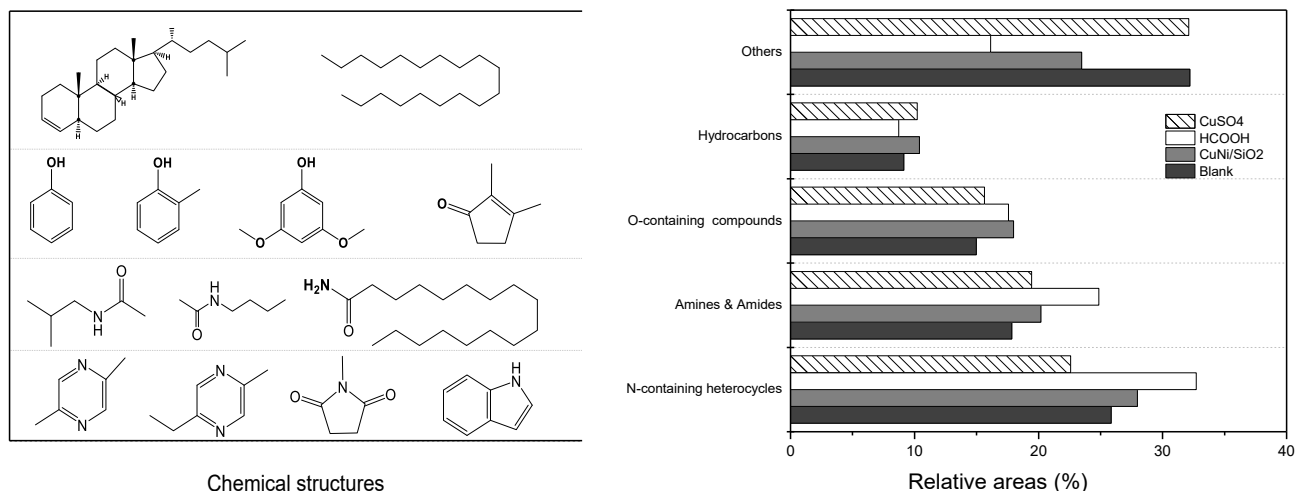

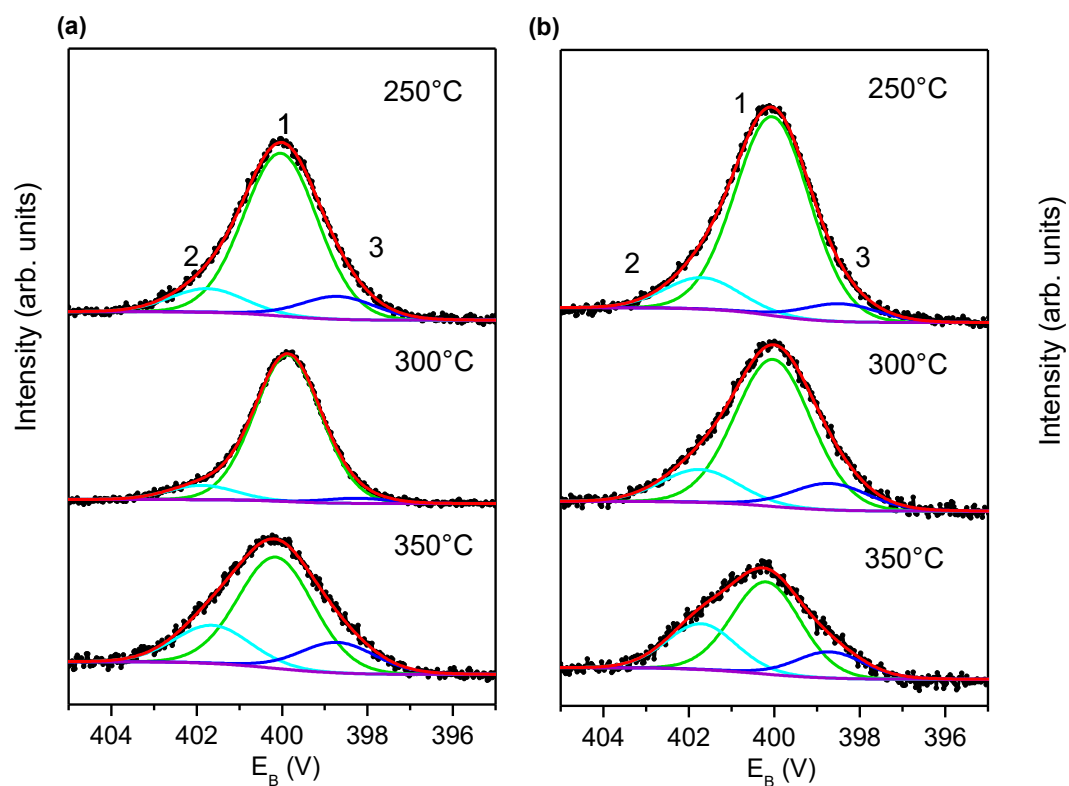Fig. 3. Component fractions of bio-crude obtained from catalytic HTL of SS under 300 °C.

Fig. 4. Evolution of N 1 s XPS spectra for representative solid residue derived from HTL of (a) blank SS and (b) in the presence CuSO$_4$ at different temperatures.
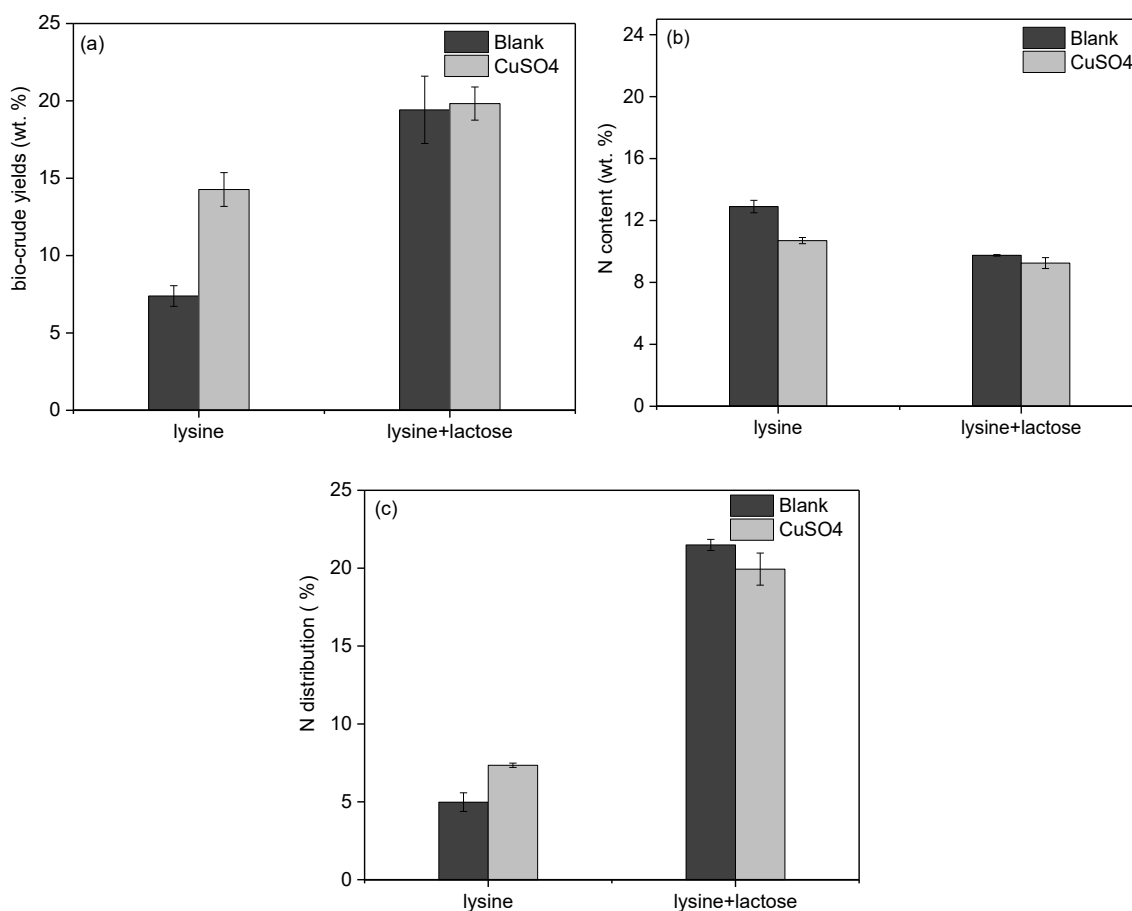

Fig. 5. HTL of single lysine and model mixtures under 300 °C, (a) the yields of bio-crude; (b) N content in the bio-crude; (c) N distribution in the bio-crude.

3.2.1. Bio-crude from model compounds

The catalytic effect on the yields of bio-crude is observed in Fig. 5 (a). The bio-crude yield for lysine alone is significantly increased with the addition of CuSO4, nearly twice than that of blank lysine. In the case of mixture, the bio-crude yield is much higher than the average yield calculated based on the mass average of pure lactose and lysine (more information seen Table S3 in SI), while CuSO4 behaves nearly no impact on the yield of bio-crude.

For lysine alone, CuSO4 decreases the N content from 12.9 to 9.8 % in the bio-crude. Compared with the pure model mixture, the N content is slightly decreased in the presence of CuSO4. Here it must be clarified that the feedstock concentrations of single lysine and the mixture were the same, which means in the mixture case, the mass of lysine is half less, leading to the input of N content in the mixture is half less than that in the single lysine. Consequently, the N content found in the bio-crude is not directly comparable, since the input is varying. Therefore, the nitrogen distribution is also depicted in Fig. 5 (c), defined as equation (2). It shows the weight percentage of nitrogen mass divided to the initial nitrogen mass of the feedstock. Contrary to the N content, the ND in the mixture is much higher than that of lysine alone, which is in accordance with the bio-crude yield. Similar to the bio-crude yields and N content, there is no big difference in the ND between the absence and presence of CuSO4 in case of the model substance mixture.

3.2.2. Bio-crude composition

Detailed chemical composition of bio-crude obtained from HTL of model compounds are also identified by GC–MS and shown in Fig. 6. Unlike the bio-crude from HTL of SS, the variety of identified chemicals from model compounds is less complex than that of real feedstock. Therefore, the results again are characterized by 5 groups of functionalities: *N*-containing heterocycles, amines, amides, O-containing compounds, and others (components shown in Table S4-5 in SI). Concerning lysine on its own, it shows the presence of CuSO4, to slightly increase the content of amides, with an enrichment of 16 %, while the decreasing the *N*-cyclic heterocycles and amines by 40 % and 92 %, respectively. A slight improvement can be found in O-containing compounds, which is also the case for the model mixture in the presence of CuSO4. Regarding the mixture, CuSO4 has a small influence on the fractions of components: *N*-containing compounds are slightly lessened, with the reduction of *N*-

containing heterocycles, amides and amines by 7.9, 13.2 and 21.5 %, respectively.

In addition, typical *N*-containing compounds are quantified by GC-FID with standard calibration. Piperidine is regarded as a cyclic amine produced from HTL of lysine. Caprolactam and octahydrodipyrido[1,2-*a*:1′,2′-*d*]pyrazine-6,12(2H,6aH)-dione (ODP) are formed as cyclic amides from lysine alone as well as from the mixture with lactose. 2,5-dimethylpyrazine and 2,3,5-trimethylpyrazine are typical pyrazine derivatives, which are confirmed as Maillard reaction products.

Table 3 shows that when adding CuSO4 to lysine, the amount of piperidine decreases from 2.6 to 1.9 wt% in agreement with Fig. 6, the relative content of amines experiences a big drop from 22.1 to 7.8 %. Caprolactam also is reduced from 5.5 to 4.5 %, while, the amount of ODP is dramatically increased from 12.2 to 24.8 wt%, resulting in an increased amide fraction. Regarding the model mixture, CuSO4 only shows a significant influence on ODP, decreasing it from 1.8 to 0.6 wt%, which is in line with the reduction of the amide fractions displayed in Fig. 6.

3.3. Mechanism of catalytic liquefaction

3.3.1. N transformation pathways

SS mainly consists of protein, carbohydrate, lipid and lignin. It is difficult to identify the reaction pathways of bio-crude production and nitrogen transformation. Some of the bio-crude components could

Table 3
Main chemicals quantified by GC-FTD.

Chemicals (wt.% g/g)[a]	lysine	Lysine + CuSO4	Lysine + lactose	Lysine + lactose + CuSO4
Piperidine	2.59	1.86	0.18	0.15
Caprolactam	5.51	4.5	0.83	0.82
ODP	12.21	24.83	1.75	0.57
2,5-Dimethylpyrazine	-[b]	-[b]	0.78	0.72
2,3,5-Trimethylpyrazine	-[b]	-[b]	0.42	0.37

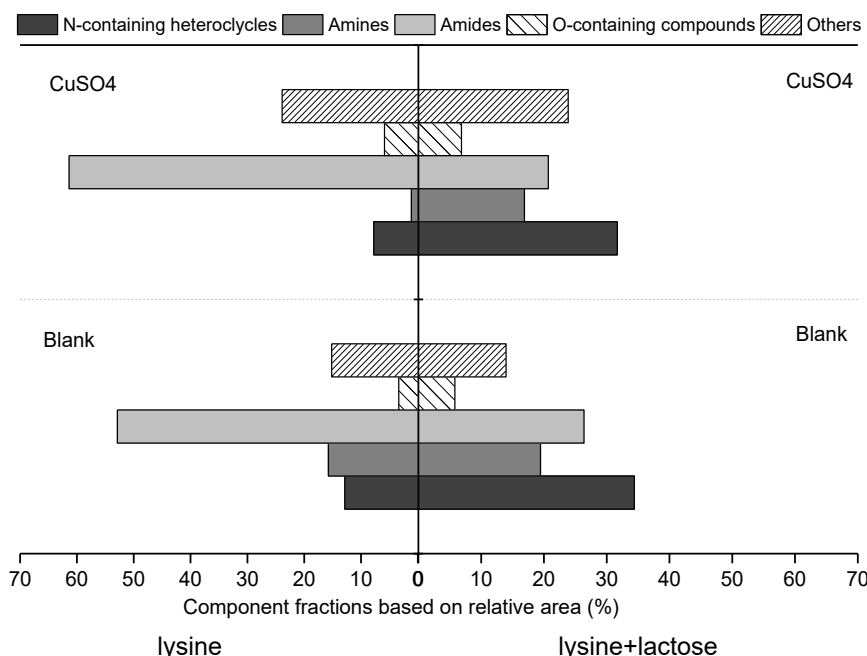[a] : based on the bio-crude.
[b] : not identified.

Fig. 6. The influence of CuSO4 on the component composition in the bio-crude obtained from HTL of model compounds at 300 °C.

originate from the raw feedstock, while others could be converted through various reactions, such as hydrolysis, depolymerization, decomposition and recombination of reactive fragments. Generally, when HTL occurs at lower temperature, the organics firstly undergoes hydrolysis to convert macromolecular organic content into dissoluble intermediates such as 5-hydroxymethyfurfural, furfural, amino acids and fatty acids. Hot compressed water breaks the bonds of materials at heteroatom sites and hydrolyzes the fragments. The hydrolysis of polysaccharides and proteins begins to occur around 190 °C, hemicellulose and lignin dissolved into liquid phase at 220 °C. Lipids or fats split at 220 °C to glycerol and fatty acids via cleavage reaction [31]. When temperature increases, the decomposition of the monomers takes place by cleavage, dehydration, reverse-aldol defragmentation, decarboxylation and deamination to reactive intermediates, involving the loss of H_2O, CO_2 and NH_3.

As a result, the macromolecules are hydrolyzed to macro form polar oligomers and monomers. At higher temperature, hydrolyzed and depolymerized reactive fragments and products usually undergo secondary reactions to generate bio-crude, aqueous phase, solid products and gases. Major reactions among these are recombination, rearrangement, cyclization, condensation and repolymerization.

The nitrogen distributes to different products by undergoing complex reaction pathways. Some amino acids generated from hydrolysis of proteins can form amines and amides by cyclization and dimerization. With increasing temperature, some protein-like species formed as quaternary-N into solid residue. With the interaction between carbohydrates, typical Maillard reactions occur at 150 °C, leading to the *N*-containing heterocycles formed as intermediates. At higher temperatures and longer reaction times, the polymerization of these products most likely happen to resulting in the formation of macromolecular chemicals. Amide formation between proteins and lipids converts nitrogen into amides and decreases the fatty acid yields [24]. To some extent, this reaction can compete with Maillard reactions to modify the distribution of components along in the bio-crude. The potential reaction mechanism of the catalysts on HTL of SS is illustrated in Fig. 7, based on our experimental result and literature.

3.3.2. Catalytic mechanism

Regarding the catalytic effects, the lowest catalytic activity was observed with CuNi/SiO₂, which conflicts with works that showed an increase in the bio-crude yield in reactions catalyzed by transition metals [17]. Here, this catalyst was found to have little effect on the bio-crude yield, in agreement with Qian et al. [21]. They observed that heterogeneous catalysts even decreased the bio-crude yield when the

temperature is higher than 300 °C. Unlike other feedstock, such as microalgae or food waste, SS is rich in ash content, especially the high S content (0.9 wt%), which could be one of the reasons for deactivation, as S is a known poisoning element to heterogeneous catalysts. Considering that the S content is decreased with increasing temperatures, as well as the addition of catalysts, desulfurization might be enhanced. This aligns with Shakya et al. [32], who stated that S is the first heteroatom to be removed from a heterocyclic compound, followed by O and eventually N. It has been suggested that unsaturated feeds cause catalyst deactivation due to their stronger adsorption and propensity for cracking, thus leading to coke deposition [33,34]. In this study, the unsaturated fatty acids could be a source for coke formation, as around 14 wt% lipids were identified in the SS sample. Unsaturated fatty acids like linoleic acid and oleic acid have been widely confirmed in SS [35,36], resulting in the surface blocking.

As a well-known hydrogen donor agent, HCOOH is consumed and therefore act more as a reagent than a catalyst. HCOOH appeared as promising acidic catalyst to increase the rates of decarboxylation and dehydration during HTL reactions [13,14]. In the current investigation, no increase in hydrogen content of the bio-crude is observed. In fact, overall there is an increase in oxygen content. The nitrogen content of the bio-crude is also consistently equal with un-catalyzed HTL. This suggests that the hydrogen generated from HCOOH is not incorporated into the bio-crudes to any significant degree. There may be more dehydration reactions occurring rather than decarboxylation leading to a high O content of the bio-crude. Posmanik et al. [13] reported that acid-catalyzed processes increased the concentrations of furan and furfurals via dehydration. However, compared with non-catalytic HTL of SS, a smaller number of O-containing compounds was identified in the bio-crude, suggesting that these furans were only intermediates, interacting with amino groups to form *N*-containing heterocycles. Instead of reacting with amino acids to generate amides, fatty acids driven by lipids hydrolysis might further convert into aliphatic hydrocarbons and CO_2 by decarboxylation, increasing the bio-crude and gas phase yields. A drastic increase of CO_2 in the gas phase compared to the blank experiment was detected (see Fig. S2). However, the formic acid-catalyzed experiments yielded an equivalent amount of aliphatic hydrocarbons in the bio-crude phase compared to the blank experiments. This can be explained in a way that the formed aliphatic hydrocarbons produced by the decarboxylation of fatty acids were cracked by the H radical provided by the HCOOH. The intermediates formed could further react with other intermediates, like ammonia to form amides or N substituted heterocycles.

Notably, with regard to CuSO₄, the highest bio-crude yields are
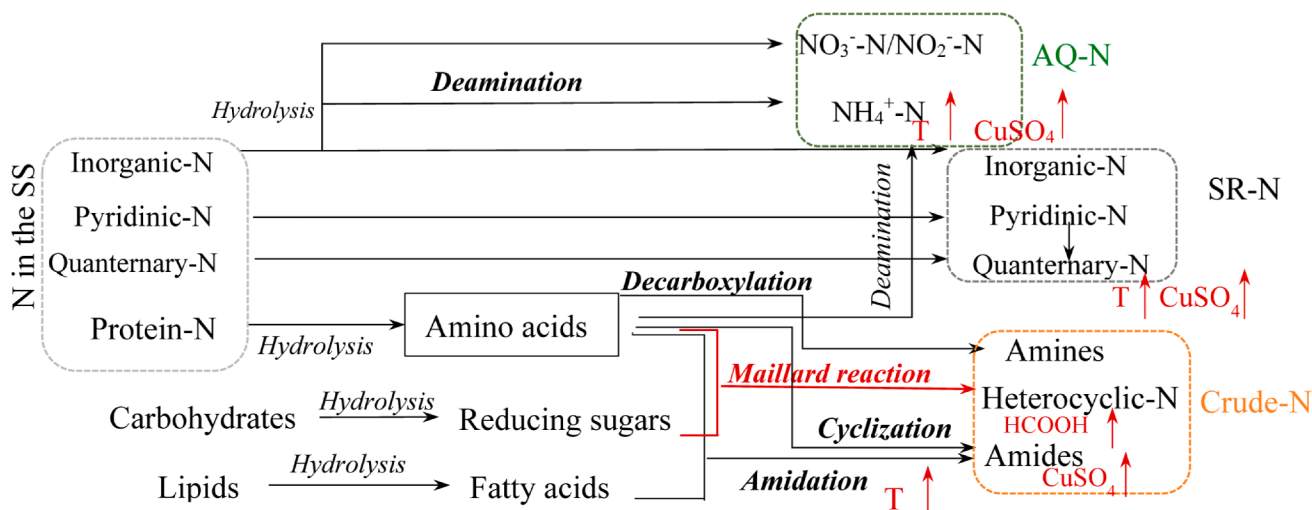

Fig. 7. Proposed transformation pathways of N during catalytic HTL of SS. (up narrow means increase).

obtained compared to other catalysts at the same conditions, which is in agreement with Wang et al. [17]. They also observed that the catalytic function was limited to the Cu^{2+} cation. In this work, the added SO_4^{2-} partly dissolves into aqueous phase with the concentration of 3000–5853 mg/L compared to that ranges from 930 to 1100 mg/L of blank HTL, when temperature increases from 250 to 350 °C. The S content in the solid residue was in the range of 0.6–2.8 wt%. If calculated in the S distribution, it was 60 %, 5 % and 25 % in the solid residue, bio-crude and aqueous phase, individually.

However, regarding the N content in the bio-crude, only a slight decrease is obtained compared to the non-catalytic reaction at lower temperatures, which results in a higher ND to the bio-crude. This can be explained by the much higher bio-crude yields, which over-compensate for the decrease of N content. Concerning the ND in the aqueous phase, the total ND is similar under all experimental conditions applied, but the fraction varies with temperature and type of catalysts. The higher ammonium concentrations indicate that Cu strongly enhances deamination of proteins to reduce organic *N*-containing compounds remaining in the water phase. Also, parts of polar *N*-containing compounds could transform into non-polar states with a subsequent accumulation in the bio-crude phase or, more likely, by an increased number of cyclization reactions of the amines and amides, as shown in Fig. 3 and Table S2 (in SI). More amides are formed with a decrease of *N*-containing heterocycles; indicating that $CuSO_4$ increases the reaction rate between amines and fatty acids. The slight decrease of N content achieved with $CuSO_4$ might be caused by some specific chemical compounds of SS. SS is rich in inorganic compounds as metal ions, like Fe, K and Cu (seen in Table 1), which can also act as catalysts. Additional Cu-based catalysts might be more than necessary to reduce the reactions' activation energy. A similar observation can be found in the work by Breunig et al. [37], where the effect of varying Fe-S-catalyst loadings (0–20 wt%) on the chemical conversion was tested without significant differences in the catalytic activity becoming visible. Catalyst loading had no significant influence on the properties of the oils.

In order to understand what happens to $CuSO_4$ during HTL, a detailed characterization of the crystalline structure of solid residue was provided by XRD. As shown in Fig. 8, only the reflections of Cu (0) at 43.30°, 50.43°, 74.13°, 89.93° and 95.14° were observed after reaction in all cases. The weak reflection peaks identified in SS are most likely due to the low concentration and complex composition, while the Cu (0) reflection peaks identified from model substances are quite clear (matching the reference code 00–004-0836). These results demonstrate that the copper (II) ion is reduced to Cu (0), deposited in the solid residue. Therefore, some organic compounds must behave as a reductant to support Cu (0) formation. This can be referred from the work revealed by Najmi et al. [38]. They studied the bio-char as reductant instead of

fossil fuels, the palm shell char is highly reactive as reductant to completely convert iron oxide to metallic iron at proper conditions. The char was directly oxidized into CO and CO_2. In the present work, more likely, $CuSO_4$ was firstly converted into cuprate-compounds as transient states, and, then completely reduced to metallic copper with hydro-char formed during HTL. Furthermore, with respect to the observation of lysine, no hydro-char was generated during HTL, which strongly indicates some organic compounds to work as reductant.

Because Cu was expected to increase the resistance to deactivation caused by coke deposition [34], Cu characterization methods by ICP and XPS methods were carried out. Firstly, the distribution of Cu (wt.%) across the solid, aqueous and bio-crude phases from HTL of feedstock with $CuSO_4$ under 300 °C was assessed (Table 4). For the SS and model system, between 63.1 % and 96.8 % of Cu were deposited in the solid residue. Under these conditions, the Cu percentage in aqueous and bio-crude phases are lower than the detection limit (1 μg/ml and 0.1 %, respectively), therefore, it demonstrates that all the Cu is transferred into the solid residue.

In addition, the surface elemental compositions in the solid residue determined by XPS are shown in Fig. 9. Regarding the Cu compositions in the solid residue, it is clear to see that only around 1 % can be identified by XPS under all the conditions, which seems to be in contradiction with the results from ICP, by which 3.79 wt% and 19.84 wt% were detected in the solid residue from HTL of SS and model mixtures with $CuSO_4$, respectively. However, Fig. 8 also shows that more than 80 % of C and O are found on the surface, indicating that, most likely, the deactivation of $CuSO_4$ was caused by the coke deposition. Another reason could be the blocking of active sites by strongly adsorbed species, like *N*-containing heterocycles, which are the most common poisons by virtue of their strong adsorption on catalyst sites. Because of their basic nature, they adsorb on catalyst acidic sites [39]. In this work, according to the effects of $CuSO_4$ on HTL of model substances, $CuSO_4$ shows positive improvement on the yields and quality of bio-crude obtained from HTL of single lysine, with excellent selectivity to amides concerning the chemical composition in the bio-crudes. Copper compounds in organic chemistry appear most frequently in the form of nucleophilic organo-copper reagents, which may cause nucleophilic

Table 4
Cu content (wt.%) and recovery in the solid residue from HTL at 300 °C.

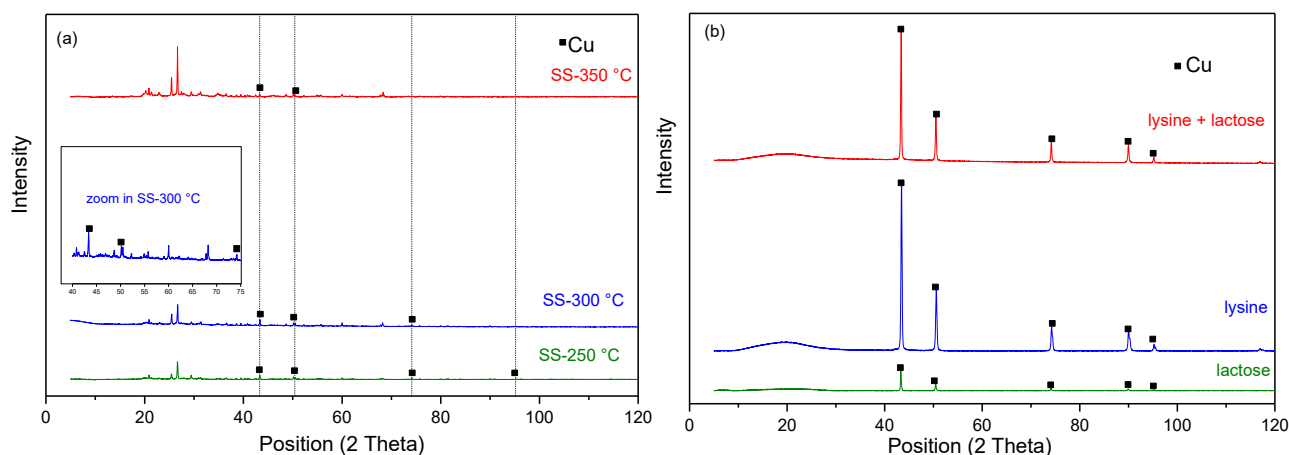| Solid residue	Cu (wt. %)	Solid residue (g)	Recovery (%)
Blank SS	0.08	1.91	96.77
SS + $CuSO_4$	3.79	1.96	88.42
Lactose + $CuSO_4$	7.67	0.58	63.11
Lysine + $CuSO_4$	92.40	0.05	92.81
Lysine + lactose + $CuSO_4$	19.84	0.31	84.54

Fig. 8. XRD patterns of solid residue derived from HTL with $CuSO_4$ (a) HTL of SS at different temperatures; (b) HTL of model mixture at 300 °C.
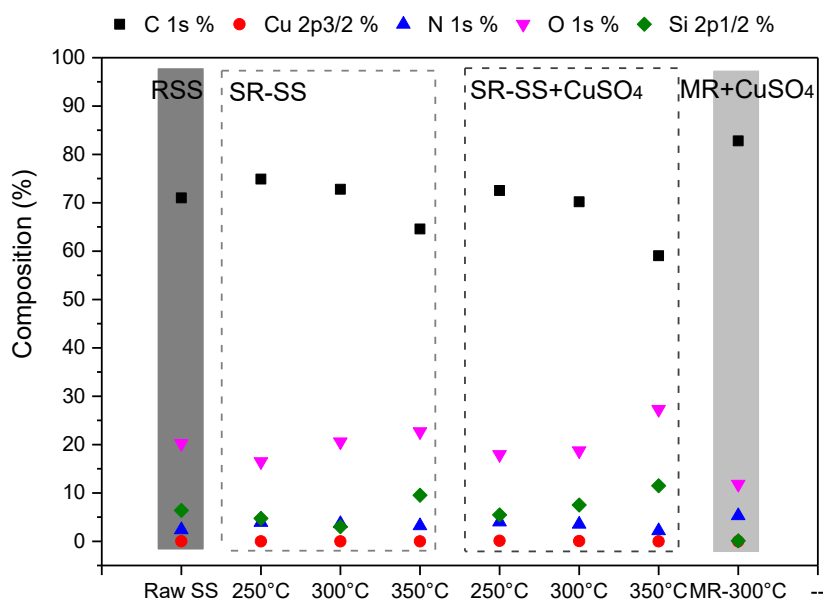
Fig. 9. Surface elemental composition (%) evaluated by XPS for original SS sample and solid residue from HTL of SS without and with CuSO$_4$, as well as model mixture with CuSO$_4$ (marked as MR).

substitution reactions, that would replace the heteroatom in heterocyclic compounds [40,41]. However, regarding the model mixtures in the presence of CuSO$_4$, only a slightly increased bio-crude yield is found; the N content does not differ from the value obtained without catalyst. A small decrease of *N*-containing compounds appears possible due to Cu deactivation caused by the accumulation of *N*-cyclic heterocycles adsorbed to its surface. This is consistent with a previous report that Cu-zeolite Y has a very strong adsorptive affinity toward *N*-containing compounds [42]. This can be attributed to the fact that N can form bonds or complexes with Cu by donating the long pair of electrons to the vacant of orbital Cu. Similar inhibitory effects of the nitrogenated compounds were observed when using the Al$_2$O$_3$ catalyst. Piperidine and pyridine strongly inhibited hydrodesulfurization pathways of 4,6-dimethyldibenzothiophene and the hydrogenation activity [43]. Thereby, it is can be concluded that Maillard reactions products are strongly adsorbed and will cause the most extensive blocking of active sites.

4. Conclusion

The obtained results show the existing challenges of catalytic liquefaction of SS. It is possible to achieve high bio-crude yields with increased HHVs at 250–350 °C. The synthetic CuNi/SiO$_2$ catalyst barely impacts the HTL conversion of SS, and is most likely rapidly deactivated by poisoning due to high S content in the SS. HCOOH increases the bio-crude yields, but without improving its quality in regard of hetero-atom content, reversely contributing to a higher *N*-heterocyclic fraction in the bio-crude. CuSO$_4$ was considered the most promising catalyst out of these three, and managed to improve the bio-crude quality by lowering the N content.

The current work has flashed light on the mechanism of catalytic effects on the fate of N during HTL of SS. Combined with a model system, the fact was revealed that the most effective catalyst in terms of bio-crude yields slightly reduce its N content. The inhibition of catalytic efficiency was not only caused by well-confirmed ash poisoning and coke deposition, but mainly by the blocking by the adsorption of recalcitrant Maillard reaction products. This may be the main reason why applied catalysts barely produce positive impacts on the reduction of N content in the bio-crude obtained from HTL of protein-enriched feedstock. However, more characterization methods should be applied to further investigate the deactivation of the catalysts.

CRediT authorship contribution statement

Yujie Fan: Conceptualization, Investigation, Writing – original draft. **Leif Meyer:** Methodology, Validation, Investigation. **Miao Gong:** Investigation, Visualization. **Bärbel Krause:** Investigation, Visualization. **Ursel Hornung:** Project administration, Supervision. **Nicolaus Dahmen:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.fuel.2022.126948.

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