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Pyrolysis of poly-L-leucine under combustion-like conditions[☆]

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Abstract

The protein poly-L-leucine has been used as a model compound for the nitrogen in biomass fuels. It was pyrolysed in a fluidised bed at 700 and 800 °C and the pyrolysis gases were analysed with a FT-IR spectrometer. HCN, NH₃ and HNCO were identified as the main nitrogen-containing species, while neither NO nor N₂O were found among the pyrolysis gases. At 700 °C, as much as 58% of the nitrogen content was converted into HCN and 31% into NH₃. The HCN/NH₃ ratio increased from about 1.9 at 700 °C to above 2.2 at 800 °C. Pyrolysis of another protein, poly-L-proline, at 800 °C gave a HCN/NH₃ ratio close to 10. This revealed that the protein's amino acid composition has a marked impact on the composition of the pyrolysate.

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Keywords: Pyrolysis; Protein; Biomass; HCN; NH₃; HNCO

1. Introduction

Wood as well as all other biomasses contains nitrogen in small amounts. The nitrogen in wood trunk is usually below 0.2 wt%. The nitrogen content in wood stems depends on distance from the centre and is higher in the sapwood than in the heartwood [1]. Bark and branches are richer in nitrogen but the concentrations are still low (below 1 wt%). Other biomass fuels have higher nitrogen contents (Table 1), but nitrogen is always a minor component on a mass basis. However, though the nitrogen content is low, it is still important since the biomass nitrogen can be transformed into the environmentally harmful nitrogen oxides under combustion. In order to develop combustion schemes aimed at reducing the formation of nitrogen oxides, it is important to know which are the primary nitrogen-containing species that are formed during the pyrolysis of the fuel.

Proteins account for most of the nitrogen in stem wood in Scots pine, about 66–87% [1,2]. The fraction of nitrogen in the form of protein decreases with time after the tree has been cut down [2]. The protein content in twigs of *Salix* was found to change with season [3] due to their biological activity. However, some proteins are structural components

of the cell walls and remain in the wood cells long after the cells biological activity has ceased [4,5]. The protein content in the stem of Red Mangrove was 1.3 wt% and another 0.04 wt% was free amino acids [6] (corresponding to about 0.2 wt% nitrogen); this nitrogen content is comparable to what is usually the total nitrogen content in wood (Table 1). Some of the nitrogen is also in the form of DNA, RNA and similar structures that are essential for all living organisms.

However, DNA also contains phosphorus and the phosphorus content in wood is low; hence only a small fraction of the nitrogen will be in the form of DNA. The molar quotient N/P ranges between 3.5 and 4 for DNA and RNA, whereas the N/P quotient is about 12–60 for wood trunk, 8–32 for wood bark and 9–30 for wood leaves/needles [7]. If all phosphorus is bound in DNA, then as much as 32% of the nitrogen in Hemlock wood is in the form of DNA, as is about 6% of the nitrogen in red maple wood. However, not all phosphorus is bound in DNA. Some of it is in, for example, ribulose-1,5-bisphosphate (in the chloroplast), essential for living biomass. DNA has amine and pyrrole as well as pyridine nitrogen functionalities. Other heterocyclic nitrogen-containing molecules found in biomass are chlorophyll (found in leaves and needles) and alkaloids [8]. Almost all of the nitrogen in needles from slash pine is in the form of proteins, while free amino acids

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Table 1
Nitrogen contents in various biomasses

Biofuel	N (wt%, daf)	Reference
Wood trunk	0.05–0.2	[1,2,7,22,23]
Wood bark	0.16–0.54	[7,10,17]
Wood leaf/needle	0.97–2.01	[7]
Olive stone	0.3	[36]
Bagasse	0.31	[19]
Straw	0.67	[37]
Brazil nut shell	0.7	[38]
Safflower seed	3.10	[29]
Rapeseed	3.91	[39]

and chlorophyll contribute only minor fractions of the total nitrogen [9].

From an X-ray photoelectron spectroscopic (XPS) study of the nitrogen functionality in bark of birch and fir, as well as for peat and coal, it was concluded that all nitrogen was in the form of pyrrolic structures (Fig. 1) in bark and that no nitrogen was in the form of pyridinic structures or amino acids [10]. However, XPS measurements cannot distinguish pyrrolic nitrogen from protein nitrogen [11], since amide nitrogen has the same electron binding energies as pyrrolic nitrogen, 400.2 eV. Furthermore, the amine ends of amino acids are protonated at room temperature (at which the XPS measurements were made). In the protonated state the amino acids electron binding energies are increased to about 401.4 eV [12]. The aromatic amine 5-amino-salicylic acid has an electron binding energy of 401.4 eV [13]. This value is usually considered to be representative of what is called ‘quaternary nitrogen’ (which is believed to be pyridinic nitrogen that has been protonated, oxidised or otherwise subjected to electron withdrawal).

Thus, one can conclude that it is not possible by means of XPS investigations to distinguish between quaternary

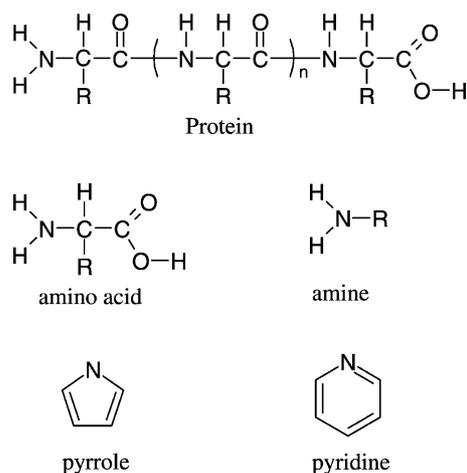


Fig. 1. The structures of proteins, amino acids, amines, pyrrole and pyridine. The letter R denotes side groups. These can be non-polar, as in poly-L-leucine (R = 2-methylpropyl), or reactive (with hydroxy, acidic or amino functionalities).

nitrogen, amino acids and amine nitrogen. Many studies regarding the nitrogen functionalities of peat [10] and coal [10,13–15] have found the ‘quaternary’ peak. In peat, amino acids are known to be present [6], and X-ray absorption near-edge spectroscopy (XANES) measurements [16] have identified amines as important nitrogen sources in coals. Furthermore, if the quaternary peak corresponds to amine nitrogen, several features of the pyrolysis process can be explained. For example, the quaternary nitrogen in coal (accounting for 20% of the fuel nitrogen) could not be found in the pyrolysis tars, neither at 600 nor at 900 °C [14]. This is surprising if the quaternary nitrogen is in the suggested heterocyclic aromatic forms, but logical if the quaternary peak corresponds to amines or amino acids. Furthermore, at 600 °C, the light gases ammonia, HCN and HNCO are formed. By contrast, heterocyclic aromatic nitrogen species does not decompose at this low temperature. Kambara et al. [13] found a positive correlation between the conversion of the ‘quaternary’ peak and the formation of ammonia from coal. The ‘quaternary’ nitrogen was less thermally stable than the pyrrole and pyridine. These facts indicate that quaternary nitrogen in coal should be amines. Hence, the XPS findings regarding nitrogen functionalities in wood barks and peat do not contradict the inference that the nitrogen in wood is mainly in the form of protein and that free amino acids are present in peat.

In biomass pyrolysis studies, both HCN and NH_3 are usually found. In some studies, more ammonia than HCN is found [10,17] and in some the opposite is true [18,19]. (One should note that the ammonia usually is analysed with acidic titration [10,17–19]. Under these conditions HNCO is transformed into NH_3 . The analysed ammonia yield is then the total yield of NH_3 and HNCO [20].) It is usually suggested that amino acids and protein should produce ammonia upon pyrolysis. The fact that HCN is formed from biomass was taken as evidence that nitrogen in biomass could not be in protein or amino acids, but rather in heterocyclic aromatic structures. However, alkylcyanides are formed as direct pyrolysis products from amino acids, while ammonia is formed from bimolecular reactions of primary pyrolysis products [21]. Thus, both ammonia and cyanides are formed from pyrolysis of amino acids. This work was aimed at proving that HCN as well as NH_3 are pyrolysis products from protein, and that proteins are the most suitable model compounds for biomass nitrogen.

2. Experimental

The pyrolysis experiments were performed in a fluidised bed (Fig. 2). The reactor is made of quartz glass to minimise the catalytic reactivity of the walls. The reactor has an inner diameter of 35 mm and it was filled with sand having sizes of 200–300 μm . The bed height was approximately 50 mm. Nitrogen is introduced in the bottom of the reactor, and is preheated before it

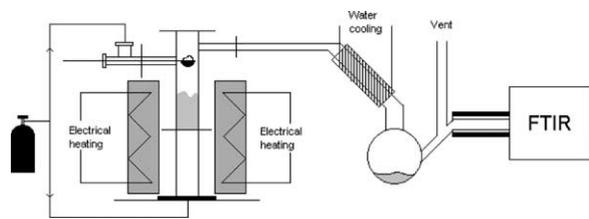


Fig. 2. The experimental set-up.

enters the fluidised bed through a quartz glass frit on which the sand bed rests. The preheating zone and the bed are electrically heated. The temperature in the bed is used to control the heating elements. The high heating rates of the reactor and the small size of the protein samples make the temperatures in the solid protein very close to the reactor temperature shortly after introduction to the reactor.

Powder of the protein poly-L-leucine is introduced from the top of the reactor by a spoon that moves horizontally through the reactor's fuel feed tube. To prevent oxygen from entering the reactor through the hole through which the spoon is running, an extra nitrogen flow is introduced into the fuel-feeding tube. This flow is also needed to dilute the pyrolysate from the reactor, since a very small carrier gas flow is used to prevent the fine protein powder from being carried away by the gas. The gas residence time in the hot reactor is approximately 2 s.

A high-performance FT-IR spectrometer (BIO-RAD, FTS 60A) was used for gas analyses. The spectrometer is combined with a long-path, low-volume gas cell (Foxboro LV7, with a cell volume of 223 cm³ and an optical path length of 7.25 m). The instrument is equipped with a MCT detector and the maximum resolution is 0.5 cm⁻¹. Spectra were obtained for wave numbers between 700 and 4000 cm⁻¹. The gas cell was heated to 120 °C.

A water-cooled tar trap of quartz glass was placed between the reactor and the FT-IR instrument. By lowering the gas temperature in the tar trap to well below the temperature in the gas cell, tars (if any in the pyrolysate) were prevented from condensing on the walls and mirrors of the gas cell and thereby blocking the IR beam. The interior of the tar trap was free from water. A teflon tube connected the tar trap with the FT-IR. The teflon tube was heated in order to avoid ammonia absorbing on the walls of the teflon tube, which it tends to do in non-heated teflon tubes. A filter prevented sand from the bed, as well as soot and unreacted sample that may follow the gases, from entering the FT-IR.

The protein used in the experiments was poly-L-leucine, delivered by Sigma–Aldrich Inc. The polymer length was claimed to be 1142 monomer units based on viscosity measurements. The protein was free from moisture and had a nitrogen content of 12.4 wt%. Complementary experiments were made with the protein poly-L-proline. This protein had a polymer length of about 150 monomer units and a water content of 3.3 wt%.

3. Results and discussion

The pyrolysis gases were continuously analysed by the FT-IR and a new spectrum was taken approximately every 2 s. It took around 1 min until the flow of pyrolysis products to the spectrometer ceased. FT-IR spectra enable identification of numerous species in the product gases. In the range

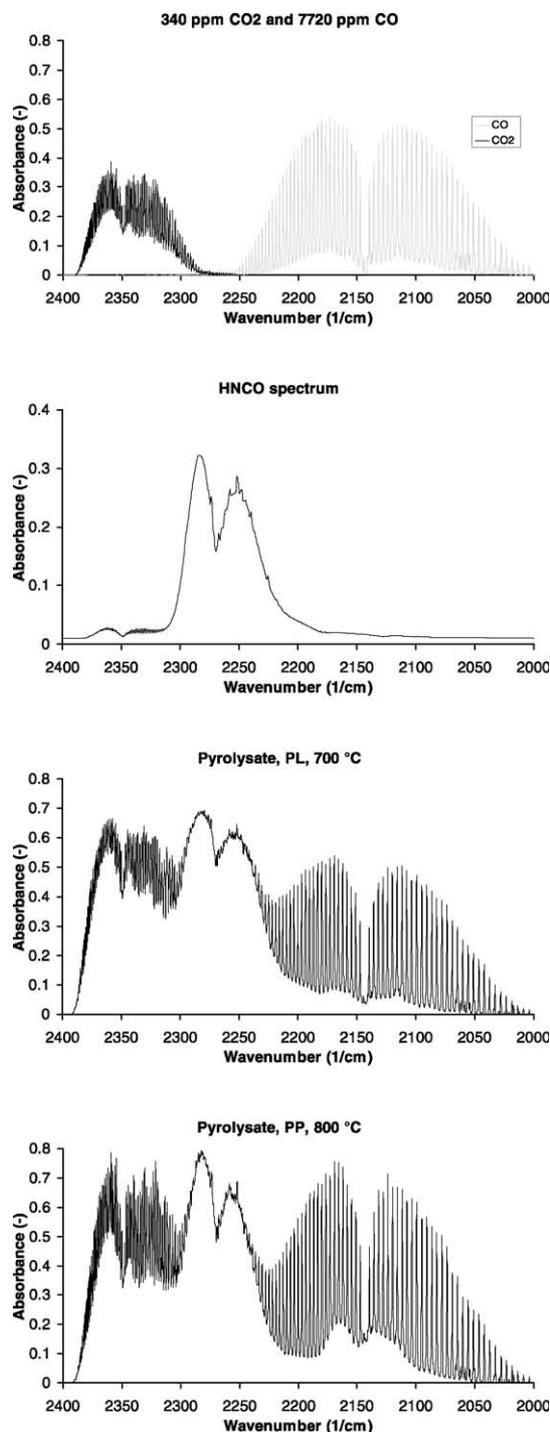


Fig. 3. From top: calibration spectra of CO and CO₂ and of HNCO (from another FT-IR spectrometer). Spectra of pyrolysate from poly-L-leucine (PL) at 700 °C and from poly-L-proline (PP) at 800 °C.

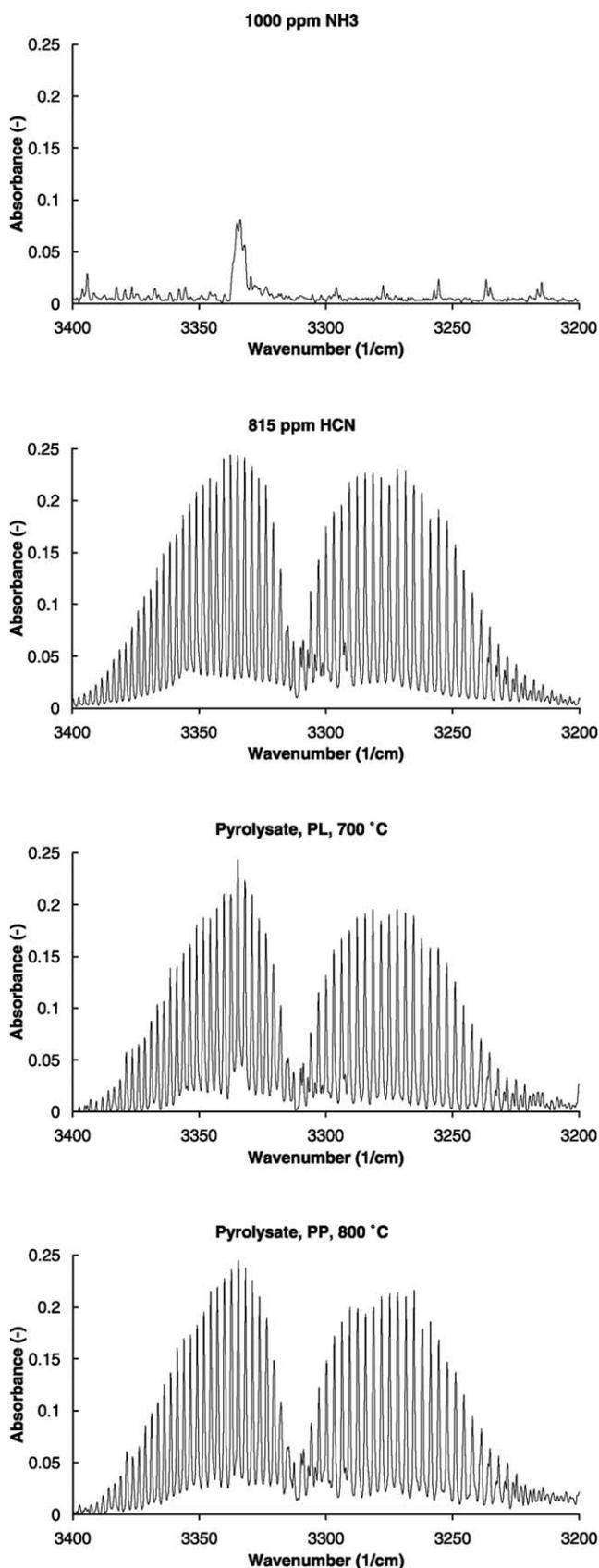


Fig. 4. From top: calibration spectra of NH_3 (1000 ppm) and of HCN (815 ppm). Spectra of pyrolysate from poly-L-leucine (PL) at 700 °C and from poly-L-proline (PP) at 800 °C.

2000–2400 cm^{-1} the gases CO, HCNCO and CO_2 are found (Fig. 3). These three gases were positively identified in all spectra from the pyrolysis of poly-L-leucine. The spectra overlap slightly, but there are regions where no interference takes place as long as the concentrations of CO_2 and CO are not very much higher than the HCNCO concentration. Unfortunately, no quantification of HCNCO was possible, due to lack of calibration gas for this species. Identification of HCNCO was made by comparing the spectra with a HCNCO spectrum from another instrument (Fig. 3).

The existence of ammonia in the product gas was seen from the high absorbance at the peaks 930 and 966 cm^{-1} , typical for ammonia. Neither N_2O nor NO could be found and it was confirmed that NO_2 is not a main nitrogen-containing species. HCN was identified through the peaks at and around 712, 2805.5 cm^{-1} and in the range 3220–3390 cm^{-1} (Fig. 4).

During the experiments, powder was usually blown off from the insertion spoon and thereby lost in the fuel feed tube when large amounts of fuel were used. This makes it impossible to close the elemental balances in some of the experiments. The total nitrogen recovery as NH_3 and HCN ranges between 60 and 89%. The highest value was achieved in the experiments with the lowest fuel load. However, the quotient between concentrations of HCN and NH_3 is constant for all experiments at a given temperature. Hence, the difference in gas recovery is most likely due to loss of solid fuel in these experiments. For the experiment with the highest nitrogen recovery, the elemental balances are presented in Table 2. The quotient HCN/ NH_3 was approximately 1.9 at 700 °C and slightly higher than 2.2 at 800 °C (Table 3).

The concentrations of CO_2 were unexpectedly high (5.2% of fuel carbon), since only the carboxylic acid at the carbon end of the polymer is expected to form CO_2 (through decarboxylation [21]). Everywhere else in the polymer chain, the oxygen groups are well separated. With a length of 1142 monomer units per protein, only 0.015% of the carbon is available to form CO_2 as a primary product. Most of the analysed CO_2 must thus originate from secondary reactions. The CO concentrations were also high. The total amount of oxygen in the analysed CO and CO_2 is about twice the amount of oxygen in the fuel. Consequently,

Table 2
Elemental balances for pyrolysis experiment on poly-L-leucine at 700 °C

Gas	N (%)	H (%)	C (%)	O (%)
HCN	58.2	5.3	9.7	–
NH_3	30.8	8.4	–	–
CO	–	–	26	156
CO_2	–	–	5.2	62
H_2O	–	12.3	–	68
CH_4	–	42.9	19.6	–
C_2H_4	–	17.2	15.8	–
Total	89	86.1	76.3	286

Table 3
Ratio between HCN and NH₃ yields

	Protein		
	Poly-L-leucine	Poly-L-leucine	Poly-L-proline
Temperature (°C)	700	800	800
HCN/NH ₃	1.7	2.2	9.5

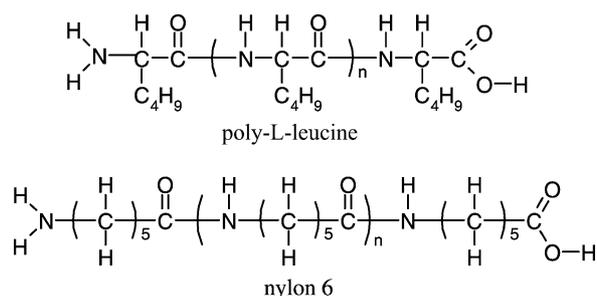


Fig. 5. The structures of poly-L-leucine and nylon 6.

oxygen must have leaked into the reactor from the surrounding air. The carbon and hydrogen in the analysed gases accounted for 76.3 and 86.1% recovery, respectively, in the experiment with the highest nitrogen recovery (Table 2).

Based on the elemental balances, a hydrocarbon containing the rest of the hydrogen and carbon would have the empirical formula (CH_{1.08})_x. Assuming that the remaining 11% of the nitrogen is HNCO alters the empirical formula marginally.

To investigate whether the HCN and NH₃ yields depend on the protein's amino acid composition, poly-L-proline was

used for comparison. This protein was in the form of a sphere with a diameter of about 3 mm. The heating was, therefore, not as instantaneous as for poly-L-leucine. It was pyrolysed at 800 °C. HNCO was identified (Fig. 3) as were HCN (Fig. 4) and NH₃ as main pyrolysis products. The HCN/NH₃ ration was approximately 9.5.

None of the two proteins used in this study produced any char. For biomass, nitrogen is always found in the char. Studies of pyrolysis of alder wood [22], birch and spruce wood [23], and wood bark [17,18] revealed that nitrogen was released more slowly [22] and to a lesser extent than the overall conversion of the biomass during pyrolysis [17,22, 23]. This was used as an indication that the nitrogen should be in stable heterocyclic aromatic structures [17,22]. However, during pyrolysis of fir bark, nitrogen was released faster than carbon [18]. A comparison between TGA experiments, with a heating rate of 10 K/min, on oak wood [24] and simple amino acids [25] reveals that amino acids with non-polar side chains decompose to a higher extent than wood (except glycine), but that amino acids with reactive side chains and glycine give char yields comparable to or higher than wood. TGA experiments by our group on poly-L-leucine, poly-L-glycine and poly-L-proline, all of which have non-reactive side chains, revealed that poly-L-glycine produces more char than wood, while the other two proteins did not produce any char, as in this study.

Proteins that do not cross-bond will decompose through depolymerisation (Fig. 6) under mild pyrolysis conditions [26], as does the related polyamide–nylon 6 [27]. The pyrolysis products from these reactions are heterocyclic: 2,5-diketopiperazine (DKP) from protein and ε-caprolactam from nylon 6 (Fig. 6). For nylon 6, it is also suggested that at elevated temperatures, ε-caprolactam can be produced from

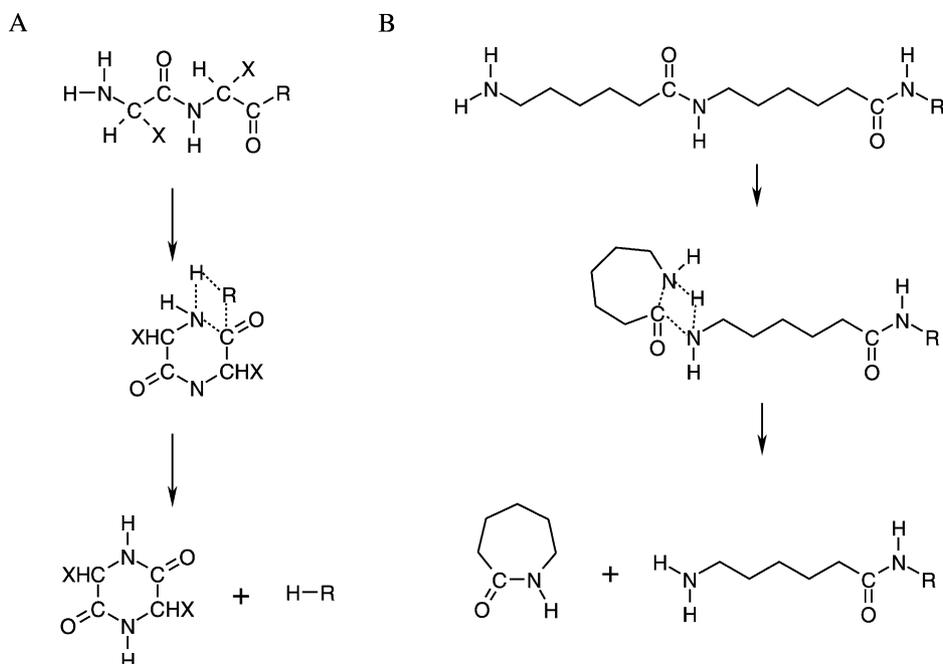


Fig. 6. Reaction mechanisms under mild pyrolysis conditions for (a) peptides and (b) nylon 6.

within the polymer chain [27]. Through this second reaction pathway, ϵ -caprolactam can also be formed from nylon 6,6 [28]. Due to the similarities in structure between nylon 6 and proteins (Fig. 5), it is likely that proteins can decompose through this second pathway as well. Both of the suggested pyrolysis pathways are effectively prevented if the side groups cross-bond. A protein that contains even small amounts of amino acids with reactive side chains will be prevented from depolymerising to any larger extent, thus producing higher char yields. About half of the amino acids in the proteins found in wood [1,2,4,5] have reactive side chains. Hence, accumulation of nitrogen in the char from biomass does not contradict the inference that protein is the main nitrogen-containing species. Indeed, mild pyrolysis of safflower seed—a biomass with a high protein content—led to accumulation of nitrogen in the char [29]. All or almost

all of the nitrogen in the safflower seed came from protein [29].

As mentioned above, the polymer nylon 6,6 resembles poly-L-leucine in many respects. The two polymers have the same elemental composition, and both polymers have their monomer units connected through amide bonds. Nylon 6,6 pyrolysed at 800 and 1000 °C, producing HCN, NH₃ and HNCO, but no NO, NO₂ or N₂O [30].

When analysing the pyrolysis gases from coal with an FT-IR spectrometer, HNCO was found to be an important nitrogen-containing product [31]. Secondary pyrolysis of the tars produced at 600 °C at higher temperatures [20] showed that HNCO was formed at the lowest temperature, followed by ammonia and hydrogen cyanide at higher temperatures. The HCN yield continuously increases with temperature, while the yields of ammonia and HNCO go

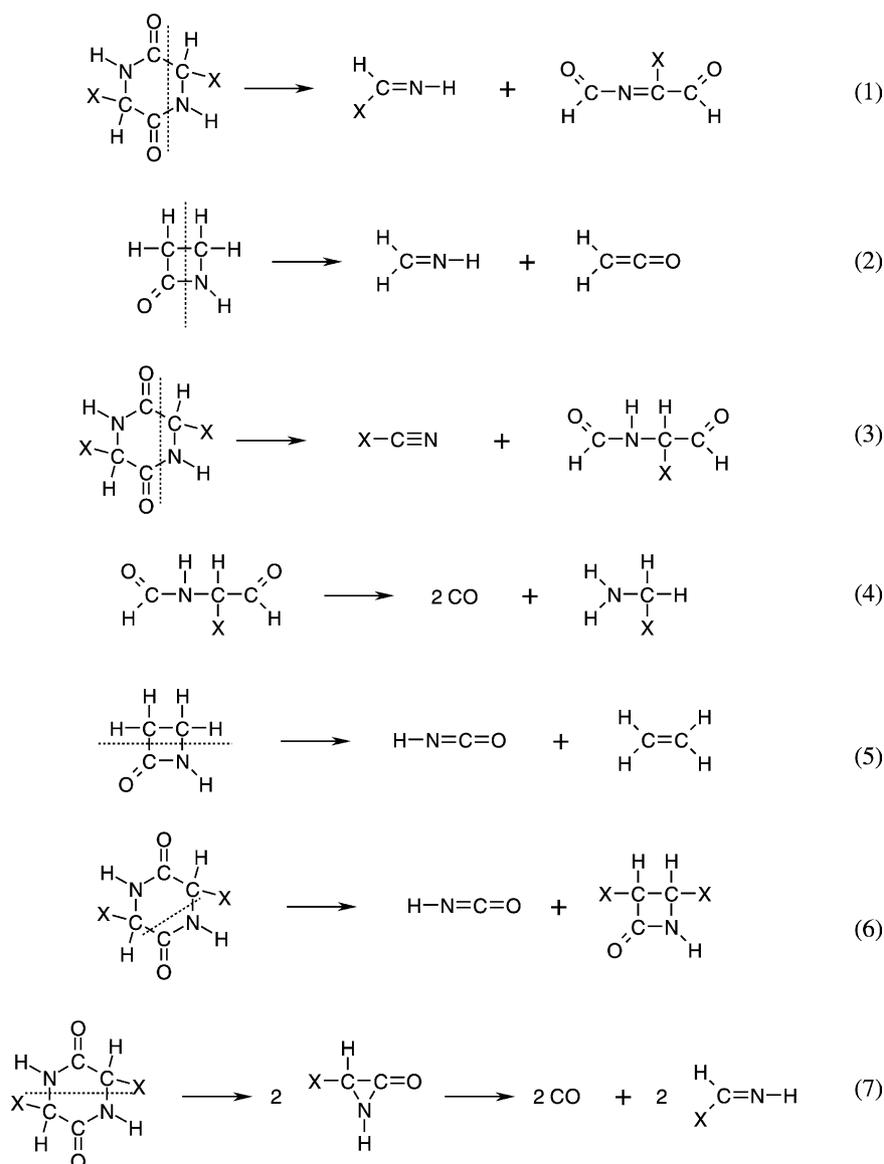


Fig. 7. Pyrolytic reactions for DKP and 2-azetidinone.

through maxima. The tar cracking seems to proceed through competing reactions where HNCO formation is favoured at low temperatures and HCN formation is favoured at high temperatures. Ledesma et al. [20] speculated that the nature of the HNCO forming tar from coal was that of pyridone or possibly pyrroline-type structures. The presence of pyridone in various coals has been verified by XANES measurements [16]. The only model compound tar found in the literature that produces both HNCO and HCN is 2-azetidinone [32]. At low temperatures it produces HNCO. At higher temperatures, both HNCO and HCN are formed.

The light gases found in this study can be formed through direct pyrolysis of the protein chain, but are probably formed mainly through cracking of primary tar products. Tar components from proteins, nylon 6 and nylon 6,6 are DKP [26] and ϵ -caprolactam [27,28]. These tars have similarities with 2-azetidinone and with pyridone in that they are all cyclic amides. Therefore, they can be expected to have similar decomposition modes. DKP is a cyclic dipeptide and is named after its amino acid composition. The DKP formed from poly-L-proline is called Pro-Pro DKP and the DKP formed from poly-L-leucine is called Leu-Leu DKP [26]. Pyrolysis of DKP has been suggested [33] to produce imine (reaction 1 in Fig. 7). This reaction is analogous with the formation of imine from 2-azetidinone [32] (reaction 2 in Fig. 7). Imine readily decomposes to cyanide and hydrogen gas, but it can also react with primary amines to give ammonia [33]. We suggest that the formation of primary amines is governed by the decomposition of DKP into cyanide and amide (reaction 3 in Fig. 7), where the amide produces amine by loss of carbon monoxide (reaction 4 in Fig. 7). The formation of HNCO can proceed through decomposition of DKP, reaction 6 in Fig. 7, which is analogous with the HNCO-forming reaction for 2-azetidinone (reaction 5 in Fig. 7). Ammonia is formed through bimolecular reactions between imine and amine [33] or through decomposition of primary amines. At high temperatures it can also be formed from HNCO through its reactions with water or hydrogen gas. Imines can also be formed through reaction 7 in Fig. 7 [33]. In reactions 1 and 3 the hydrogen atom on one of the nitrogen atoms is transferred to an adjacent carbon atom. DKP deriving from imino acids (proline and hydroxyproline) differ from DKP from amino acids in that the nitrogen atoms do not bond to hydrogen atoms. Consequently, Pro-Pro DKP cannot decompose through reactions 1 or 3, and since reaction 4 involves the amide formed in reaction 3, no primary amines can be formed through reaction 4 for Pro-Pro DKP. Formation of ammonia from Pro-Pro DKP is therefore suppressed. Reaction 6 is possible, providing a route for HNCO and pyrroline formation. Reaction 7 is not possible, but it has been suggested [34] that a similar reaction can proceed through breakage of the amide bonds. This reaction would produce two pyrroline molecules from Pro-Pro DKP. Pyrroline can be cracked into an imine or a cyanide. It can also be transformed into pyrrole by loss of

a hydrogen molecule. The pyrrole nitrogen is almost entirely converted into hydrogen cyanide [35], but at 800 °C this reaction is slow. Thus, the main pyrolytic reaction routes for poly-L-proline are the ones yielding HCN and HNCO, whereas poly-L-leucine and other proteins that do not contain imino acids have additional reaction routes, one of which leads to the formation of ammonia.

The findings regarding the temperature dependence of the HCN/NH₃ ratio for poly-L-leucine pyrolysis are the same as previously found for nylon 6,6 and coal. From nylon 6,6 as well as from our study, HNCO could be found but not quantified. For 2-azetidinone and coal tars, HNCO is formed at low temperatures, while HCN formation competes with HNCO formation at higher temperatures, we expect proteins to have the same temperature dependence on the selectivity between formation of HNCO and HCN.

4. Conclusions

Most of the nitrogen in biomass comes from proteins. The main pyrolysis gases from protein at high temperatures are HCN, NH₃ and HNCO. The product yields depend on temperature and also on the protein's amino acid composition. For poly-L-leucine, the HCN/NH₃ ratio is increased from 1.9 at 700 °C to 2.2 at 800 °C. For poly-L-proline pyrolysed at 800 °C, the HCN/NH₃ ratio is 9.5. Proteins that have no reactive side chains are completely volatilised at the temperatures used in this study. For proteins with reactive side chains, char formation competes with devolatilisation. Since the amino acid composition is of importance for the pyrolysis of proteins, with regard both to how much nitrogen is retained in the char and to which light gases are formed, one should use proteins with an amino acid composition that resembles the composition found in the biomass of interest, when making model compound studies.

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