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Nitrogen products and reaction pathway of nitrogen compounds during the pyrolysis of various organic wastes

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The nitrogen compounds in tars were investigated at temperature of 500 °C during the pyrolysis of three organic wastes (sewage sludge, food waste, wood) and their mixture, representatives of a common municipal waste. The analyses of both gaseous and condensed tars related the formation of up to respectively 14 and 72 nitrogen compounds, with widely forms of compounds. In gases, light nitriles (acetonitrile, propanenitrile) seemed to be the main products whereas, in condensed tars, several chemical families were represented: long chain nitriles and amides, pyrrolic and pyrrolidinic compounds and diketopiperazines (DKPs). Moreover, several compounds, rarely previously detected, were observed, such as oximes. All those nitrogen compounds probably originated from proteins but also from fatty acids and sugars. The nature of those compounds was found to be only slightly influenced when wastes have similar nitrogen functionalities contents, such as food waste and sewage sludge. That would suggest that reaction pathways for nitrogen compounds are similar for such wastes. For wood, its low nitrogen content hindered the detection of nitrogen products, which could be also due to a different reaction pathway for nitrogen. The mixture of those wastes had only slightly effects on nitrogen products and thus on the reaction pathway. Using nitrogen products, this paper was concluded with a possible reaction pathway for the nitrogen of sewage sludge and food waste during pyrolysis.

1. Introduction

Pyrolysis is a thermochemical decomposition of organic materials without oxidant. It can happen in the case of an incomplete combustion, for example during incineration of wastes. It can also be directly used as a thermal treatment to transform materials into valuable products, i.e., gases, tars and chars. Thus, pyrolysis is a promising way to energetically valorize organic wastes. Many studies were carried out in order to investigate the products of pyrolysis. Various organic wastes were used: cereal cakes [1–3], castor seeds [4], tobacco [5,6], soybean protein [7], polyamides [8], animal bones [9], fermented tea [10], lake sediments [11], dissolved organic matter (DOM) [12], tanning wastes [13], mycelial waste [14], etc. However, majority of the previous studies were dedicated to sewage sludge pyrolysis [14–23]. The aims of the studies on pyrolysis products can be the production of bio-oils or chemicals [1–5,15,17–20], the production of nitrogen chemicals [21,22], the characterization of the by-products from activated carbon pro-

duction [9], the characterization of the original pyrolyzed products [10–12] or the optimization of the energetic process [13].

Several researches also investigate pyrolysis products in order to evaluate the environmental impact of pyrolysis. In fact, the transformations of materials during pyrolysis produce many pollutants, such as sulfurous compounds, heavy metals, dioxins, furans, nitrogen compounds, etc. Nitrogen compounds are particularly monitored since they can lead, by combustion, to the formation of nitrogen oxides (NO_x) and then, in the atmosphere, to the formation of ozone and acid rains.

Therefore, the understanding of reaction pathways is helpful to limit the formation of these pollutants. In order to determine reaction pathways, it is crucial to understand the sources of nitrogen pollutants. The presence of nitrogen in the wastes (fuel-N) contributes to pollutants production. In organic wastes, nitrogen is mainly included in proteins [7,24]. During pyrolysis, these proteins undergo successive transformations which lead to many nitrogen species. To the understanding of these transformations, these species are analyzed [14,16]. They can be contained in gaseous phase, in condensable (tar-N compounds) or in chars. The main products are the lightest gaseous nitrogen compounds, i.e. ammonia (NH₃) and hydrogen cyanide (HCN) [7,14,16,23–27]. Isocyanic acid (HNCO) and nitrogen (N₂) can also be among the main prod-

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ucts [14,23–26]. Many others nitrogen-containing compounds are formed and are classified among tar-N compounds [6,7,14,16,23].

The distribution of nitrogen between char, tars and gaseous products varies between the studies. This can be explained by the differences in operating conditions, in the characteristics of the waste or in the type of nitrogen-containing compounds in the waste [14]. Because they are the main products, the distribution of fuel-N into HCN and NH₃ were mainly focused. Some studies showed a preponderance of HCN [23,27] whereas others showed a higher production of NH₃ [28]. As instance, Chen et al. showed that HCN is predominant with a fast pyrolysis and increases with temperature, especially for sewage sludge [14]. Trends for NH₃ were less pronounced but it also tended to increase with temperature, and then to fall for temperatures higher than 700–800 °C. NH₃ was predominant during the slow pyrolysis of mycelial waste from antibiotic production [14].

Even if NH₃ and HCN are the main products, the analysis of tar-N compounds is necessary to understand reaction pathways since tar-N compounds often constitute reaction intermediates. Moreover, tar-N compounds constitute a large part of the nitrogen-containing products. As instance, Fullana et al. showed that conversion of sewage sludge nitrogen into tar-N can reach 75% [16]. These compounds are often classified in three classes: (i) amines, (ii) heterocyclic compounds and (iii) nitriles [7]. They are numerous and often differ across studies. Some studies used these compounds to propose a reaction pathway for the transformation of nitrogen during pyrolysis [7,16,29]. For example, Tian et al. proposed a reaction pathway for sewage sludge-N until the formation of final products HCN and NH₃ [29]. This pathway involves various temperature-dependent stages and key intermediates such as nitriles and heterocyclic compounds.

However, further works are needed in order to improve this reaction pathway. Particularly, the majority of studies on nitrogen products and reaction pathway are carried out with sewage sludge. It would be interesting to compare results from various organic wastes and to determine the influence of the waste nature on the nitrogen products formation and the reaction pathway. Moreover, pyrolysis reactors and incinerators are often fed with municipal wastes which are composed in a large part of sludge, food waste, wood and paper. To our knowledge, the pyrolysis of food waste was never studied until now. Further investigations are then needed to study the pyrolysis of municipal wastes and particularly food waste.

Thus, this study aims to compare the pyrolysis nitrogen products and nitrogen reaction pathways of three different organic wastes and of their mixture, characteristic of a common municipal waste: (i) a nitrogen-poor waste, wood, (ii) a nitrogen-rich waste, intensively studied, sewage sludge, and (iii) a nitrogen-rich waste, never studied, food waste.

For this purpose, an experimental set-up was developed, composed of a tubular reactor, a sampling device and an analytic system. The analytical method was especially optimized in order to maximize the number of identified reaction intermediates. In fact, a lot of compounds have already been identified in previous studies. However, each study gives different compounds, which do not show a repeated trend. Moreover, they are often analyzed into the condensed phase while they are also presents in the gas phase [15]. This work aimed to identify as much as possible tar-N compounds by analyzing both gaseous and condensed tars.

2. Experimental methods

2.1. Wastes

Experiments were carried out by using organic wastes characteristic of a common municipal waste, supplied in batch, consisting

of (i) wood (paper and cardboard are not included but their compositions are similar to wood), (ii) sewage sludge and (iii) food waste. The wood was a common softwood (from gymnosperm trees) used in the construction of pallets for loading and transportation of food that, after its work-cycle life, has been chipped in particles of an average size of 3 cm in diameter and stored indoors. The sewage sludge and the food waste came from cruise ships. To avoid any influence on the process of pyrolysis, the size of the particles was optimized at an average equivalent diameter of 4 mm for the wood and even much smaller for the sewage sludge and the food waste, that looked like a homogeneous powder [30–32]. Moreover, before the beginning of the experiments, wastes were pretreated by drying at 120 °C during at least 10 h. Thus, water initially composing wastes was not taken into account in the mass balance and did not reacted during the pyrolysis process.

Table 1 summarizes the main characteristics of the wastes: (i) moisture was measured using an iodine solution by a Karl Fisher apparatus; (ii) ashes compositions were evaluated in terms of residual mass after combustion of the sample at 550 °C; (iii) the elemental composition was determined by a Thermo Finnigan AE1112 Series Flash elemental analyzer (C, H, N, S fractions by measure and oxygen were obtained by mass difference). Incertitudes on weight percentages are calculated on the average of several samples analysis. The advantage offered by the three wastes consisted of a very similar ultimate composition in terms of carbon and hydrogen amounts and in a large difference in the content of nitrogen between wood and the two others wastes. The mixture of the three wastes was prepared with a wood/sewage sludge/food waste fraction of 0.5/0.25/0.25, respectively.

2.2. Pyrolysis reactor

The experimental set-up is shown in Fig. 1, it mainly consists of a reactor, a sampling apparatus and an analytical system.

The reactor was a stainless-steel tube of 1.5 m length and 4 cm diameter, surrounded by three heating elements made of insulated resistances on 70 cm length. Before experiments, 5 g of waste were placed in the middle of the reactor into a crucible. The reactor was heated at 20 °C.min⁻¹ until 500 °C, while swept by argon as a carrier gas with the constant flow rate of 0.5 L min⁻¹ to purge out air. While heated, wastes were transformed into char, tars and gas. Samples were kept at 500 °C till incondensable gases were no more detected at the output of the reactor.

At the output of reactor, tars and gas were sent to a sampling apparatus consisting of: (i) a 2 L flask, to sample gaseous atmosphere dedicated to an analysis by a gas chromatograph connected to a mass spectrometer (GC/MS), (ii) a trap which consisted in three bubblers at ambient temperature (20 °C) filled with 200 mL of acetone to absorb tars, dedicated to an elemental analysis and to an analysis by GC/MS, (iii) a M&C Portable gas conditioning CSS-M system, which pumped a fraction of the gas with at a flow rate of 200 mL min⁻¹, cooled it at 5 °C and filtered it, (iv) a micro GC, connected to the pump outlet, which analyzed major components constituting the gas phase, cleared of its tars.

2.3. Analytical procedure

Several analytical methods were developed to determine the nature of pyrolysis products. The elemental composition of chars was determined by the same elemental analyzer than for wastes. Gas in the 2 L flask was immediately sampled by a 50 µL gas syringe and injected into a PerkinElmer GC/MS in order to identify nitrogen compounds. Tars were recovered in the tar trap filled with acetone and by washing the tubing and the air sampling flask with acetone. Acetone and water, part of the condensable pyrolysis products, were then evaporated at ambient temperature (20 °C) during

Table 1
Ultimate composition of wastes and moisture.

Weight %	Dry basis						Moisture
	N	C	H	O	S	Ashes	
Wood	0.8 ± 0.7	50.0 ± 0.6	5.9 ± 0.1	42.9 ± 1.3	0.0	0.4 ± 0.2	10.1 ± 2.0
Sewage sludge	6.1 ± 0.5	44.6 ± 1.3	5.7 ± 2.0	26.7 ± 2.3	0.4 ± 0.4	16.5 ± 0.8	17.8 ± 1.7
Food waste	5.4 ± 0.4	48.8 ± 0.4	6.2 ± 0.2	24.9 ± 0.9	0.4 ± 0.4	14.3 ± 0.5	9.4 ± 1.5

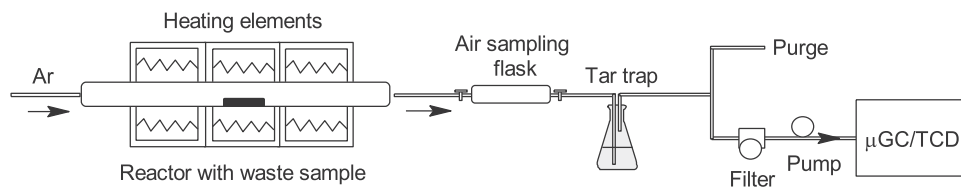


Fig. 1. Experimental set-up.

Table 2
Characteristics of the GC/MS methods used for the analysis of tars.

	Gaseous tars	Condensed tars
Manufacturer	PerkinElmer	PerkinElmer
GC model	Auto System XL	Clarius 680
Injector temperature	250 °C	275 °C
Injection mode	Split (ratio: 1/10)	Split (ratio: 1/10)
Column model	Rxi-624SilMS (Restek fused capillary column)	SPB-5MS (Supelco fused capillary column)
Stationary phase	poly 6% cyanopropyl phenyl/94% dimethyl polysiloxane	poly 5% diphenyl/95% dimethyl polysiloxane
Column dimensions	60 m, 0.32 mm i.d., 1.8 μm film	30 m, 0.25 mm i.d., 0.25 μm film
Carrier gas	Helium (constant flow: 2 mL min ⁻¹)	Helium (constant flow: 0.9 mL min ⁻¹)
Temperature program	35 °C (10 min) to 280 °C (10 min) at 10 °C min ⁻¹	45 °C (1 min) to 330 °C (10 min) at 5 °C min ⁻¹
MS model	Turbo Mass Gold	Clarius 600 S
MS acquisition	Full scan under electron ionization (70 eV) at 3 scan s ⁻¹ in the 10–300 m/z range	Full scan under electron ionization (70 eV) at 3 scan s ⁻¹ in the 20–500 m/z range

Table 3
Micro-GC parameters for the analysis of incondensables.

	First module	Second module
Injector temperature	90 °C	90 °C
Column model	MS5A (Molar sieves 5 Å, 10 m)	PPQ (PolarPlot Q, 10 m)
Carrier gas	Argon (constant pressure: 28 psi)	Helium (constant pressure: 25 psi)
Column temperature	100 °C	75 °C
Quantified gas	H ₂ , O ₂ , N ₂ , CH ₄ , CO	CO ₂ , C ₂ H ₂ +C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₁₀

at least 24 h until stabilization of product mass. This evaporation method triggers a loss of volatile compounds but the use of ambient temperature limits this loss. After the elimination of volatile fractions, the ultimate compositions of those tars were determined by the Thermo Finnigan elemental analyzer previously mentioned. After the dilution in a small volume of acetone, nitrogen compounds were identified by another GC/MS. Characteristics of both GC/MS methods are given in the Table 2.

Main incondensable gaseous products, for example carbon dioxide (CO₂) and nitrogen (N₂), were monitored with a frequency of 3 min by an Agilent Technologies 3000 A micro GC composed of two column modules. Each module was connected to a thermal conductivity detector (TCD). Detection limits for all compounds were around several ppm. GC details are given in the Table 3.

Table 4
Fractioning of wastes during pyrolysis.

Mass fraction (%)	Wood	Sewage sludge	Food waste	Mixture
Char	25.7	33.3	26.7	29.1
Condensed tars	50.9	36.5	36.3	51.3
Incondensable gases	13.0	11.7	15.0	15.4
Unknown products	10.4	18.5	22.0	4.2

An attempt to analyze HCN and NH₃ by a Fourier transformed infrared spectrometer (FTIR) was carried out. However, tar compounds including all sorts of chemicals saturated IR spectra so that interferences hindered interpretable results.

3. Results and discussion

3.1. Partitioning and major products

Table 4 shows the fractioning of the three wastes and the mixture into the different pyrolysis products: char, condensed tars and incondensable gases. Mass of char was measured at the end of experiments. Mass of condensed tars was obtained by the weighing of condensed tars after evaporation of acetone and water. Mass of gases was calculated on the basis of incondensable gases analysis. In fact, the curves of incondensable gases concentrations' temporal evolution (Fig. 2) were integrated by the least squares method in order to obtain each gas total mass. By addition of these masses, the mass of gases was obtained. Mass of unknown products is the difference between mass of initial waste and masses of char, condensed tars and incondensable gases. These results of wastes fractioning show that char represents one third of the products. Tars present

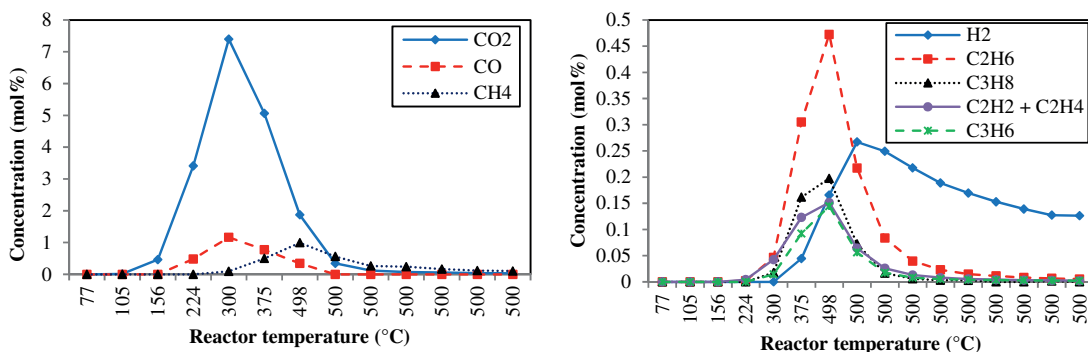


Fig. 2. Evolution of gas concentrations from the pyrolysis of food waste as a function of reactor temperature.

Table 5

Fractions of wastes transformed into gaseous products during pyrolysis (micro-GC analysis).

Mass fraction of waste (%)	Wood	Sewage sludge	Food waste	Mixture
CO ₂	7.9	9.2	11.9	11.2
CO	4.0	0.8	1.1	2.6
CH ₄	0.72	0.65	0.72	0.79
C ₂ H ₆	0.12	0.40	0.52	0.31
C ₃ H ₈	0.03	0.22	0.30	0.17
C ₂ H ₂ + C ₂ H ₄	0.09	0.18	0.17	0.14
C ₃ H ₆	0.06	0.21	0.21	0.14
H ₂	0.04	0.03	0.07	0.04

the higher fractions, particularly for wood, raising more than 50% of the initial mass. Gases represent small fractions but are relatively similar for the three wastes and the mixture. Despite the efforts to recover a maximum of products, the fraction of unknown products varies from 4% for the mixture to 22% for the food waste. These unknown products are light products that have not been trapped into acetone during experiments or that have been evaporated during the step of acetone evaporation. They probably are the water produced during pyrolysis and light tars such as volatile organic compounds (VOC). Lack of agreement between fractions of the waste alone and the mixture shows the uncertainty on tars masses, due to the partial trapping of tars.

Gaseous products concentrations were measured continuously. They are represented as a function of reactor temperature in Fig. 2 for the pyrolysis of food waste. The same trends were observed for the two other wastes and the mixture. Raising 7.5%, CO₂ is the main gaseous product. It reaches its maximum formation for a temperature of 300 °C, like carbon monoxide (CO), whereas hydrocarbons concentrations only decrease when temperature reaches 500 °C and H₂ even after several minutes at 500 °C. Those results show that, while temperature increases, oxygen atoms are firstly liberated with peaks of CO and CO₂, then carbon atoms and finally hydrogen atoms with peaks of hydrocarbons and H₂. It is in accordance with the theory of pyrolysis mechanism that substrate is firstly reduced into simple molecules, losing its oxygen and a part of its carbon and then it is aromatized, losing its hydrogen [33]. N₂ was also measured but its concentration was below its detection limit, 200 ppbv.

The fraction of each gaseous product was calculated by integrating concentration profiles as a function of time. The results are given in the Table 5. Ratio between CO₂ and CO is approximately 10 for sewage sludge and food waste whereas it is only 2 for wood. Furthermore, the majority of light hydrocarbons fractions are higher for sewage sludge and food waste than for wood. These similarities between both nitrogen-rich wastes could indicate that their thermal decompositions are similar. On the contrary, that of wood

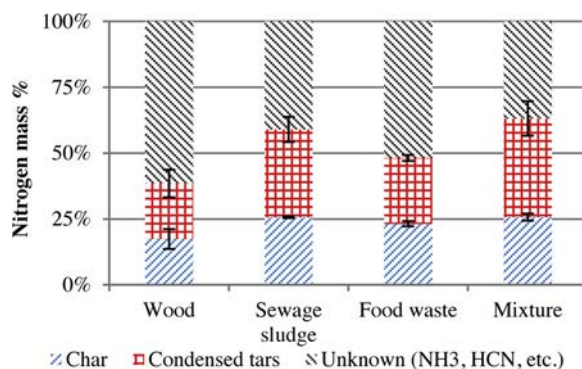


Fig. 3. Nitrogen distribution in pyrolysis products.

would differ from the other ones. Those assumptions will be asked again for the analyses of nitrogen products, Sections 3.3 and 3.4.

The maximum fraction of N₂ was also calculated, taking into account that its concentration is below 200 ppbv. It results that this nitrogen compound represents less than at least 1% of nitrogen initial quantity in wastes. Thus, it is not a major gaseous nitrogen product of pyrolysis.

In order to complete a mass balance for nitrogen, ultimate compositions of tars and chars were determined. They are given in Table 6. As already noticed for incondensables formation, while transforming into chars, wastes lost oxygen and hydrogen and gained ashes. Oxygen and hydrogen are liberated into incondensables but also into tars, as it is seen by their high levels of oxygen and hydrogen. Moreover, carbon fraction in char is higher than in initial substrate for wood but lower for sewage sludge and identical for food waste. Thus, aromaticity of wood char is more promoted than for the two other wastes. It could be due to the higher levels of ashes in sewage sludge and food waste, which would inhibit aromatization. Concerning nitrogen, a particular behavior is observed. In fact, its fraction in solid decreases only slightly and its fraction in tars is close to solid one. It could be a consequence of higher stable nitrogen functionalities in wastes.

3.2. Nitrogen distribution in pyrolysis products

From ultimate compositions of initial wastes, and of chars and tars, nitrogen distribution in pyrolysis products was calculated. Fig. 3 gives the distribution for the three wastes and the mixture. It shows that chars contain between 17% and 26% of initial nitrogen, condensed tars between 21% and 38% and unknown nitrogen forms represent 36–62%. These unknown nitrogen products are probably NH₃, HCN or other light nitrogen compounds. Indeed, NH₃ and HCN were the main nitrogen products in several previous studies on pyrolysis of wood [24–26] and sewage sludge [7,16,23,27].

Table 6
Ultimate composition of tars and chars.

Mass%	Char				Tars			
	Wood	Sewage sludge	Food waste	Mixture	Wood	Sewage sludge	Food waste	Mixture
N	0.5 ± 0.1	4.7 ± 0.1	4.6 ± 0.2	2.9 ± 0.2	0.33 ± 0.08	5.6 ± 0.8	3.7 ± 0.2	2.4 ± 0.4
C	79 ± 3	37.0 ± 0.5	48.0 ± 0.7	60 ± 9	58 ± 4	64 ± 6	69.0 ± 0.9	64 ± 5
H	2.9 ± 0.3	2.2 ± 0.1	1.9 ± 0.0	2.4 ± 0.2	8.0 ± 0.5	9.4 ± 0.7	10.0 ± 0.1	9.1 ± 0.6
O	16.0 ± 0.2	7.1 ± 0.8	5.6 ± 0.4	11.0 ± 0.6	33 ± 4	21 ± 2	17 ± 1	25.0 ± 1.3
Ashes	1.6 ± 0.5	49 ± 4	40 ± 3	24 ± 3	0	0	0	0

However, the results of these previous studies are not always in agreement regarding the distribution of the nitrogen products. Some results at high temperatures (800 °C) showed that HCN is the main nitrogen product [23,27]. Others showed that NH₃ is predominant over the entire temperature range (400–1000 °C) [14,28]. Hansson et al. observed that NH₃ is predominant at 700 °C but HCN becomes predominant at 1000 °C [24]. Several studies showed that parameters such as temperature, temperature rate, waste nature have a great influence on nitrogen distribution [7,14,28,34].

Here, the fraction of unknown products is higher for wood than for the other wastes. It probably signifies that the selectivity toward light nitrogen products is higher for wood. Moreover, tars always being among the main fractions of nitrogen products [7,14,23,27,28], it is crucial to identify them. This point will be the subject of Sections 3.3 and 3.4.

Two types of GC/MS analysis were carried out in order to identify nitrogen compounds: (i) analysis of gas and (ii) analysis of condensed tars dissolved into acetone. Chromatograms from sewage sludge pyrolysis are shown in the Fig. 4. Table 7 gives several results from those analyses. Up to 176 peaks were obtained in a single chromatograph. The number of peaks from gas was lower than the number of peaks from tars, indicating that tars analysis was more sensitive than gas analysis. Moreover, at least 69% of peaks were identified. The majority of analysis permitted to identify more than 90% and until 97% of MS area. Total MS area of nitrogen compounds was between 4 and 21%, except for wood, in which quantity of nitrogen compounds was probably too low to be detectable. These results show that the majority of nitrogen compounds present in chromatograms were identified.

3.3. Nitrogen compounds in gaseous tars

18 nitrogen compounds were identified in pyrolysis gas. They are listed in Table 8, with their area percentages and the previous studies where they were already identified in pyrolysis tars of organic substrates. The majority of identified compounds were previously identified, as noted in Table 8. Among the compounds; NH₃ was detected in the gases of sewage sludge and food waste, whereas HCN was detected in the gases of the mixture. The sensitivity of GC/MS to these compounds is low. Thus, both were probably formed from the three wastes.

Apart from NH₃ and HCN, three types of compounds were identified: (i) nitriles, (ii) heterocyclic compounds and (iii) amides. These classes of compounds were previously identified [7]. They are typical products of pyrolysis. The major products are acetonitrile and propanenitrile, which are light nitriles. These compounds were already detected during previous studies on pyrolysis. Fullana et al. also identified them [16]. Velghe et al. quantified them by analyzing tars dissolved in methanol [20]. They showed that they were not the main nitrogen products: aliphatic amides and particularly acetamide were the most abundant. In the condensable phase obtained from sewage sludge, Cao et al. also identified acetamide as one of the main nitrogen compounds, with 2,5-pyrrolidinedione [21]. We detected also acetamide but its peak area is low, compared with light nitriles ones. Differences between these results

can be explained by analytical methods. In fact, tars are generally analyzed after trapping in solvents, whereas we directly analyzed gaseous phase. Light nitriles being very volatiles and amides being moderately volatiles, light nitriles are better analyzed in gaseous form and amides in condensed form after solvent trapping. Another possibility is that proportions vary with pyrolysis temperature [7]. Peaks of heterocyclic compounds have also relatively high areas. Among them, pyrrole has the higher peak area. It was one of the most recurrent compounds in the previous studies, as can be seen by the high number of previous detections in literature in Table 8. Results thus confirm previous findings on nitrogen compounds.

Compounds identified here are also formed during pyrolysis of amino acids and proteins. For example, acetonitrile, 2-propenenitrile and pyrrole were formed during the pyrolysis of tyrosine, an amino acid [35]. Likewise, heterocyclic compounds were often detected during pyrolysis of amino acids such as glutamine, proline or asparagine [37,42]. Moreover, heterocyclic compounds can be a source of light nitriles [36]. Amino acids are known to produce by dimerization other nitrogen compounds called diketopiperazines (DKP) [25,46]. When pyrolyzing DKP, amides and then nitriles are produced [25]. Thus, reaction pathway probably involves a transformation of amino acids and proteins into heterocyclic compounds and particularly DKP and then a rupture of cycles, forming nitriles and amines. However, several other sources of these compounds are possible. For instance, acetamide would also be a typical product from the pyrolysis of microbial cell walls and chitin, and would probably form from other precursors such as thermally labile proteins and amino sugars [21].

Furthermore, nitrogen compounds formed from sewage sludge and food waste are similar and have close distributions. The nitrogen compositions of both wastes are similar. Nitrogen is probably in protein form in both wastes. On the contrary, the quantities of nitrogen compounds seem to be impacted by the nature of wastes since no nitrogen compounds were detected in gases of wood pyrolysis and since the quantities of these compounds seem to be higher for sewage sludge than for food waste. The absence of detectable nitrogen compounds from wood pyrolysis could mean: (i) that compounds which are formed during the pyrolysis of sewage sludge and food waste are under the detection limits or (ii) that produced compounds are different from the ones detected from the pyrolysis of the others wastes and are non-detectable. However, nitrogen in wood is mainly in the protein form, as in sewage sludge and food waste [25]. Hence, nitrogen products of wood should be the same than other wastes. Thus, reaction pathways are close for wastes having similar nitrogen functionalities and contents but could be modified with wastes with different nitrogen contents. Results from analysis of condensed tars in Section 3.4 will continue that discussion.

3.4. Nitrogen compounds in condensed tars

Table 9 gives a list of nitrogen compounds found in the condensed tars. 72 compounds were identified in the tars of sewage sludge, food waste and mixture. Several compounds were only

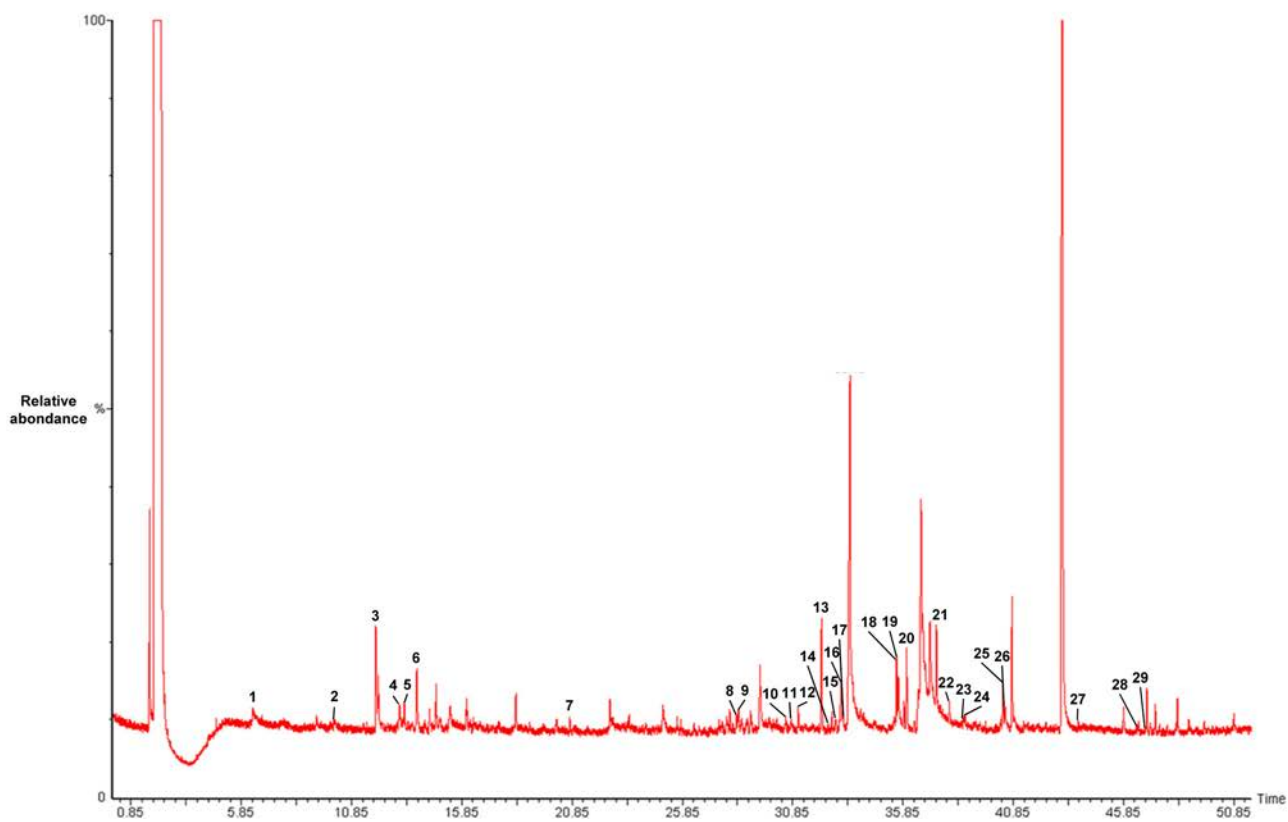
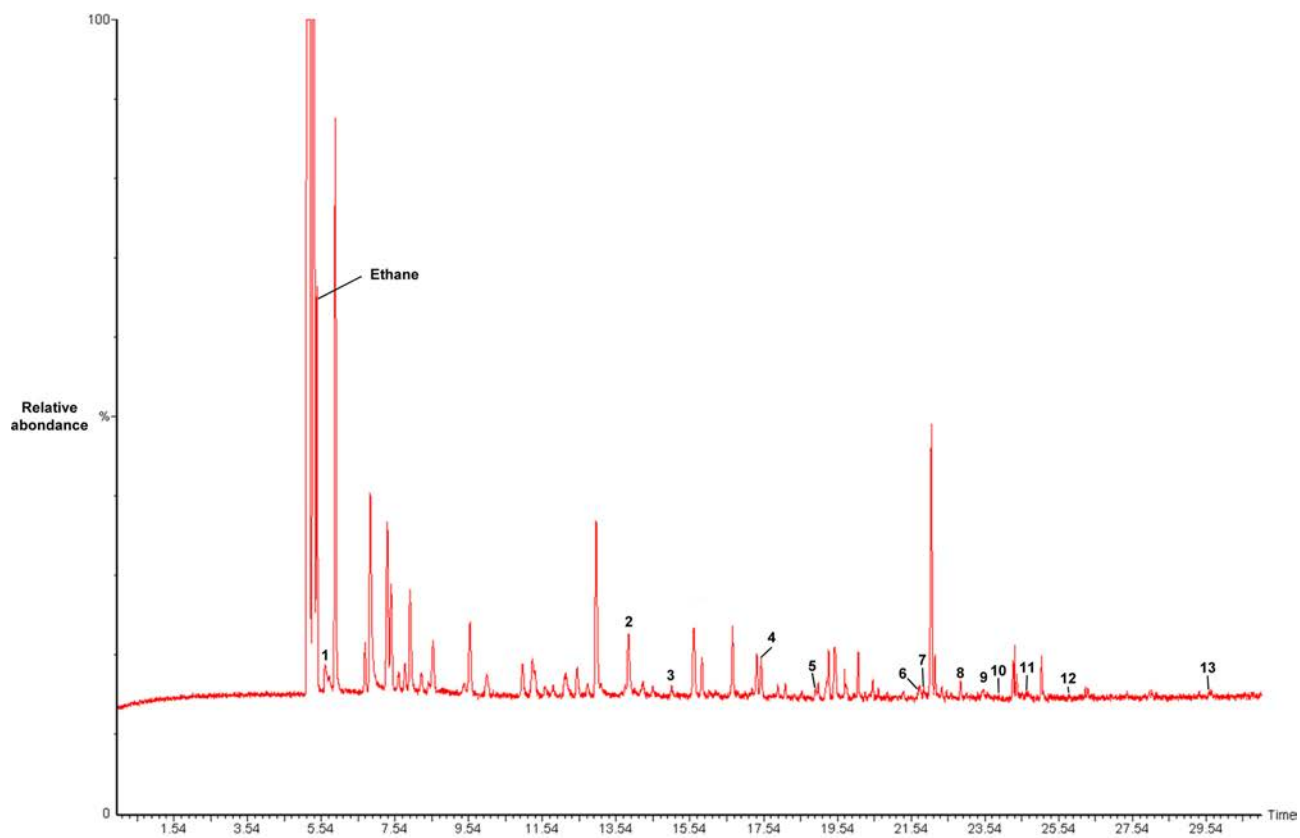


Fig. 4. Chromatograms of pyrolysis gas (up) and tar (bottom) from sewage sludge (N-compounds peaks are numbered and listed in Table 8 and Table 9).

Table 7
MS peaks of gas and tars compounds.

	Wood		Sewage sludge		Food waste		Mixture	
	Gas	Tars	Gas	Tars	Gas	Tars	Gas	Tars
Peaks amount	45	95	86	99	138	176	99	154
Identified peaks (%)	69	73	86	73	85	72	90	73
MS area of identified peaks (%)	74	95	96	90	93	95	97	95
MS area of nitrogen compounds (%)	0	0	10	18	4	21	5	8

identified by their family. In Table 9, these compounds are accompanied by the mass/charge (m/z) ratios of their major mass peaks.

Nitrogen compounds found in condensed tars can be divided into six families as can be seen in Table 9: (i) nitriles, (ii) heterocyclic compounds with one nitrogen atom, (iii) DKPs, heterocyclic compounds with 2 nitrogen atoms, (iv) amides, (v) amines and (vi) oximes. The number of compounds is higher than in the gases and their diversity is different. Thus, the analysis of condensed tars complements the analysis of gases.

Nitriles in condensed tars differ from the ones identified in the gases. Main nitriles have between 16 and 19 carbon atoms, while, in the gases, main nitriles have only 2 or 3 carbon atoms. This type of nitriles was previously only detected as products of wastes pyrolysis, as can be seen in Table 9, and never in pyrolysis of amino acids or proteins. Thus, they have not the same origin than the light nitriles identified in gases. Indeed, they come from the reaction between ammonia and fatty acids [21]. Long chain amides, also found among the nitrogen compounds, are probably intermediates between fatty acids and nitriles. However, they are also found naturally in the organic substrates. For example, 9-octadecenamide is a naturally occurring lipid in living organisms [1]. Thus, long chain amides could also directly vaporize from wastes.

Among heterocyclic compounds, pyrrolic and pyrrolidinic compounds are found in condensed tars, as in the gases. Some indolic and piperidinic compounds are also detected. These kinds of compounds were previously observed. For example, indole was identified as one of the major products of rapeseed oil cake pyrolysis [3]. Heterocyclic compounds are generally believed to be derived from proteins. As instance, indoles derivatives were detected during the pyrolysis of several amino acids, like asparagine, proline and tryptophan [36–38,41,44]. However, they could also be produced from another biochemical sources such as melanoidin structures [11,12]. The presence of DKPs in condensed tars, identified through a study on the pyrolysis of dipeptides [46], is an excellent marker of proteins. They are exclusively detected in condensed tars, probably due to their low volatilities. As previously mentioned, they probably are among the major sources of several amines and nitriles.

Several amines and oximes were also detected. Some have relatively high area peaks. That is consistent with previous findings on nitrogen compounds, relating that the cracking of proteins produces amines [7]. Some of these compounds were never previously identified, showing the multitude of nitrogen compounds being able to form from pyrolysis.

As in gases, the same major nitrogen compounds of condensed tars are detected for sewage sludge, food waste and mixture. Thus, that confirms that the reaction pathways of thermal decompositions are similar for both wastes. Moreover, the analysis of wood tars did not lead to the identification of nitrogen compounds, leading to the same conclusions than for the gases.

3.5. On the complementarity of the two analysis

One of the originalities of this work was to combine analysis of condensed tars and gaseous tars. Tars are generally collected by trapping in a solvent, so into condensed form. Tars were rarely previously analyzed directly into gaseous form. This work shows

that the two different analytical methods permit to detect different compounds. In fact, several compounds were detected by only one method. It is the case for volatile compounds such as acetamide and light nitriles, which were only detected by gaseous method. It is also the case for non-volatile compounds, such as DKPs, long-chain nitrogen compounds and oximes, which were only detected by condensed method. Further work could be focused on the improving of the analytical methods. For example, condensed tars could be analyzed without evaporating water and solvent, which eliminate some volatile compounds. Gaseous tars could also be concentrated into an adsorbent in order to increase the sensitivity of the analysis. Finally, more studies on pyrolysis products could adopt the analysis of gaseous tars in order to identify and quantify more volatile compounds, which could be major products.

3.6. Reaction pathway

In order to resume the findings of this study, a simplified reaction pathway can be proposed, valid for food waste and sewage sludge. It is schemed in the Fig. 5. It is focused on identified tar-N compounds. It gives a complementary point of view for previously published reaction pathways of sewage sludge [7,29]. It also enlarges reaction pathway to another waste, i.e., food waste.

In organic wastes, the main sources of nitrogen are the proteins [7,24]. So they can be considered as the main sources of nitrogen products. It would explain why products are similar between two different sources, such as food waste and sewage sludge. The pathway proposed here is based on the degradation of proteins.

During pyrolysis, proteins, as macromolecules, are cut to form smaller molecules. Several products are probably directly issued from these ruptures of proteins. The most frequent amino acids in proteins are glycine, alanine, leucine and valine, which contain few carbon atoms. The fragments issued from these amino acids could be light amides and amines, such as acetamide. These fragments could be transformed by electrons reorganisation into light nitriles, such as acetonitrile. Likewise, several heterocyclic compounds could directly originate from rupture of proteins. Pyrrolidinic and pyrrolic compounds are typically issued from fragments of proline and pyrrolysine, amino acids which are included in proteins. Indolic compounds are tryptophan fragments.

Proteins can also react with sugars to form Amadori compounds by the Maillard reaction [38]. Then, these Amadori compounds are able to cyclise and to form oxygenated heterocyclic compounds such as DKPs. They could also be broken and form light amino compounds.

Another possible pathway for heterocyclic compounds formation is the cyclisation of proteins fragments and the formation of heterocyclic compounds. DKPs are typically the result of the condensation between two amino acids of proteins [46]. Pyrrolic, pyrrolidinic, indolic and piperidinic compounds are probably also formed from the condensation of proteins fragments. Then, heterocyclic compounds can undergo a rupture of their cycle. They would give light linear nitrogen compounds, such as amides, nitriles, amines or oximes.

Ammonia and hydrogen cyanide, as major products, would be formed from light nitrogen compounds. Moreover, they could be

Table 8
Nitrogen compounds identified in pyrolysis gas and fractions of their area peaks.

	Ratio between peak areas of compound and C ₂ H ₆ (%)		Ratio between peak areas of compound and all compounds (%)		Previous detections in literature	Peak number in Fig. 4		
	Sewage sludge		Food waste				Wastes	Chemicals
	Food waste	Mixture	Food waste	Mixture				
Gas								
HCN								
NH ₃	19.1	14.6	5.5	2.08		1		
Nitriles								
Acetonitrile	29.6	9.6	9.8	1.37	Sewage sludge [16,20] Tobacco [5]	2		
Propanenitrile	13.0	3.7	4.1	0.53	Polyamides [8] Sewage sludge [16,20] Animal bones [9]	4		
2-propenenitrile	6.4	0.9	1.4	0.13		3		
Isobutyronitrile	3.7	0.7	0.7	0.10		5		
Heptadecanenitrile	2.9	1.5	1.5	0.16				
4-methylpentanenitrile	2.4	0.9	0.7	0.13		11		
Total	58	17.5	15.8	2.26	Fermented bones [10] Sewage sludge [18] Soybean protein [7] Sewage sludge [18,21] Sesame cake [1] Animal bones [9] Sesame cake [1] Sewage sludge [18]			
Heterocyclic compounds								
Pyrrrole	8.2	5.5	5.5	0.32		8		
2-pyrrolidinone	5.0	2.2	2.2	0.32	Soybean protein [7] Animal bones [9] Rape cake [3] Lake sediments [11] DOM [12] Sewage sludge [17] Tobacco [6]			
Pyridine	4.8	0.8	0.8	0.08	Sewage sludge [20,22] Soybean protein [7] Sewage sludge [15,18-20] Lake sediments [11] Animal bones [9] DOM [12] Lake sediments [11] Lake sediments [11] Sewage sludge [21] Lake sediments [11]	13		
1-methyl-1H-pyrrole	4.5	0.3	0.3	0.43		6		
2,5-pyrroledione	4.4	0.7	0.7	0.10		7		
3-ethyl-1H-pyrrole	2.9	1.9	0.24	0.27		9		
2,3,4-trimethylpyrrole	1.5	0.12	0.12	1.12		12		
Total	31.3	6.6	7.8	1.12	DOM [12]			
Amide								
Acetamide	1.6	0.1	0.1	0.1	Tobacco [6] Sewage sludge [20,21] Rape cake [2] Lake sediments [11] DOM [12]	10		
Total				5				

Table 9
Fractions of MS area (%) for nitrogen compounds in tars.

	Sewage sludge	Food waste	Mixture	Previous detections in literature	Peak number in Fig. 4
Nitriles					
Heptadecanenitrile	1.77	2.67	0.60	Soybean protein [7] Animal bones [9] De-oil cakes [1] Sewage sludge [18,21] De-oil cakes [1] Tanning waste [13] Castor seeds [4]	13
9-octadecenitrile	0.91	2.05	0.14		19
9-octadecenitrile	0.93	1.61	0.15	Mustard cake [1]	18
Nonadecanenitrile	1.19	1.54	0.49		20
Hexadecanenitrile	0.16	0.24	0.06		
4,8,12-trimethyl-3,7,11-tridecatrienitrile	0.09	0.12			
Octadecanenitrile	0.09	0.02			
Ethoxyacetoneitrile	4.8	8.0	1.4		
1,10-dicyanodecane					
Total	1.85	1.02	1.22		
Heterocyclic compounds with one nitrogen atom					
2-pyrrolidinone	1.19	0.49	0.32	Tobacco [6] Sewage sludge [20,22]	3
2,5-pyrrolidinedione	0.31	0.85	0.27	Sewage sludge and mycelial waste [14]	6
2,2,6,6-tetraméthyl-4-piperidinone	0.53				5
3-pyridinol	0.26				4
Pyrrolidine (m/z: 55, 113, 111, 129, 187)		0.36		Sewage sludge [17]	
1,2,3-trimethylpiperidin-4-one		0.27	0.12		7
3-methyl-1H-indole		0.13	0.06	Rapeseed oil cake [3] DOM [12]	
Indole					
Indole	0.07	0.11		Sewage sludge [17,18] De-oil cakes [1] Rapeseed oil cake [3] Lake sediments [11] DOM [12] Castor seeds [4] Sewage sludge [17] Sewage sludge [17]	27 28 29
Pyrrolidine (m/z: 113, 126, 55, 43)	0.10	0.06			
Pyrrolidine (m/z: 113, 126, 55, 70, 72)	0.10	0.05			
Pyrrolidine (m/z: 113, 126, 70, 41)	0.06	0.08			
Proline derivative (m/z: 84, 41, 56)		0.03	0.07		
1-methyl-2,5-pyrrolidinedione		0.04	0.06		
Hexahydropyrrrolizin-3-one		3.4	3.1		
Total	4.4				
DKP					
DKP (m/z: 70, 154, 194, 41)	0.95	0.59	0.27		16
DKP pro-ala	0.46	0.17	0.10		9
DKP (m/z: 42, 113, 99, 43, 70)		0.43			
DKP pro-arg	0.36				12
DKP pro-gly		0.34	0.36		
DKP pyrrocoll	0.33	0.09	0.13		8
DKP pro-val	0.32	0.23	0.15		10
DKP (m/z: 154, 70, 125, 41, 86, 69)					
DKP (m/z: 70, 69, 97, 41, 125, 169)	0.29	0.25	0.20		17

Table 9 (Continued)

	Sewage sludge	Food waste	Mixture	Previous detections in literature	Peak number in Fig. 4
DKP pro-ile	0.20	0.15			15
DKP (m/z: 42, 113, 70)		0.18	0.11		
DKP val-val	0.17				11
DKP pro-ile	0.11				14
DKP pro-phe		0.15	0.05		
DKP pro-val		0.14	0.06		
DKP (m/z: 156, 113, 95, 170)		0.12	0.06		
DKP (m/z: 70, 168, 44, 97, 125)		0.11	0.06		
DKP pro-ile		0.07	0.10		
DKP (m/z: 154, 86)	0.08	0.09	0.07		
DKP (m/z: 44, 99, 56, 71, 125)		0.03	0.07		
DKP (m/z: 70, 43, 69, 97, 125)		0.06			
DKP (m/z: 126, 42, 85, 43, 154, 113)		0.04	0.05		
DKP (m/z: 56, 41, 70, 125, 127, 113)		0.04			
DKP phe-val		0.03			
Total	3.2	3.3	1.8		
Amides					
Heptadecanamide	1.07	1.05	0.40		21
2-hydroxypropanamide	0.36	0.81	0.97		2
9-octadecanamide	0.69	0.90	0.33	Animal bones [9] De-oil cakes [1] Rapeseed oil cake [3] Castor seeds [4] Sewage sludge [17-19] Swine manure [47]	25
9-octadecanamide	0.53	0.51	0.13		26
Octadecanamide	0.52		0.13	Animal bones [9] Sesame cake [1] Sewage sludge [17-19]	
N,N-dimethyldodecanamide	0.17				23
N,N-dimethyldodecanamide	0.14				24
Amide (m/z: 59, 72, 43, 41, 44)		0.12			
N,N-dimethyldodecanamide		0.13			
5-hydroxypentanamide		0.06	0.10		
Propanamide		0.08			
Amide (m/z: 87, 72, 100, 46)		0.06			
3-methylbutanamide		0.06			
Amide (m/z: 59, 42, 41, 86, 57, 127)		0.05			
Total	3.0	3.7	1.9		
Amines					
Amine (m/z: 58, 43, 42, 100, 83)		0.85			1
4-amino-4-methyl-2-pentanone	0.74	0.04			
Amine (m/z: 84, 42, 126)	0.28				
Amine (m/z: 44, 42, 56, 84)	0.21				
Amine (m/z: 58, 79, 69, 40)	0.04				
Amine (m/z: 59, 44, 43, 42)					
Total	1.1	0.04	0.17		
Oximes			0.2		
O-methylloxime (m/z: 73, 86, 58, 55)		0.38		Swine manure [47]	22
O-methylloxime (m/z: 73, 86, 58, 43)	0.33	0.27			
O-methylloxime (m/z: 73, 56, 58, 67)		0.15			
O-methylloxime (m/z: 73, 86, 43, 58)		0.14			
O-methylloxime (m/z: 73, 69, 43, 55)		0.06			
Total	0.3	1.0	0		

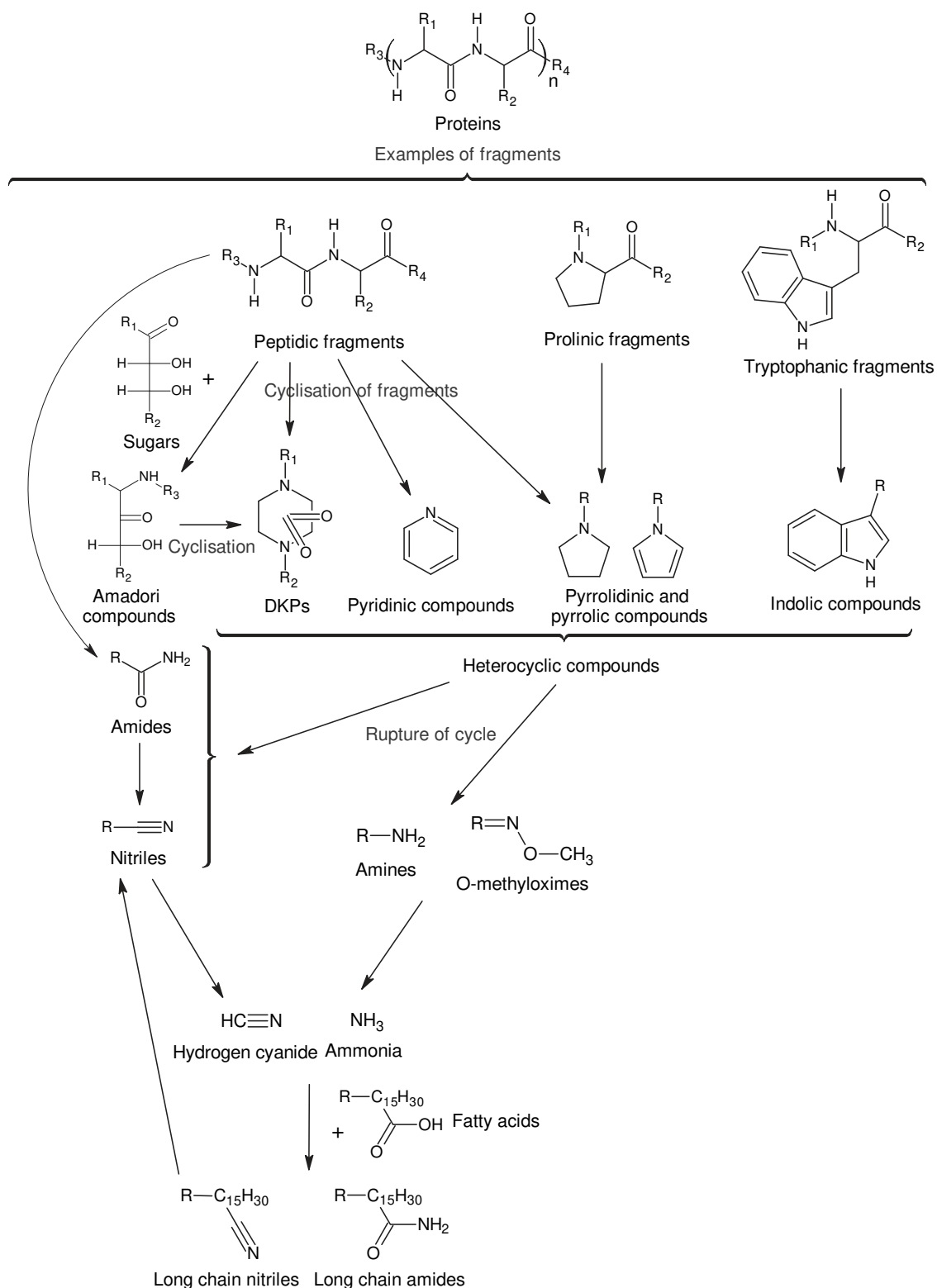


Fig. 5. Reaction pathway for nitrogen compounds during pyrolysis of organic wastes.

partly responsible for the formation of long chain nitrogen compounds, such as amides and nitriles [21]. As previously mentioned, these long chain nitrogen compounds could also be constituents of organic wastes. Likewise, organic wastes contain others sources of nitrogen compounds, such as melanoidin structures [11,12]. So other pathways surely exist but this pathway is probably the main pathway of nitrogen compounds formation.

4. Conclusion

This work focuses on the nitrogen products from the pyrolysis of three wastes, representatives of a common municipal waste. The temporal profiles of major products and partitioning into tars and chars are firstly presented. Those results show that the release of products follows a particular order: (i) oxygen atoms, (ii) carbon

atoms, (iii) hydrogen atoms. The nitrogen distribution in condensable products, i.e., char and tars, is high, compared to oxygen and hydrogen atoms, so that the nitrogen in the wastes is presumably stable.

The analysis of both gaseous and condensed tars related the formation of up to 14 and 72 nitrogen compounds respectively in the gases and in the condensed tars, with widely forms of compounds. In gases, light nitriles seemed to be the main products whereas, in condensed tars, several chemical families were represented: long chain nitriles and amides, pyrrolic and pyrrolidinic compounds and DKPs. Moreover, several compounds, rarely previously detected, were observed, such as oximes.

Those nitrogen products were found to be only slightly influenced when wastes have similar nitrogen functionalities contents, such as food waste and sewage sludge. However, with wastes with lower nitrogen content, such as wood, nitrogen products were not detected. Thus, reaction pathway could be different for nitrogen in wood. The mixture of wastes have only slightly effects on nitrogen products and thus on the reaction pathway.

Based on identified nitrogen products, a reaction pathway is proposed. It is based on the fact that proteins are the main sources of nitrogen. The compounds in both gaseous and condensed tars are in accordance with the reaction pathway of proteins thermal decomposition.

This work has to be continued by improving analytical methods in order to increase sensitivity and to quantify nitrogen products, particularly NH₃ and HCN. Other wastes could also be added in the study. Then, it would serve for the understanding of the nitrogen oxides formation.

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