Journal of Analytical and Applied Pyrolysis 114 (2015) 222–234

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

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

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ARTICLE INFO

Article history:
Received 27 February 2015
Received in revised form 20 May 2015
Accepted 1 June 2015
Available online 5 June 2015

Keywords:
Nitrogen compounds
Organic wastes
Pyrolysis
Reaction pathway
Tars

ABSTRACT

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 production [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 (NH_3) and hydrogen cyanide (HCN) [7,14,16,23–27]. Isocyanic acid (HNCO) and nitrogen (N_2) can also be among the main prod-

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http://dx.doi.org/10.1016/j.jaap.2015.06.002
0165-2370/

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 NH_3 were mainly focused. Some studies showed a preponderance of HCN [23,27] whereas others showed a higher production of NH_3 [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 NH_3 were less pronounced but it also tended to increase with temperature, and then to fall for temperatures higher than 700–800 °C. NH_3 was predominant during the slow pyrolysis of mycelial waste from antibiotic production [14].

Even if NH_3 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 NH_3 [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