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Pyrolysis of Furfural Residues and Possible Utilization Pathway

George Ngusale

Abstract

The manuscript attempts to understand the evolution of NO_x precursors: NH₃ and HCN from Pyrolysis of furfural residue (FR). The pyrolysis process was carried out in a thermogravimetric analyzer (TGA) coupled to Fourier-transform infrared (FTIR) spectrometer. The combination revealed insightful information on the evolution of NH₃ and HCN. This could help us better understand the characteristics of FR derived from furfural production especially with regard to NH₃ and HCN. Nitrogen is considered a minor component in biomass wastes; in this study nitrogen content is about 0.57%. However, the pollution potential poised by low nitrogen content is huge through both direct and indirect processes. Thus, this study presents results that were found with regard to FR pyrolysis in pure nitrogen environment. At the heating rate of 40°C/min⁻¹, the only NO_x precursor detected was HCN at 713 cm⁻¹ as per the database provided by National Institute of Standards and Technology (NIST). NH₃ was not detected. The particle size of FR used ranged between 0.15–0.25 mm.

Keywords: furfural residues, pyrolysis, NO_x precursors, TGA, FTIR

1. Introduction

In China, there exists abundant biomass in terms of agricultural crop residues that until now remain unutilized or under-utilized as shown **Figure 1**.¹ The crop residues range from rice husks/straws, wheat husks, corn cobs and many others. However, crop residues such as corn cob are greatly used in furfural industries for furfural production. Furfural production produces waste, herein referred to as Furfural Residue.

Furfural residues are in abundant supply in China [1]. It is estimated that a furfural processing plant with an annual furfural production of 1000 t produces about 13000 t/a of FR [2]. The residuals are derived from corncob through an acid hydrolysis process as shown in **Figure 2**. The process eliminates hemicellulose component retaining the cellulose and lignin components, with probably a few traces of hemicellulose [3].

With the increasing demand for energy in China, FR has been undergoing research to determine its utilization in various aspects such as ethanol production, soil conditioning to mention but a few [2, 3]. The research has been motivated by the great need to avoid open burning of FR in open fields. Worldwide, the open burning and/or disposal of any given waste or residue has been known to be a major

¹ <http://dimsums.blogspot.com/2010/12/69-of-crop-residues-utilized.html>. 2010. [accessed 2016-02-16].

China's utilization of crop residues

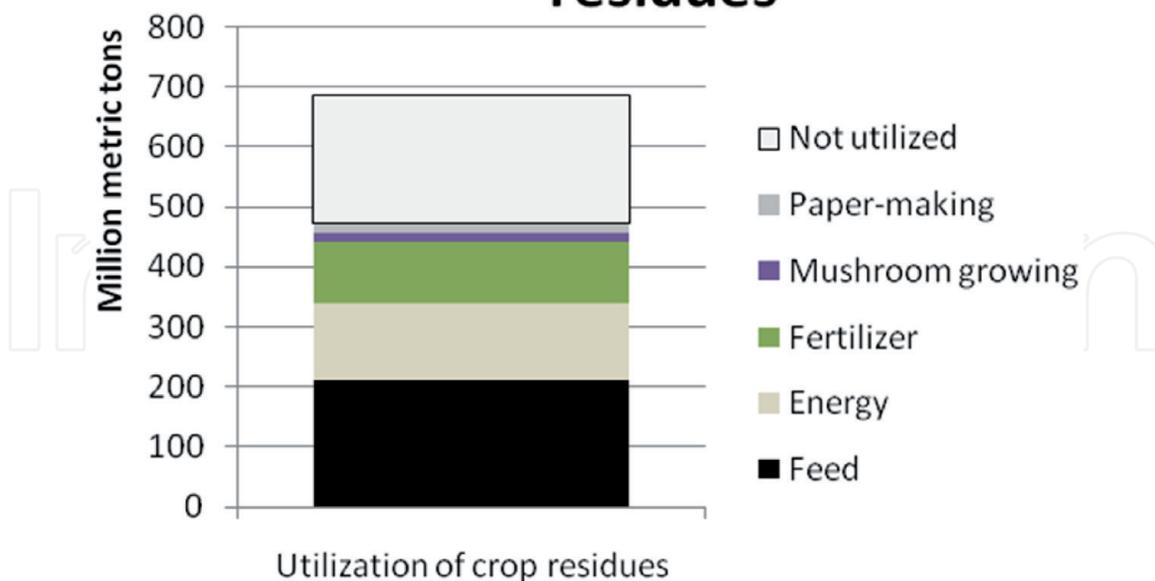


Figure 1.
Utilization of crop residues in China.

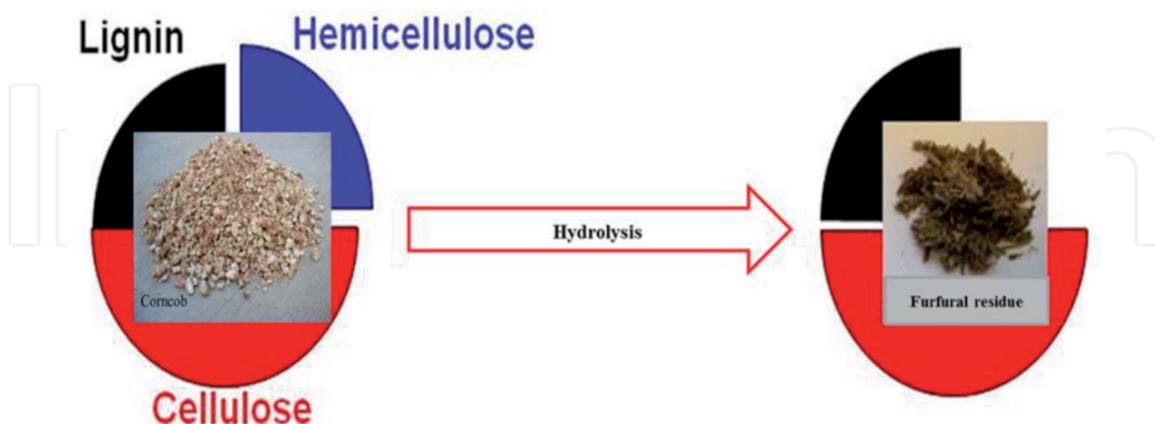


Figure 2.
Furfural residue formation.

environmental pollutant [4, 5]. On the other hand, limited literature currently exists on thermal-chemical utilization of FR for energy production.

However, for FR to undergo any thermo-chemical process (pyrolysis, gasification or combustion), knowledge on fuel-N is crucial. Fuel-N is normally converted into NO_x which is environmentally harmful [6, 7]. In this regard, the manuscript considers the formation of NO_x precursors mainly NH₃ and HCN. Previous studies

have indicated that different types of biomass have different intrinsic properties especially nitrogen functionalities [8]. Furthermore, some studies have found that biomass pyrolysis yields more NH_3 more than HCN while others the vice-versa is true [7]. Therefore, this study aims to provide information on conversion of FR-Nitrogen during pyrolysis. This would offer a platform for comparability with previous studies on pyrolysis of other biomass wastes [9]. The results so obtained would go a long way in investigating the mechanism of NO_x precursors for specific biomass wastes during pyrolysis process. The study used TG coupled to FTIR to investigate NH_3 and HCN. Given the low nitrogen content in FR (about 0.57%), the only NO_x precursor detected was HCN at 713 cm^{-1} as per the database provided by NIST² [10].

2. Experiment

The proximate and ultimate analyses on FR carried out at Shanghai Jiao tong University are as shown in **Table 1**. Thereafter, about 5 mg of the samples whose diameter range from 0.15–0.25 mm were measured and then loaded in an inert platinum crucible placed on a balance. According to one of the manufacturers' Engineer of the TGA Q5000 (in Shanghai, China), no more than 5 ± 0.5 mg should be loaded to ensure decomposition takes place in the kinetic regime. Then, the correct positioning of the sample holder was ensured to avoid or minimize significant

Proximate analysis (wt. %)				Ultimate analysis (wt.%, dry basis)				
Fixed carbon ^a	Volatile	Ash	Moisture	s	H	O	N	S
39.13	23.31	6.95	30.61	46.51	4.94	35.09	0.51	2.09

^aBy difference.

Table 1.
Proximate and Ultimate analysis of FR.

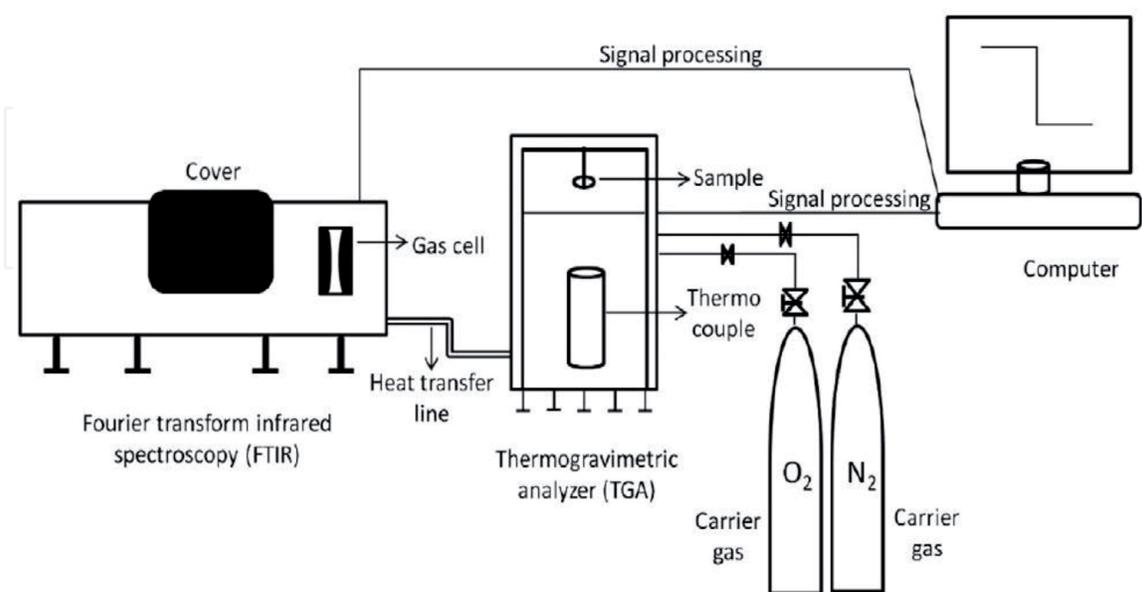


Figure 3.
Schematic diagram of the TGA coupled to FTIR spectrometer [13].

² National Institute of Standards and Technology (NIST) chemistry WebBook Database of organic chemistry compounds.

temperature shifts/errors that would have occurred [11]. Pyrolysis was carried out at a heating rate of 40°C/min from ambient room temperature to final temperature of 1000°C. Though the low heating rate selected does not correspond to realistic thermal conditions, the value is necessary for analysis and understanding the experimental results. Nitrogen gas was used as the purge gas to sweep the pyrolysis gases and prevent secondary reactions and tar deposition on the FR sample while providing an inert atmosphere. The flowrate was set at 50 ml/min as the value does not have significant effect on amount of collected gaseous products [5]. Evolved gases from TGA were transmitted to a Bruker Tensor FTIR (vertex 70) spectrometer via a heated transfer line kept at a constant temperature of 180–190°C to prevent the condensation of less volatile compounds [12]. FTIR spectra were collected with 1 cm⁻¹ resolution, in the range of 4000-600 cm⁻¹ IR absorption band. A schematic setup of the complete TGA coupled to FTIR spectrometer is shown in **Figure 3**.

3. Results and discussion

3.1 Fuel properties

From **Table 1**, the percentage results of both proximate and ultimate analysis of FR were used to calculate the empirical formula (EF): CH_{1.2746}O_{0.5659}N_{0.009}S_{0.0169}. Then, using the EF, the value of the stoichiometric weight air-to-fuel ratio, Rs was obtained as 5.62. The formula for Rs assumes complete conversion to water vapors and carbon dioxide. Rs value for FR is approximately the same as that obtained for nutshells (Rs = 5.6) [14]. Similarly, the moisture content is high at 30.61% while nitrogen content is at 0.51%. This nitrogen content is within the range measured by other researchers [2, 15].

3.2 TGA—FTIR

TGA coupled to FTIR spectrometer has been known to provide insightful information on the composition of gaseous products evolved from the pyrolysis of solid fuels [13, 16]. In this study, a heating rate of 40°C/min was selected high enough to ensure the quality of the FTIR data obtained [12].

3.2.1 TGA curves for FR

Figure 4 shows TGA curves for both weight loss and the corresponding derived weight of FR. Owing to limited literature on FR pyrolysis, the Authors attempted to learn some relevant information on FR [3, 17]. The information helped deduce the thermal decomposition behavior of FR. The initial temperature rise necessitated moisture release from FR. The moisture released contributes about 10% of weight loss. Volatile matter started to be released from FR at temperatures of about 239°C. When the temperature reached about 748°C, more than 65% of the weight of FR was released under pure pyrolysis condition (using nitrogen as the medium). A final high temperature of 1000°C was selected to ensure complete FR degradation. This might be due to higher thermo-stability of lignin in FR due to occurrence of more condensed polymeric structures in its composition [3]. Similarly, derived weight curve shows four peaks: one major peak and three minor ones. First minor peak occurs between 62 and 93°C with a maximum decomposition rate of 0.88%/°C. This indicates the released moisture from within

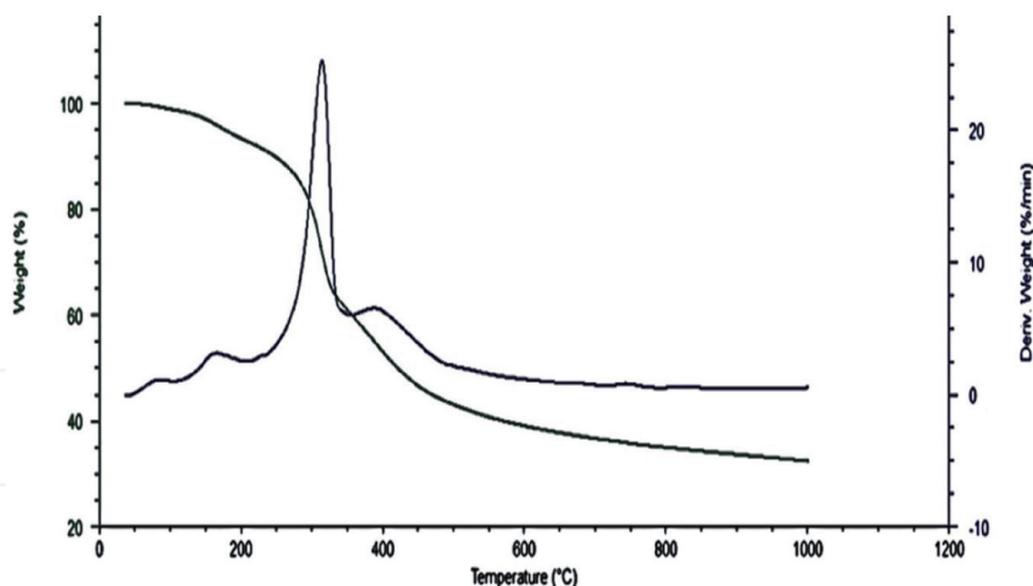


Figure 4.
TGA curves for both the weight loss and derived weight of FR.

FR material. The second peak occurs between 137 and 195°C with a maximum decomposition rate of 3.1%/°C, indicating the degradation of hemicellulose traces left in FR material after hydrolysis. The third peak is the major one as it represents the greatest weight loss at temperatures between 275 and 334°C with a maximum decomposition rate of 25.2%/°C. Last but not least, fourth peak is attributed to lignin degradation in FR material at a broad temperature range of 369–416°C with a maximum decomposition rate of 6.53%/°C. This could be as a result of hemicellulose extraction that tampered with the lignin content or rather a hypothesis that lignin undergoes a phase transition [18]. Some studies have found that at high temperatures (>400°C) the aromatic rings of char matrix in lignin are rearranged [19, 20]. However, the occurrence of the different peaks solely depends on the percentages of hemicellulose, cellulose and lignin contained in the original material, which in this case is FR [21].

3.2.2 FTIR analysis of HCN and NH₃ in the pyrolysis gas composition

The gaseous emissions measured with the FTIR system are as shown in **Figures 5 and 6**. **Figure 5** shows the three-dimensional (3D) diagram corresponding to FR pyrolysis while **Figure 6** shows IR spectrum of pyrolysis products obtained at the maximum evolution rate for each decomposition FR.

The system has built-in calibrations for various gaseous emissions. Since the focus of this study was on HCN and NH₃, the other emissions were not identified and analyzed. The wave number ranges for HCN and NH₃ selected were 712–714 cm⁻¹ and 930–966 cm⁻¹ respectively [9, 22]. At these wave numbers no major moisture content interference especially for HCN apart from the normal bending vibrations in the fingerprint region.

HCN, NH₃ and other nitrogenous species are known to be present in low amounts [23–25]. **Figure 7** shows HCN released from pyrolysis of FR in nitrogen atmosphere. The initial HCN released began at a temperature of about 152°C and then increased sharply to a maximum temperature of 353°C. However, a sharp rise in HCN released was evident within the temperature range of 286–386°C then slightly stabilized up to 420°C before gradual decline up to 822°C. Thereafter,

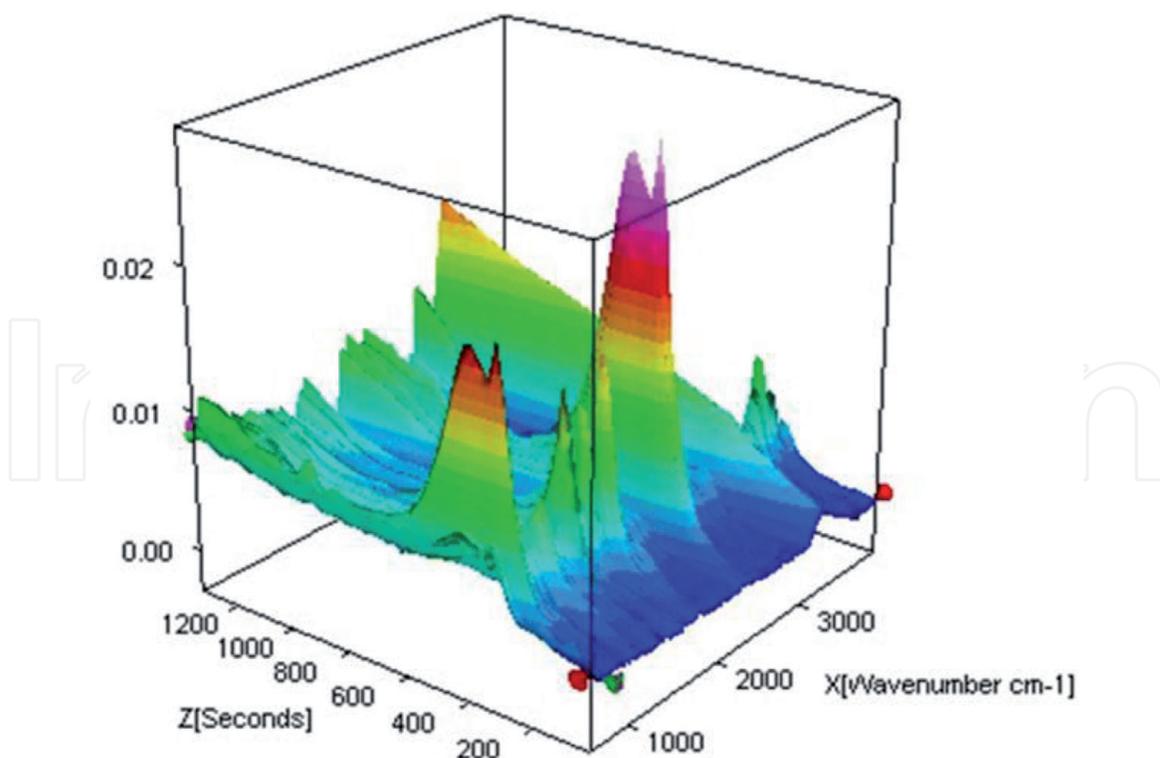


Figure 5.
3D IR spectrum of Furfural residues.

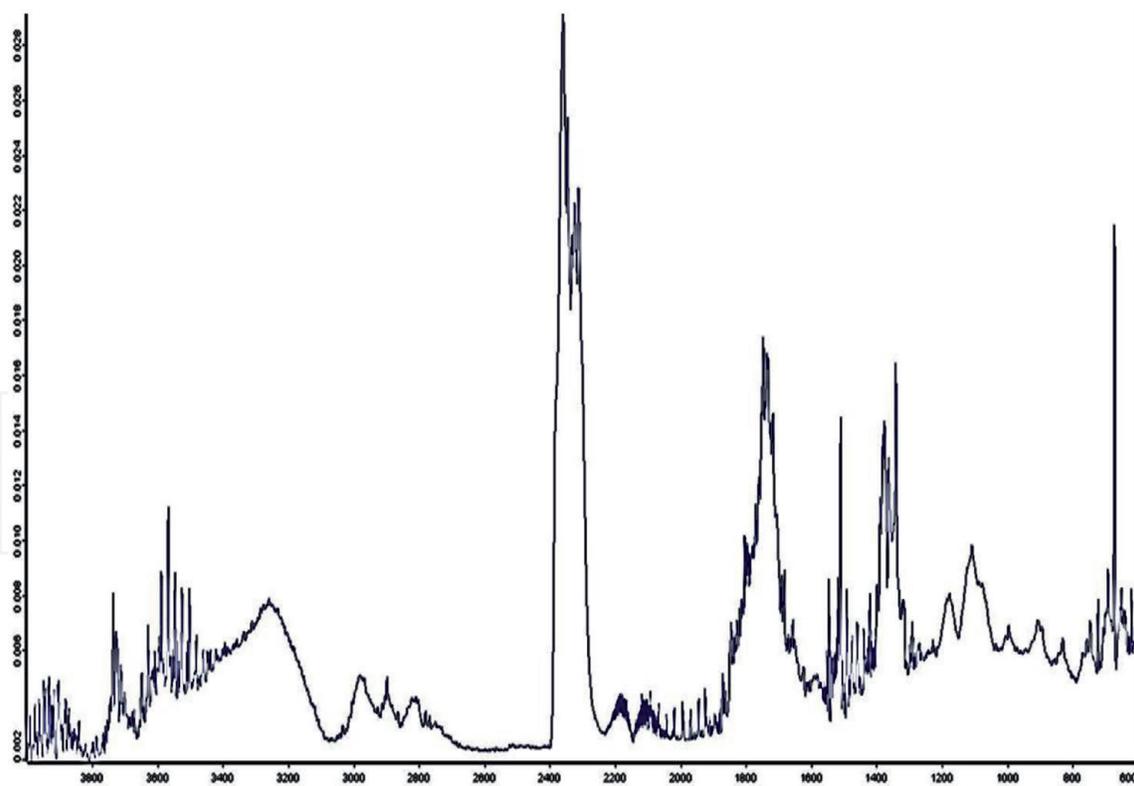


Figure 6.
IR spectrum of pyrolysis products obtained at the maximum evolution rate for each decomposition Furfural residues.

a gradual rise took place up to 1000°C. NH₃ released could not be conclusively detected as per the NIST webBook. The study however, showed similar trends of previous detection of HCN, NH₃ and other nitrogenous species with regard to pyrolysis of other biomass wastes [26, 27].

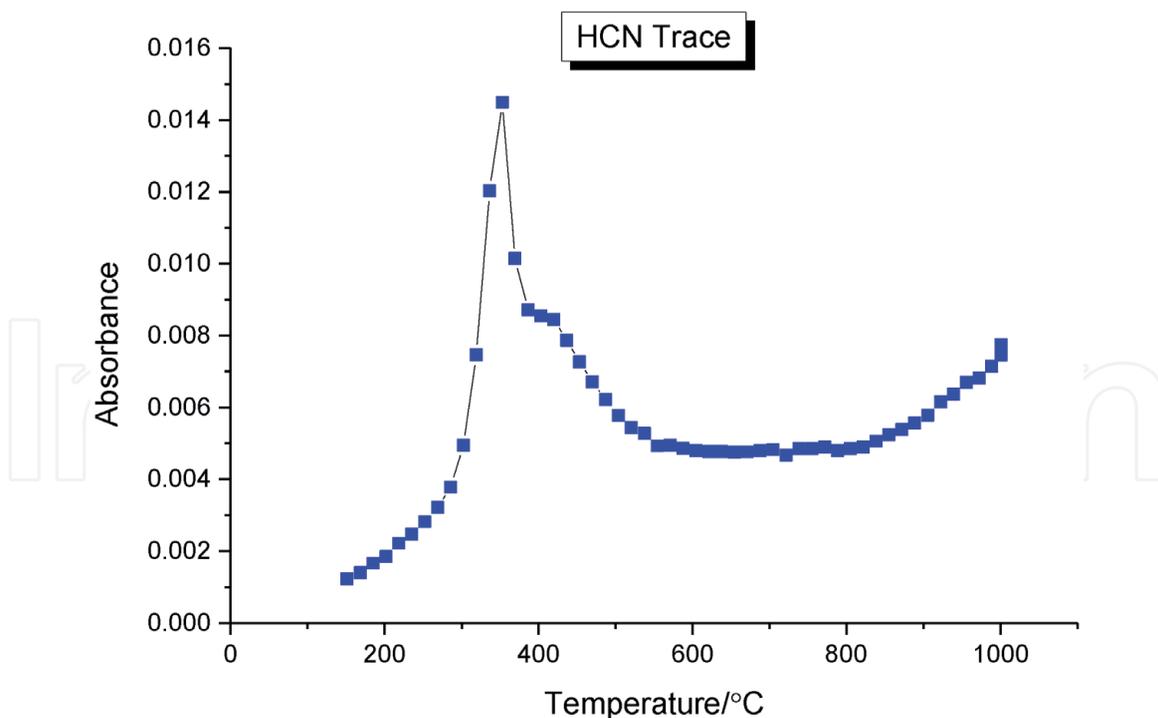


Figure 7.
Release of HCN in nitrogen atmosphere.

4. Conclusion

The evolution characteristics of NH_3 and HCN released from the pyrolysis of FR were investigated by TGA-FTIR. The pyrolysis temperature range of 200–485°C led to a maximum release of HCN at 353°C. At the heating rate of $40^\circ\text{C}/\text{min}^{-1}$, the only NO_x precursor detected was HCN at 713 cm^{-1} as per the database provided by NIST. NH_3 was not detected while HCN was released from pyrolysis of FR in nitrogen atmosphere. The particle size of FR used ranged between 0.15–0.25 mm.

Also, percentage results of both proximate and ultimate analysis of FR obtained an empirical formula (EF): $\text{CH}_{1.2746}\text{O}_{0.5659}\text{N}_{0.009}\text{S}_{0.0169}$. Then, using the EF, the value of the stoichiometric weight air-to-fuel ratio, R_s , was 5.62.

As the focus of this study could not factor the effect of both varying particle size and heating rate, further research is recommended.

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