Faculty of Chemical Engineering and Technology
University of Zagreb

FKITMCMXIX

*in cooperation with*

Hrvatske vode, Legal entity for water management (HR)
Department of Civil & Environmental Engineering, College of Science, Engineering and Technology, Jackson State University (USA)
Croatian American Society (HR)
Slovenian Biomass Association (SLO)
ODRAZ, Sustainable Community Development (HR)

# 3rd International Symposium on Environmental Management

## Towards Sustainable Technologies

SEM 2011

# Conference Proceedings

October 26 - 28, 2011
Faculty of Chemical Engineering and Technology, Zagreb, Croatia

# DETERMINATION OF AMMONIA AND CARBON DIOXIDE IN EXHAUST GASES DURING COMPOSTING OF TOBACCO WASTE IN A CLOSED REACTOR

Dajana Kučić*, Nina Kopčić, Ivana Ćosić, Marija Vuković, Felicita Briški

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10000 Zagreb

*e-mail: dkucic@fkit.hr, tel:+385 1 4597 270, fax: +385 1 4597 260

**Abstract**

Solid waste accumulated during the processing of tobacco for cigarette manufacture mostly contains tobacco particles and flavouring agents. The main characteristic of that waste is a lower than optimal C/N ratio and a high content of nicotine as a toxic substance. Tobacco waste is classified as agro-industrial waste and as such can be decomposed by composting. Ammonia is one of the main compounds responsible for generation of offensive odours, and atmospheric pollution when composting organic wastes with high nitrogen content.

The objective of this work was to determine amount of ammonia and carbon dioxide in the exhaust gases during composting of tobacco waste. Composting process was carried out with forced aeration (0.66 L $min^{-1}$ $kg_{VS0}^{-1}$) in column reactor (10 L) under adiabatic conditions during 26 days. During the process, temperature changes in the reactor, pH value, C/N ratio and mesophilic and thermophilic microorganisms in the mixed microbial culture were closely monitored while evolved $CO_2$ and $NH_3$ were analyzed periodically. Ammonia was measured both in the condensate and in 4 % boric acid trap while $CO_2$ was trapped in 1 M NaOH.

It was found that emission of carbon dioxide depended on temperature while emission of ammonia mainly depended on pH value in composting mass. The most of carbon dioxide was evolved in the first several days of composting process due to the highest activity of microorganisms. At the end of the process total $CO_2$ evolved (per kilogram of initial volatile solids) was 302.0 g $kg_{VS0}^{-1}$. No significant amount of ammonia was detected until day fifteen. Total $NH_3$ evolved during 26 days of composting was 2.972 g $kg_{VS0}^{-1}$ and it was found that condensate contained approximately 80% of that amount.

***Keywords:*** *composting, tobacco waste, adiabatic closed reactor, ammonia and carbon dioxide emissions*

## 1. INTRODUCTION

Industrial wastes include solid or liquid mass and contain considerable amounts of organic matter. Classification of industrial wastes of organic origin includes tobacco wastes, which are generated during different processes of the tobacco and cigarette production cycle. These wastes frequently contain residues of tobacco leaves [1].

Composting is an environmentally friendly and effective technology to treat or manage organic wastes. It is a biological treatment in which aerobic mesophilic and thermophilic microorganisms transform the biodegradable organic matter into $CO_2$, $H_2O$ and a stable organic matter-compost [2]. Carbon dioxide is identified as a biogenic gas, because $CO_2$ is a measure of microbial respiration and ammonia is generated as product of microbial transformation of organic nitrogen [3].

Composting the toxic tobacco waste would minimise waste and the compost could be useful for agricultural purposes. However, mismanagement of the composting process results in emission of harmful gases and corresponding environmental problems. [4]. Two major polluting gasses during tobacco composting are carbon dioxide ($CO_2$) and ammonia ($NH_3$). $CO_2$ is a greenhouse gas with the largest impact on climate changes, while ammonia is one of the main compounds responsible for generation of offensive odours and atmospheric pollution when composting organic waste with high nitrogen content [5].

The aim of this work was to determine the evolution of ammonia and carbon dioxide in the exhaust gases during composting of tobacco waste in a laboratory–scale column reactor.

## 2. ELABORATION

### 2.1. Materials and methods

#### *2.1.1. Tobacco Waste*

Tobacco waste, which is used in the composting experiments, was obtained from Cigarette Company in Croatia. Table 1 presents the main characteristics of the initial composting mixture.

Table 1. Characteristics of the initial tobacco waste

| Parameter | |
|---|---|
| Moisture (%) | 65 |
| Dry matter (%) | 35 |
| Volatile matter (%) | 78,43 |
| N-Kjeldhal (% dry matter) | 1,96 |
| C/N ratio | 21 |
| pH-value | 6,5 |

#### *2.1.2. Composting Experiments*

The composting experiment of tobacco waste was conducted in a closed thermally insulated column reactor with effective volume of 10 L. The reactor was operated at an airflow rate of 0.66 L $min^{-1}$ $kg^{-1}_{volatile\ solids\ (VS)}$ and the temperature was monitored by thermocouples connected to the data logger during the 26 days of composting period. Condensate and exhaust air were collected in volumetric flasks, ammonia was trapped in boric acid solution and carbon dioxide in sodium hydroxide solution. All experiments were performed in duplicate.

#### *2.1.3. Analytical Methods*

Composting samples, taken periodically from reactor, were tested for pH, moisture, volatile solid contents, carbon and nitrogen (C/N) ratio and microbial diversity. The moisture content and volatile solids in the composting mass were determined gravimetrically, pH-value was measured with pH meter and the total nitrogen content using Kjeldahl method [6].

Ammonium from the exhaust gas was absorbed into 4% boric acid [7] and carbon dioxide in 1 M sodium hydroxide. The graduated cylinder was used for measuring daily production of condensate. In condensate pH-value and presence of ammonium was checked regularly. The growth of both mesophilic and thermophilic bacteria and fungi were determined. The incubation time was 24-48 h for mesophilic and thermophilic bacteria and 72 h for mesophilic and thermophilic fungi. The temperature was 37$^{o}$C and 28$^{o}$C for mesophilic bacteria and fungi and 50$^{o}$C for thermophilic bacteria and fungi. The results were expressed as CFU per 1 g of dry matter [8].

### 2.2. Results and Discussion

#### *2.2.1. Temperature Profile and Growth of Microorganisms*

Temperature is one of the most important parameters for maintaining the efficiency of composting process. Biological activity is an indicator of biodegradation of organic matter because aerobic microorganisms produce heat in composting mass [7]. The temperature undergoes considerable changes due to a calorific effect, resulting from oxidative cleavage of covalent bonds in the substances during composting [9]. All composting processes are known to go through tree stages: mesophilic, thermophilic, and cooling.

The initial temperature of the composting mass was 25$^{o}$C and after 48 hours rapidly increased to 56$^{o}$C. The third day of composting, the temperature dropped to 39$^{o}$C and the day after increased again to a peak of 44$^{o}$C. Afterward, the composting mass started to cool until the compost and ambient temperatures levelled (Figure 1).

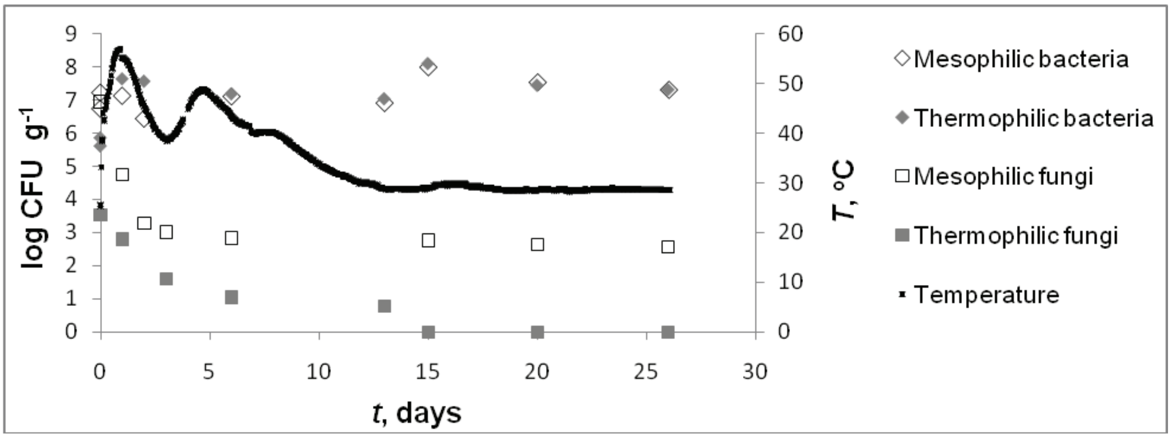



Figure 1. Temperature variations in composting mass and growth of microorganisms during 26 days of composting

The mesophilic stage usually starts at the beginning of a process during which the microorganisms undergo adaptation and proliferate [9]. The temperature levels in the composting mass tended to increase and reached 50-60°C due to the energy released from the biochemical reactions of the mesophilic microorganisms. Increased temperature enabled the growth of thermophilic microorganisms and their activity. In this phase, metabolic heat started to decrease as a result of biodegradation of macromolecules that uses a large amount of energy, and temperature started to drop [1]. It enabled the regrowth of mesophilic microorganisms. The secondary temperature peak that occurred were possibly a result of delayed microbial growth (recovered mesophilic microbial population) in the outer portions of composting mixture, either due to the water leached from the top, or lower heat removal rate due to the predominance of low constant aeration rate, or both [10]. At the end of the experiment, the organic components of waste undergo their final degradation and the temperature curve was typical of laboratory composting process and indicated that the system was operating satisfactorily.

The growth of both the mesophilic (20-45°C) and thermophilic (45-70°C) bacteria and fungi, at various stages of the composting process, was determined (Figure 1). The microbial species involved in the degradation of the substrate and their number has been changing with the change of the temperature in reactor. During the first day of the experiment, the number of mesophilic bacteria increased from $5.49\times10^6$ to $1.35\times10^7$ and at day fifteen up to $9.83\times10^7$. After that, their number slowly started to decrease. The exponential growth ($4.17\times10^5$ to $4.23\times10^7$) of thermophilic bacteria started after the first day because the temperature was about 50°C and until the end of composting their number increased no further. Bacteria are mostly responsible for starting the composting process because they consume the available soluble nutrients, which produces metabolic heat [11]. From the start of experiment, the number of mesophilic ($5.48\times10^4$) and thermophilic ($3.43\times10^3$) fungi decreased and until the end of process only mesophilic fungi were detected ($6.31\times10^2$).

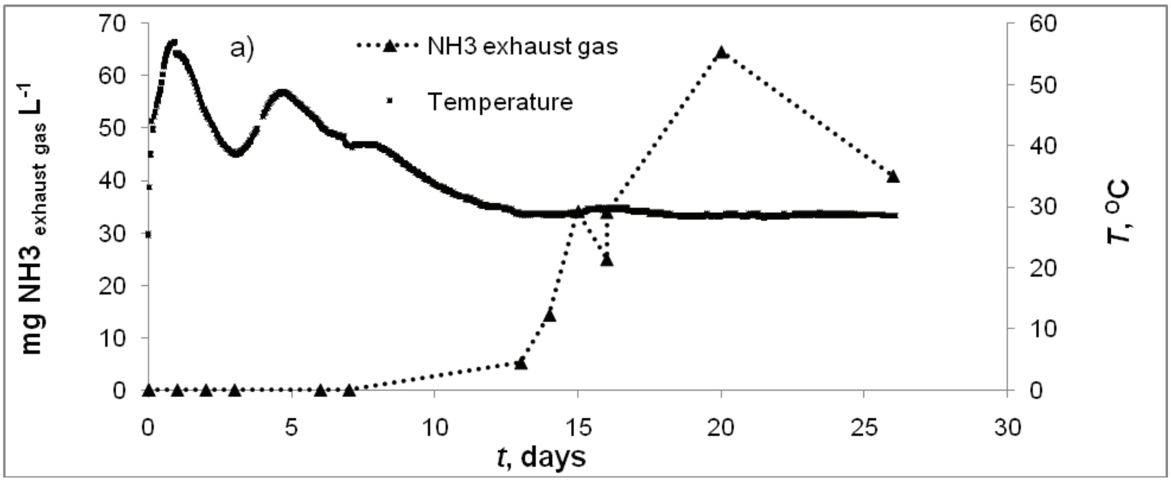
***2.2.2. Emission of Ammonia and Carbon Dioxide***

Ammonia and carbon dioxide are the main gases released during composting of tobacco waste and the obtained results of experiments are presented in Figures 2, 3 and 4.

*2.2.2.1. Ammonia Evolution and Influence of pH Value on its Emission*

Ammonia emissions have been proposed in some works as an indicator of the biological activity in composting materials with high nitrogen content [5]. Tobacco waste has high nitrogen content and low C/N ratio. It is known that temperature and pH are two main factors, which have influence on ammonia emission from the composting mass. High temperature and pH value affects ammonia volatilization, thus non-volatile ammonium ions are converted to the volatile ammonia form [5]. The pH values of composting mass ordinarily vary from weakly acidic to neutral. Due to the formation of ammonia it becomes alkaline, what is closely related to the activity of microorganisms participating in the process of compost formation [9].

Figure 2 (a) and (b) shows the evolution of ammonia in the exhaust gas and presence in condensate depending on temperature in reactor. It can be seen that concentration of ammonia in the exhaust gas and in condensate is lower during the initial phase with high temperature. In later phase of process, the ammonia emission was higher due to the transformation of biodegradable organic N to ammonium [5].



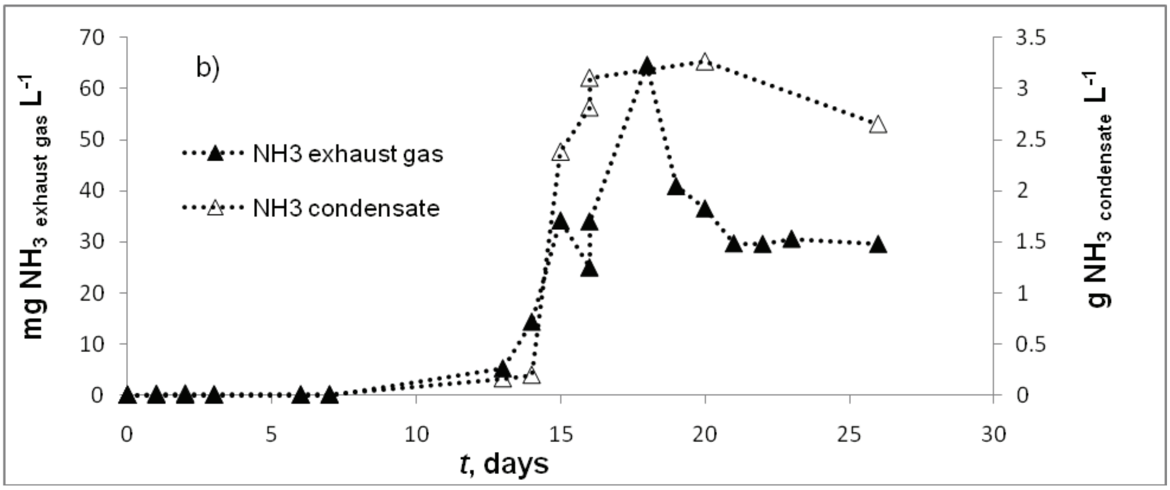




Figure 2. Presence of ammonia in condensate versus temperature (a) and correlation of evolution of ammonia in exhaust gases and in condensate (b) during 26 days of composting

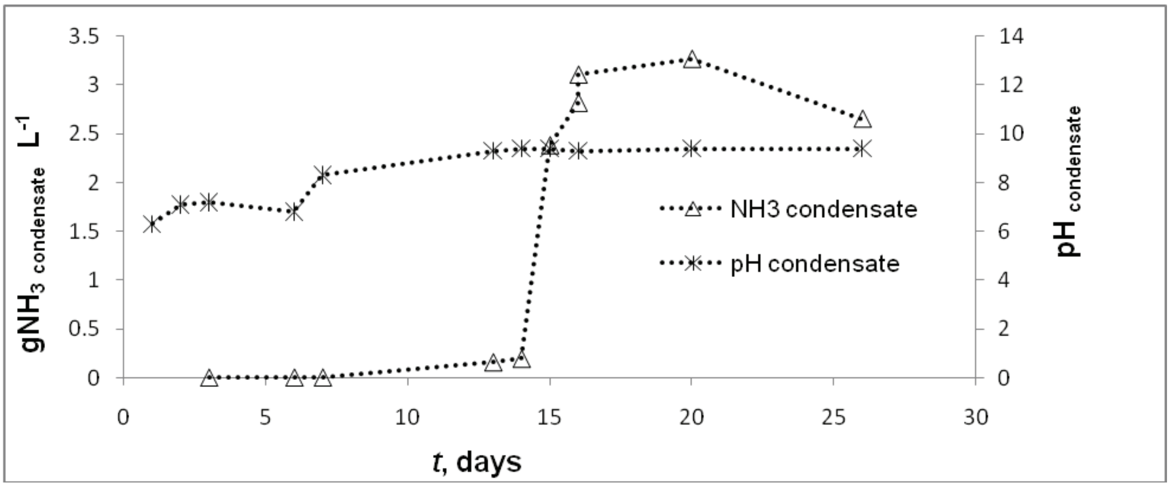



Figure 3. Evolution of ammonia in condensate and pH value of condensate during composting

From Figures 2 (b) and 3 it can be seen that on day 13 the concentration of ammonia in exhaust gas and in condensate increased with increasing of pH value of condensate. The increase of pH value during the composting process is due to the production of ammonium ions as a result of the ammonification process [12]. At day twenty, the emission of ammonia was still high. Apparently, the emission of $NH_3$

was influenced by pH condition of composting mass and its moisture content, microbial activity and continued aeration [13].

During the composting process, the pH value of condensate increased from an initial pH of 6.3 to 7.2 in the first 3 days and after 10 days to pH=9. Changes in pH value of condensate over reaction time corresponded well with variations in concentration of ammonia in condensate evolved from the biodegradation of the organic nitrogenous compounds [14]. These results correspond well with the general theory that variations in pH value are in relation with ammonia-ammonium equilibrium in the compost mixture. Furthermore, the pH value (pH = 9) of compost and condensate increased no more, but maintained in the same alkaline range during the subsequent period (Figure 3).

*2.2.2.2. Evolution of Carbon Dioxide*

The dynamics of $CO_2$ release in the compost reactor is highly influenced by the temperature regime. Equation (1) and (2) describe the production of $CO_2$, and equation (3) the absorption of $CO_2$ in the hydroxide solution [15].

$$C_5H_{19}O_3N + 12.5O_2 \rightarrow 10CO_2 + NH_3 + 8H_2O \quad (1)$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \quad (2)$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (3)$$

Figure 4 shows that emission of carbon dioxide is proportional with temperature and high microbial activity during the first 6 days. $CO_2$ evolved in the exhaust gases peaked at the same time. Thus, the emission rate of $CO_2$ during first two days was around 30.0 g $CO_2$ $kg_{VT0}^{-1}$ and reached maximum value at day 6 with amount of 55.0 g $CO_2$ $kg_{VT0}^{-1}$.

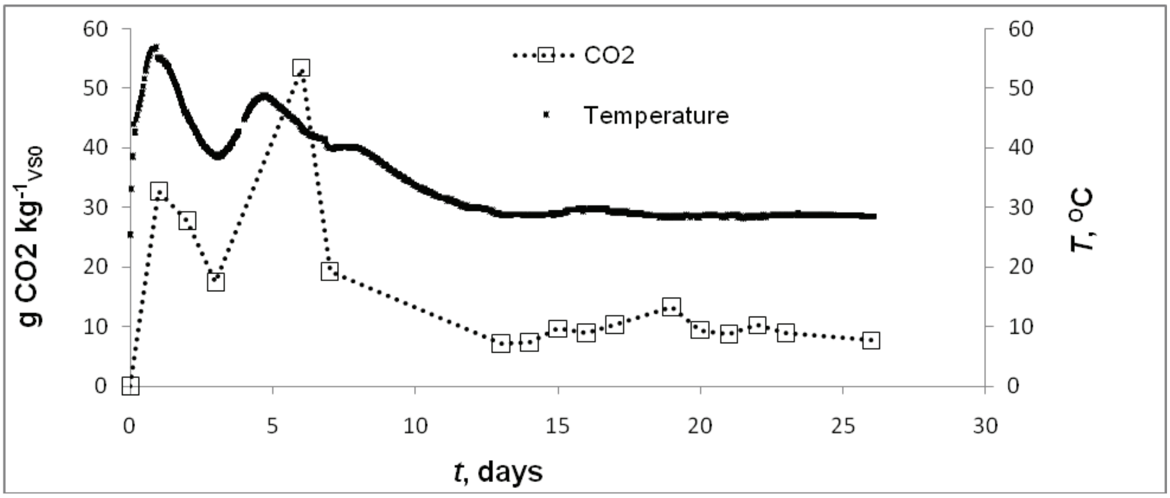



Figure 4 The evolution of carbon dioxide versus temperature during the composting of tobacco waste

Because of the intense biodegradation of organic fraction of waste between the second and the sixth day the temperature and evolution of $CO_2$ increased. The variation of $CO_2$ concentration during that period is in correlation with bacterial activity and with reaction temperature (Figures 1 and 4). After 10 days, the concentration of carbon dioxide became lower and until the end of process remained between 8.0 and10.0 g $CO_2$ $kg_{VS0}^{-1}$.

***2.2.3. C/N Ratio and Conversion of Substrate during Composting of Tobacco Waste***

The C/N ratio has frequently been used to describe the course of organic waste degradation and it is widely accepted that a high substrate C/N ratio implies a low mineralization rate due to N deficiency [16]. The initial carbon and nitrogen ratio is the most important index of compost quality. Based on the nutritional requirements of the microbes that are active in composting, C/N ratio of the organic matter should be in the order of 20-25 parts carbon to 1 part nitrogen; a declination from this ratio leads to slow composting process [1].

The initial C/N ratio of tobacco waste was 21 and it was gradually decreasing with increasing of conversion of volatile solids, expressed as degradation of organic matter in waste solid (Figure 5). The most intense degradation is evident in the first 13 days, i.e. in the first half of the composting process.

The nitrogen as ammonium ions remained in composting mass until the day 15 when the volatilization of ammonium ions start (Figure 3). At the end of composting the conversion of substrate was 45%, C/N ratio was 10 and the compost as a product possessed a satisfactory agronomic value.

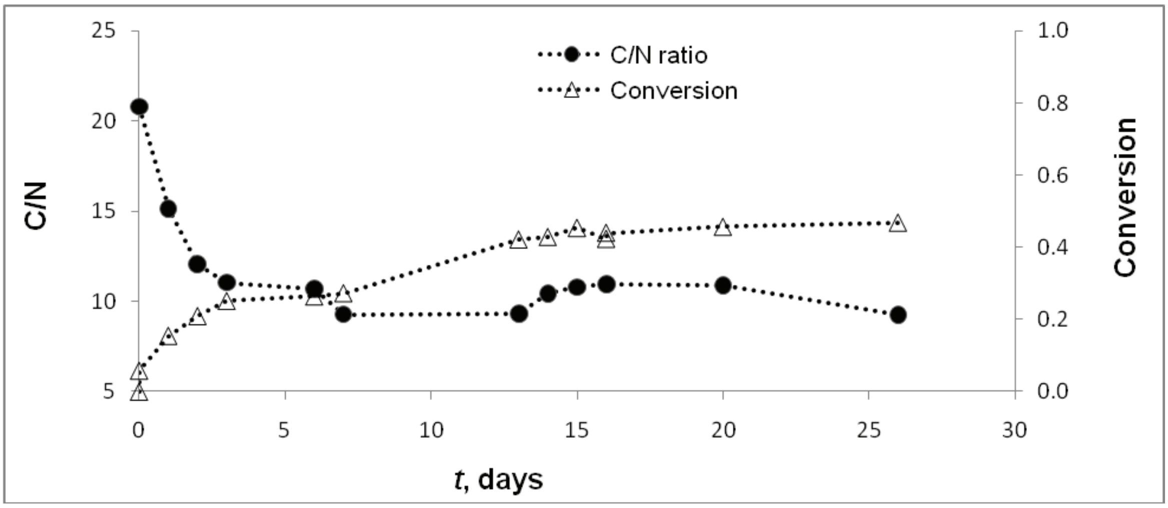



Figure 5 C/N ratio versus conversion of tobacco waste during 26 days of composting

## 3. CONCLUSIONS

During 26 days of composting of tobacco waste in a closed reactor the following has been recorded. Initial pH value of compost substrate was 6.5 and initial C/N ratio 21 and at the end of composting process was 9 and 10 respectively.

From the second to fifth day temperature oscillated between 56°C and 50°C, due to delayed microbial growth in lower portions of tobacco waste. At different stages of composting noticed were a change in the number and type of microorganisms.

The C/N ratio, pH value and temperature influenced on ammonia emissions. At the beginning of process the concentration of volatile ammonia was low and then was increased with increasing of pH value (pH = 9) of composting mass. The total concentration of ammonia in condensate was 2.972 g $kg_{VS0}^{-1}$ after 26 days.

The most of carbon dioxide evolved during the first 6 days of composting process due to the highest activity of microorganisms. The cumulative evolved $CO_2$ during 26 days of composting was 302.0 g $CO_2$ $kg_{VS0}^{-1}$.

**Acknowledgement**
This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia under the Research Project 125-1251963-1968.

## REFERENCES

[1] N. Saithep, S. Dheeranupatana, P. Sumrit, S. Jeerat, S. Boonchalearmkit, J. Wongsanoon and C. Jatisatienr, Composting of tobacco plant waste by manual turning and forced aeration system, Journal of Science and Technology 02 (2009) 248-260.

[2] N. Saithep, S. Dheeranupatana, P. Sumrit, S. Jeerat, S. Boonchalearmkit, J. Wongsanoon and C. Jatisatienr, Composting of tobacco plant waste by manual turning and forced aeration system, Journal of Science and Technology 02 (2009) 248-260.

[3] T.-J. Hu, G.-M. Zeng, D.-L. Huang, H.-Y. Yu, X.-Y. Jiang, F. Dai, G.-H. Huang, Use of potassium dihydrogen phosphate and sawdust as adsorbents of ammonical nitrogen in aerobic composting process, Journal of Hazardous Materials 141 (2007) 736-744.

[4] E. Pagans, X. Font, A. Sanchez, Biofiltration for ammonia removal from composting exhaust gases, Chemical Engineering Journal 113 (2005) 105-110.

[5] E. Pagans, R. Barrena, X. Font, A. Sanchez, Ammonia emissions from the composting of different organic wastes. Dependency on process temperature, Chemosphere 62, (2006) 1534-1542.

[6] Institute, Austrian Standardization, Austrian Standard S 2023, Analytical methods and quality control for waste compost, Vienna 1986.

[7] T. Osada, K. Kuroda, M. Yonaga, Determination of nitrous oxide, methane, and ammonia emissions from a swine waste composting process, J Mater Cycles Waste Manag. 2 (2000) 51-56.

[8] S. Duraković, S, Opća mikrobiologija, Zagreb, Zagreb 1996

[9] A.D. Neklyudov, G.N. Fedotov, A.N. Ivankin, Aerobic Processing of Organic Waste into Compost, Biochemistry and Microbiology 42 (2006) 341-353.

[10] Y. Liang, J.J. Leonard, J.J.R. Feddes, W.B. Mcgill, Influence of carbon and buffer amendment on ammonia volatilization in composting, Bioresource Technology 97 (2003) 748-761.

[11] F. Briški, Z. Gomzi, A. Hublin and M. Vuković, Aerobno kompostiranje otpadaka voća i povrća: modeliranje procesa, Kemija u industriji 52 (2003) 95-102.

[12] B. Beck-Friis, S. Smars, H. Jonsson; H. Kirchmann, Gaseous Emissions of Carbon Dioxide, Ammonia and Nitrous Oxide from Organic Household Waste in a Compost Reactor under Different Temperature Regimes, J. agric. Engng Res. 78 (2001) 423-430.

[13] Y.-K. Jeong, S.-J. Hwang, Optimum doses of Mg and P salts for precipitating ammonia into struvite crystals in aerobic composting, Bioresource Technology 96 (2005) 1-6.

[14] S.-H. Kwon, D.-H. Lee, Evaluation of Korean food waste composting with fed-batch operations II: using properties of exhaust gas condensate, Process Biochemistry 39(2004) 1047-1055.

[15] T. Haug, Roger, The Practical Handbook of Compost Engineering, Chapter 9, Lewis Publishers, United States of America 1993, pp. 326-327.

[16] M.P. Bernal, C. Paredes, M.A. Sanchez-Monedero, J. Cegarra, Maturity and stability parameters of composts prepared with a wide range of organic wastes, Bioresource Technology 63 (1998) 91-99.