Adsorption of HCN from Pyrolysis of Tobacco Leaves with Na\textsubscript{2}CO\textsubscript{3}, NaHCO\textsubscript{3}, and Proline

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Abstract
Hydrogen cyanide (HCN) was produced by flameless combustion of dried tobacco leaves for investigating the adsorption on Na\textsubscript{2}CO\textsubscript{3}, NaHCO\textsubscript{3}, and proline (HNC\textsubscript{4}H\textsubscript{7}COOH). The concentration of HCN could be produced steadily at 0.73 mg/dm\textsuperscript{3}. For the given 245 cm\textsuperscript{3} of smoke with the flow rate of 17.5 cm\textsuperscript{3}/s, the efficiency of adsorption of HCN was improved to 80% by the addition of the optimal amounts of Na\textsubscript{2}CO\textsubscript{3}, NaHCO\textsubscript{3}, and proline (HNC\textsubscript{4}H\textsubscript{7}COOH), which were 10, 20, and 30 mg respectively. In the circumstances, the breakthrough concentration was reduced to 0.15 - 0.20 mg/dm\textsuperscript{3}.

Keywords
Adsorption, HCN, Tobacco Leaves, Sodium Carbonate, Sodium Bicarbonate, Proline

1. Introduction
The increase in population requires more energy and food. To reduce the costs, industrial factories look for changing waste materials; such as wood, bark, bagasse, rice husk and agricultural straw, to energy instead of conventional fossil fuels. Meanwhile, cultivators might burn the remaining crop after cultivation for replantation. Various toxic gases can be produced by combustion of this biomass [1]-[13]. As this biomass has nitrogen as a constituent, besides carbon and hydrogen, nitrogen compounds, such as HNCO, HCN, NO\textsubscript{x}, N\textsubscript{2}O, and NH\textsubscript{3}, can be generated by combustion [1] [2] [3].

Hydrogen cyanide, HCN, is generally produced by the combustion of various synthetic materials containing nitrogen constituent, such as polyamide (nylon), 1,3,5-triazine-2,4,6-triamine (melamine) and polycrylonitrile. It can also be produced by the pyrolysis of biomass containing amino acids, heterocyclic compounds of nitrogen or dicarboxylic acids [8] [9] [10] [11] [12]. Even though...
the amount of hydrogen cyanide, HCN, from biomass pyrolysis is small, it is harmful to public health. It is so toxic asphyxiating that it inhibits the metabolism process. Moreover, cyanide ions might block oxidative respiration and might also cause cancer [14] [15] [16].

Historically, various substances, such as carbon, activated carbon, zeolite, catalysts, nanotube and architectural materials, were studied for the adsorption of hydrogen cyanide [17]-[33]. Oliver et al. [30] revealed that copper containing synthetic activated carbons produced from porous sulfonated styrene/divinylbenzene resins could adsorb hydrogen cyanide gas effectively without the formation of (CN)_2. Rajakovic et al. [31] researched that the carbon materials impregnated with metal organic compounds could adsorb hydrogen cyanide, especially copper (II)-tartrate. Furthermore, the impregnated organic compounds had more efficiency than inorganic compounds. While R. R. Kottawala et al. [32] exposed that the polar compounds, containing carboxyl, hydroxyl or carbonyl groups, had high efficiency for adsorbing hydrogen cyanide, depending on their induced dipole and charge-dipole interactions. Peter Branton et al. [33] reported that the efficiency of the adsorption of hydrogen cyanide depended on physisorption or chemisorption.

According to the previous researches on the pyrolysis of tobacco leaves, hydrogen cyanide, HCN, could be generated directly by the pyrolysis of dried tobacco leaves, which was used for this study. The direct adsorption of hydrogen cyanide on sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3) and proline (pyrrolidine-2-carboxylic acid, HNC_4H_7COOH) compounds was investigated without producing porous adsorbents. In addition to their chemical structures, the influence of both amounts of compounds and pyrolysis gas on the adsorption of hydrogen cyanide could be investigated more conveniently than porous adsorbents.

2. Material and Methods

2.1. Material

Dried tobacco leaves were used as raw materials for producing hydrogen cyanide (HCN). They were cut into fine strips. A gram of strips of dried leaves was packed in a paper cylinder with a diameter of 8 mm. and length of 84 mm. All packs of dried leaves were kept in a container at 22˚C with 60% relative humidity in order to control moisture contents of dried leaves.

The glass fiber filter pads, with 2 mm thick and 44 mm diameter, were dipped into the solutions of sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3) or proline (pyrrolidine-2-carboxylic acid, HNC_4H_7COOH) for adsorption experiment. The concentration of these solutions could be varied for variation of amounts of compounds on the pads for investigating the influence on the adsorption of HCN. The pads were dried at 100˚C for 3 hours. They were put in the adsorption experimental set, consisting of hydrogen cyanide generation with flameless combustion HCN, adsorption on an investigated compound,
collecting the unadsorbed hydrogen cyanide in the 0.625 M sodium hydroxide solution, and a piston vacuum pump, respectively, as shown in Figure 1.

### 2.2. The Adsorption Experimental

Each pack of dried leaves was combusted flamelessly, while the combustion gas was pumped by the piston vacuum pump through the pad containing a selected adsorbing compound with the flow rate of 17.5 cm³/s. The unadsorbed hydrogen cyanide was collected in the 40 cm³ of 0.625 M NaOH solution for analyzing the breakthrough amount of hydrogen cyanide. Each condition of adsorption was repeated at least 4 times.

### 2.3. Quantifications

The NaOH solution, which collected the unadsorbed amount of hydrogen cyanide, was analyzed by the continuous flow analyzer, Skalar, with the detection limits of CN⁻ of 0.02 mg/dm³. In addition, the amount of hydrogen cyanide, which was adsorbed on the pad was analyzed in the same manner as the unadsorbed hydrogen cyanide above, by dissolving the adsorbing pad in 40 cm³ of 0.625 M NaOH solution. The adsorption efficiency was evaluated by Equation (1).

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\text{Adsorption Efficiency} = \frac{\text{Amount HCN adsorbed} \times 100}{\left(\text{Amount HCN adsorbed} + \text{Amount HCN unadsorbed}\right)} \quad (1)
\]

### 3. Results and Discussion

#### 3.1. The Adsorption of HCN on Na₂CO₃, NaHCO₃, and Proline

Hydrogen cyanide was generated by flameless combustion at the end of a cylindrical pack of dried strips of tobacco leaves. Meanwhile, the combustion gas was pumped steadily through the other end of the pack via the adsorption zone at the flow rate of 17.5 cm³/s by the piston vacuum pump. The unadsorbed hydrogen cyanide was collected cumulatively in the 0.625 M NaOH solution after passing the adsorption zone as shown in Figure 1. With consecutive flameless combustion of up to 6 packs of dried leaves, the total amount of hydrogen cyanide which was, collected in the NaOH solution, increased proportionally to the cumulative amount of smoke passing the adsorption zone, as shown in Figure 2. This demonstrated that hydrogen cyanide was produced steadily at the average concentration about 0.73 mg/dm³ by the apparatus for adsorption investigation. In addition, the analysed results of the amount of HCN adsorbed on the pad revealed that the cumulative amount adsorbed on the pad was slightly more than a half of the amount of HCN flowing through the adsorption zone for the whole range of investigation. This has demonstrated the unsaturated adsorption for the total amount of HCN investigated.

With only the filter pad in the adsorption zone, the cumulative amount of hydrogen cyanide adsorbed on the pad increased proportional to the cumulative volume of smoke flowing through the adsorption zone in the same manner as
Figure 1. The experimental set for adsorption of hydrogen cyanide from combustion of dried stripes of tobacco leaves.

Figure 2. The relation of cumulative total and adsorbed amount of hydrogen cyanide generated by flameless combustion with the cumulative smoke volume flowing through the adsorption zone with flow rate of 17.5 cm³/s.

The total amount of HCN produced as shown in Figure 2. The concentration of HCN was reduced at least 70% by adsorption on the filter pad for the first 245 cm³ of smoke, which was produced by the first pack of dried leaves, hence the breakthrough concentration of HCN dropped below 0.20 mg/dm³, as shown in Figure 3. For additional amount of smoke produced by the second to the sixth pack of dried leaves, the concentration of HCN was reduced slightly more than 50% by further adsorption on the filter pad. Consequently, the breakthrough concentration of HCN increased to just below 0.35 mg/dm³. In the circumstances, the amount of HCN adsorbed on the pad was increased from 0.24 mg/g of pad for the first pack of dried leaves to 1.93 mg/g of pad for the additional 5 more packs of dried tobacco leaves.
Figure 3. The breakthrough concentrations of hydrogen cyanide of the adsorption systems containing 10 mg Na₂CO₃, NaHCO₃ and proline (HNC₄H₇COOH), respectively, relative to the filter pad only, with flow rate of 17.5 cm³/s.

With 10 mg of sodium carbonate (Na₂CO₃) on the filter pad, the breakthrough concentration of HCN dropped below 0.10 mg/dm³ for the first 200 cm³ of smoke, as shown in Figure 3. This corresponded to at least 85% of HCN in the smoke was adsorbed on the pad containing 10 mg sodium carbonate. The breakthrough concentration of HCN increased gradually to just above 0.25 mg/dm³ with further adsorption of HCN in smoke beyond 200 cm³ up to 1500 cm³. The breakthrough concentration approached to the values of the filter pad without sodium carbonate. The results indicated that most sodium carbonate on the pad almost reached the saturated adsorption. With the similar amount of sodium bicarbonate (NaHCO₃) or proline (HNC₄H₇COOH) on the filter pad instead of sodium carbonate, the breakthrough concentrations of HCN were similar to that of sodium carbonate. The similar breakthrough concentration of HCN might relate to the presence of common carbonyl group on these compounds [32].

3.2. The Effect of Amounts of Na₂CO₃, NaHCO₃, and Proline

As the breakthrough concentration of HCN increased drastically within the range of the first 245 cm³ of smoke, of which could be produced by each pack of dried tobacco leaves with the flow rate of 17.5 cm³/s, the influence of the amount of these compounds on the adsorption of HCN was investigated. For sodium carbonate (Na₂CO₃), the adsorption efficiency was almost constant at 80% by increasing the amount more than 10 mg, as shown in Figure 4. In the circumstances, the breakthrough concentration of HCN was reduced to just below 0.15 mg/dm³, as shown in Figure 5. By reducing the amount of sodium carbonate on the filter pad, the efficiency dropped drastically to 70%, 60% and just above 50% respectively. The maximum adsorption efficiency for the smoke produced by
Figure 4. The total adsorption efficiency of hydrogen cyanide on Na₂CO₃, NaHCO₃ and proline (HNC₄H₇COOH), for 245 cm³ of smoke with flow rate of 17.5 cm³/s.

Each pack of dried tobacco leaves was achieved by 10 mg sodium carbonate. In other words, the optimum amount of sodium carbonate for adsorption of HCN from 245 cm³ of smoke was 10 mg.

By using 10 mg of sodium bicarbonate (NaHCO₃) on the filter pad, the adsorption efficiency was about 70%, as shown in Figure 4. With the double
amount of sodium bicarbonate (NaHCO₃) on the filter pad, the adsorption efficiency was improved from 70% to almost 80%. In the circumstances, the breakthrough concentration of HCN dropped in the same manner as that of sodium carbonate but was above 0.15 mg/dm³, as shown in Figure 5. By reducing the amount of sodium bicarbonate to a half of the base condition, the adsorption efficiency was just above 50%, while the breakthrough concentration became just below 0.3 mg/dm³. The atomic polarization of H atom on sodium bicarbonate was much lower than that of Na atom on sodium carbonate [34] [35], therefore, the adsorption efficiency on sodium bicarbonate was less than that of sodium carbonate for the same amount on the filter pad. The maximum adsorption efficiency could be achieved by adding the amount of sodium bicarbonate as double amount of the optimum amount of sodium carbonate.

With 10 mg of proline on the filter pad, the adsorption efficiency was just 60% under the given conditions. This was influenced by the presence of organic functional group (HNC₃H₇-) on proline molecule, of which the polarizability was much less than those of Na and H atoms sodium carbonate and sodium bicarbonate, respectively. It could be improved quite proportionally to the increasing amount of proline. The maximum adsorption efficiency at 80% could be achieved by adding 30 - 40 mg proline on the filter pad, as shown in Figure 4. In the circumstances, the breakthrough decreased gradually from just above 0.2 mg/dm³ to just above 0.15 mg/dm³, as shown in Figure 5. By reducing the amount proline on the pad, the adsorption efficiency dropped drastically to just above 50% in the same manner as both sodium carbonate and sodium bicarbonate. Therefore, the optimum amount of proline for adsorption of HCN from 245 cm³ smoke was 30 mg.

4. Conclusion

Hydrogen cyanide could be produced steadily by flameless combustion of dried stripped tobacco leaves with concentration of 0.73 mg/dm³. With the flow rate of 17.5 cm³/s, a half of hydrogen cyanide produced could be adsorbed on the filter pad, with specific adsorption of 0.24 mg HCN/ g pad, under which the breakthrough was reduced to 0.3 - 0.4 mg/dm³ at the room temperature. With the addition of Na₂CO₃, NaHCO₃, or proline (HNC₃H₇COOH) on the pad, the maximum efficiency for adsorption of HCN in the smoke of 245 cm³ could be improved to about 80%. In the circumstances, the optimum amounts of Na₂CO₃, NaHCO₃, and proline were 10, 20, and 30 mg, respectively. While the breakthrough concentration of HCN was reduced to the range of 0.15 - 0.20 mg/dm³.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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