Method for the Control of NO_x Emissions in Long-Range **Space Travel**

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The wheat straw, an inedible biomass that can be continuously produced in a space vehicle has been used to produce activated carbon for effective control of NO_x emissions from the incineration of wastes. The optimal carbonization temperature of wheat straw was found to be around 600 °C when a burnoff of 67% was observed. The BET surface area of the activated carbon produced from the wheat straw reached as high as 300 m²/g. The presence of oxygen in flue gas is essential for effective adsorption of NO by activated carbon. On the contrary, water vapor inhibits the adsorption efficiency of NO. Consequently, water vapor in flue gas should be removed by drying agents before adsorption to ensure high NO adsorption efficiency. All of the NO in the flue gas was removed for more than 2 h by the activated carbons when 10% oxygen was present and the ratio of carbon weight to the flue gas flow rate (W/F) was 30 g·min/L, with a contact time of 10.2 s. All of NO was reduced to N₂ by the activated carbon at 450 °C with a W/F ratio of 15 g·min/L and a contact time of 5.1 s. Reduction of the adsorbed NO also regenerated the activated carbon, and the regenerated activated carbon exhibited an improved NO adsorption efficiency. However, the reduction of the adsorbed NO resulted in a loss of carbon which was determined to be about 0.99% of the activated carbon per cycle of regeneration. The sufficiency of the amount of wheat straw in providing the activated carbon based on a six-person crew, such as the mission planned for Mars, has been determined. This novel approach for the control of NO_x emissions is sustainable in a closed system such as the case in space travel. It is simple to operate and is functional under microgravity environment.

Introduction

In long-range space travels, such as the travel to Mars, life support cannot depend on storage alone; rather, it requires a fully regenerative system as well, i.e., waste must be reclaimed for reuse. The waste includes inedible portions of crops and human feces.

Among various reclamation technologies under investigation for use in space travel, incineration is perhaps the most promising technology because it rapidly and completely converts the waste to carbon dioxide, water, and minerals. Also, incineration is already the most thoroughly developed technology for use in a terrestrial environment. The major difficulty with the use of incineration, particularly in a closed environment, is the emission of pollutants, such as NO_x and SO₂ that can accumulate, thus necessitating a flue gas cleaning system.

To conserve nutrients for life support, NO_x should be converted to N₂, NH₃, and/or nitrates. The N₂ can be used to replace cabin N2 leakage and/or the loss of N2 during combustion, while the NH₃ and nitrates can be recycled as part of plant hydroponics nutrient solutions. The SO₂ should be converted to sulfate for recycling as part of nutrient solutions as well.

Many flue gas cleanup technologies have been developed to remove NO_x and SO₂ from terrestrial incineration exhaust streams.²⁻²¹ Most of the technologies

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require expendable materials, making them unsuitable for space applications. In addition, the safety, energy requirements, sustainability, and functionality under microgravity conditions need to be addressed. For example, processes using catalysts $^{3-5}$ might be undesirable due to the possibility of catalyst poisoning which limits the life span of a catalyst. Also, it is difficult to use wet processes $^{6-15}$ that handle liquids because of the microgravity environment. In addition, using potentially hazardous high-pressure systems and/or systems that require excessive amounts of electric energy is unwarranted for space travel.

In view of the aforementioned constraints and requirements, we are investigating an approach involving the use of hydroponically grown wheat straw, an inedible biomass that can be continuously produced in a space vehicle, to clean up flue gas pollutants generated during incineration. Previously, we have found that flue gas from the incineration of biomass contains an insignificant amount of SO₂ and that most of the sulfur in the biomass ends up as sulfate in flyash. Presumably, SO₂ reacts with the alkali metal in the biomass; thus, this study focuses on the control of NO_x emissions. The approach involves the carbonization of inedible biomass to produce activated carbon for the adsorption of NO_x and the subsequent reduction of the adsorbed NO_x to N₂ by the activated carbon. The sufficiency of the wheat straw produced in a space vehicle for the control of NO_x emissions is also addressed.

Experimental Section

Apparatus. The preparation of the activated carbon, the adsorption of NO_x and the reduction of NO_x by the activated carbon were performed in a furnace system. The main component of the system is either a 5.08-cm-i.d. tube reactor (for the preparation of char) or a 1.91-cm-i.d. stainless steel tube reactor (for adsorption, de-adsorption, and regeneration), all 76 cm in length. The tubular reactors are put into a tube furnace (Thermolyne, type F121100) for heating. The furnace has the function of running an automatic set-point-ramping program.

Materials. The following materials were used: NO (5% with N_2 as the balance, Scott Co.), standard NO (500 ppm with N_2 as the balance, Scott Co.), CO₂, N_2 , O₂ (Airgas Co.), and hydroponically grown wheat straw (WS).

Preparation of Carbon. Wheat straw was cut into needle-shape pieces with dimensions ranging 2-6~mm in length, 1-2~mm in width, and 0.2-2~mm in thickness, using a blender. After the biomass was shredded, it was packed tightly into a stainless cylinder for pyrolysis and activation. Nitrogen and carbon dioxide were used as the pyrolysis and activation gases, respectively. The gas flow rate was 0.5-1.0~L of nitrogen per

minute for pyrolysis and 0.25 L of carbon dioxide per minute for activation. The amount of biomass used was approximately $50.0-60.0\,$ g for each batch. The pyrolysis and activation temperature (between 300 and 800 °C) and times (between 0.5 and 6 h) were varied during carbonization to determine optimal activation conditions. The activation temperature was $50\,$ °C higher than the pyrolysis temperature. After the carbonization treatment, the dimension of the wheat strawderived activated carbon did not exhibit noticeable change compared with wheat straw materials before the treatment. The notation of the activated carbon "WS-2-600-1-650" indicates that the activated carbon was prepared from wheat straw with a 2 h pyrolysis time at 600 °C followed by 1 h of activation at 650 °C. Once activation was complete, CO_2 was supplied to the sample until it could be sealed in a container.

Biomass on a space mission would likely come from a hydroponic system. The mineral content of hydroponic biomass can be much higher than that of field-grown biomass if nutrients are supplied luxuriously to the hydroponic solution. A typical hydroponic plant solution^{22,23} has a nutrient ratio of N:K:Ca:P:S:Mg =16:6:4:2:1:1 and contains micronutrients of B, Mn, Zn, Cu, Co, Mo, and Fe. The concentration of potassium (K) in the solution is about 6 mM. Thus, hydroponic activated carbon adsorption efficiencies may differ significantly from field-grown biomass. Field grown biomass generally has less than 10% mineral (ash) content, while hydroponic biomass can have as much as 30% mineral content. Because of this, many of the experiments were performed using char, which had been soaked in deionized water for 2 h to remove the soluble minerals. After soaking, the char was drained and dried at 150 °C for 1 h before use.

Characterization. The specific surface areas of each sample was determined by gas adsorption using an automated adsorption apparatus (Micromeritics, ASAP 2010). Nitrogen adsorption/desorption was measured isothermally at $-196\,^{\circ}\mathrm{C}$. Before any such analysis, the sample was degassed at 250 $^{\circ}\mathrm{C}$ in a vacuum at about $10^{-3}\,\mathrm{Torr}$. The nitrogen isotherms were analyzed with the BET equation to determine the surface areas of the chars. The BJH²⁴ that allows the computation of pore sizes from equilibrium gas pressures and provides the adsorption cumulative pore size distributions of the samples were also determined.

Adsorption. Most of the NO_x in flue gas from combustion is in the form of NO. Also, NO_2 is readily adsorbed on activated carbon. Consequently, efforts were made to determine conditions for maximum removal efficiency of NO. The effect of oxygen and moisture in the flue gas on the NO adsorption efficiency of the activated carbon was studied.

The adsorption experiments were performed by using a simulated flue gas with variable concentrations of N_2 , carbon dioxide, oxygen, NO, and H_2O . The NO and NO_2 concentrations were analyzed by a chemiluminescent NO_x analyzer (Thermo Environmental Instruments Inc., model 14A). The amount of NO adsorbed by the activated carbon was determined from the difference in the NO concentrations of the inlet and outlet gases. It was assumed that missing NO was adsorbed onto the activated carbon.

In a typical adsorption run, the activated carbon, ranging between 5 and 30 g, was placed inside the stainless steel tube reactor (1.91-cm-i.d.). A simulated flue gas, with a flow rate of 0.5 or 1 L/min, passed through the reactor and the outlet gas was directed to a NO_x analyzer. The superficial velocity of gas in the reactor is 2.78 cm/s with a flow rate of 1 L/m. The volume of the carbon is 85 cm³ for a 15 g batch because

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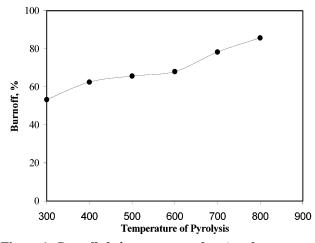


Figure 1. Burnoff of wheat straw as a function of temperature under anaerobic conditions.

the density of the carbon was measured to be 0.176 g/cm³. Thus, the empty bed contact time is 5.1 and 10.2 s for a ratio of the amount of the carbon to the flue gas flow rate, W/F, of 15 and 30 g·min/L, respectively.

Reduction and Regeneration. Reduction of the NO and regeneration of the activated carbon were performed by heating the NO-loaded char in the absence of oxygen. To evaluate the behavior of the process over time, a purge gas flow of nitrogen was applied during experiments, while the outlet gas was directed to a gas analyzer. The sample was heated from room temperature to 600 °C at a rate of 40 °C/ min. The gas flow rate for reduction and regeneration was 0.5 or 1.0 L of nitrogen per minute.

Results and Discussion

Preparation and Characterization of Activated Carbon. Burnoff. To determine the optimal carbonization temperature, samples of wheat straw were heated at 100 °C intervals between 300 and 900 °C for 2 h during pyrolysis and between 350 and 950 °C for 1 h for activation. Afterward, percent burnoff was measured. Higher carbonization temperatures caused larger portions of the samples to burn off, as shown in Figure 1. The burnoff was 68%, 86%, and 100% at 600, 800, and 900 °C, respectively. The percent burnoff increases only slightly with the increase of temperature from 400 to 600 °C. However, pyrolysis and activation temperatures above 700 °C were observed to cause significant amounts of wheat straw to burn to ash. All of the wheat straw was burnt to ash (100% burnoff) with a pyrolysis temperature of 900 °C. It is recommended that reactions not be run at temperatures exceeding 600 °C.

Surface Area and Cumulative Pore Area. Each activated carbon was characterized by measurements of its average pore size and surface area. Three types of pores developed in the carbon particles: micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm). The BET surface area of wheat straw char carbonized at temperatures between 300 and 700 °C is shown in Figure 2. The surface area passes through a maximum of 105 m²/g at a pyrolysis and activation temperature of 600 and 650 °C, respectively. The decrease in surface area beyond 600 °C is caused by sample burning off. Using temperatures much lower than 600 °C would compromise the maximum amount of effective adsorption surface area attainable. It is not only important to

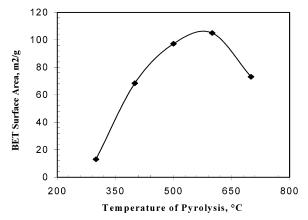


Figure 2. BET surface areas of the activated carbon produced from wheat straw at a variety of temperatures.

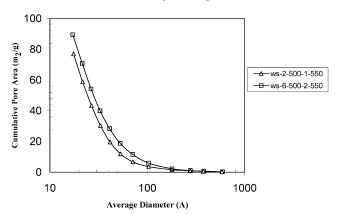


Figure 3. BJH cumulative pore area of the activated carbon produced from wheat straw at different pyrolysis and activation times.

run reactions at temperatures low enough to prevent burnoff and ash formation but also at temperatures high enough to generate effective surface areas, which would be at 600 °C for wheat straw. The BET surface area of the activated carbon after the removal of water-soluble minerals was determined to be as high as 300 m²/g.

Figure 3 shows the BJH adsorption cumulative pore area of wheat straw activated carbon generated at different pyrolysis and activation times. It is evident from the plot that samples derived from longer pyrolysis and carbonization times exhibited a higher micropore count compared to shorter times. However, too long pyrolysis and activation reaction times cause an adverse increase in burnoff percentage. Though wheat straw carbonized with a pyrolysis time of 6 h and activation time of 2 h still demonstrated a higher cumulative pore area than the shorter times, it also produces larger amounts of burnoff. The optimum condition to generate a high micropore count, but at the same time minimize material loss, was determined to be 2 and 1 h for the pyrolysis and activation, respectively.

Determining the Optimal Temperature and Time for Carbon Preparation. Optimal pyrolysis and activation temperatures and times for carbon preparation were determined on the basis of the amount of NO_x that could be adsorbed by the activated carbon. The NO adsorption efficiency of wheat-straw-derived activated carbons generated by different pyrolysis and activation temperatures are shown in Figure 4. A gas mixture containing 250 ppm of NO, 5% O₂, 10% CO₂, with N₂ as the balance

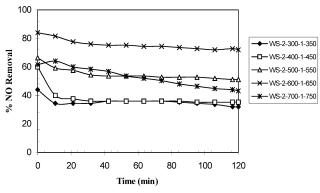


Figure 4. NO removal efficiency by wheat straw-derived activated carbon produced with different pyrolysis and activation temperatures. Flue gas composition: 250 ppm NO, 5% O₂, 10% CO₂, N₂ the balance; flow rate: 0.2 L/min; WF = 8 g·min L⁻¹ with an empty bed contact time of 3.4 s.

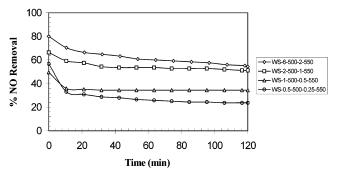


Figure 5. NO removal efficiency by wheat straw-derived activated carbon produced with different pyrolysis and activation times. Flue gas composition: 250 ppm NO, 5% O₂: 5%, 10% CO₂, N₂ the balance; flow rate: 1 L/min; WF = 8 g·min L⁻¹ with an empty bed contact time of 2.72 s.

was passed, at a flow rate of 250 mL/min, through a tubular reactor containing 2 g of activation carbon (WF = 8 g·min/L) at 25 °C. It is evident from the plots in Figure 4 that the WS-2-600-1-650 activated carbon had the best adsorption efficiency. The activated carbons derived above 600 °C have higher ash concentrations than those derived below, while those derived below have lower percent micropore counts and surface area—both explaining why wheat straw generated at 600 °C had the best adsorption efficiency.

The NO adsorption efficiencies of samples carbonized for differing pyrolysis and activation times are shown in Figure 5. It is evident from these plots that activated carbons carbonized for prolonged pyrolysis and activation times have better adsorption efficiencies than those carbonized for shorter times. Although the micropore count and the surface area of activated carbon increases with an increase of the preparation time, prolonged activation results in higher burnoff rates and the production of ash. A balance must be reached when setting carbonization time, one that will generate the largest surface area without significant burnoff. We have found that the optimal pyrolysis and activation times for wheat straw are 2 and 1 h, respectively. However, because of the amorphous nature of the activated carbon, we found that a quantitative mathematical expression on the NO adsorption capacity as a function of the carbonization/activation temperature and time, the NO adsorption temperature and time, and

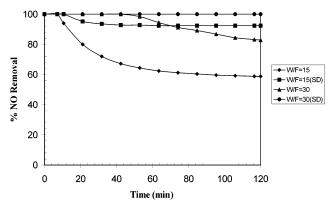


Figure 6. NO removal efficiency by wheat straw-derived activated carbon, WS-2-600-1-650, before and after soaking and drying (SD). Flue gas composition: 250 ppm NO, 10% CO₂, 10% O₂: 10%, with N₂ the balance; flow rate: 1 L/min; WF= 15 and 30 g·min L⁻¹ with an empty bed contact time of 5.1 and 10.2 s, respectively; at 25 °C.

the concentrations of NO and O_2 cannot be reliably reproduced.

The hydroponic biomass possesses high mineral content. The effect of the minerals on the NO adsorption efficiency by activated carbon was studied. The activated carbon was first soaked in water to dissolve the soluble minerals and then dried to remove the moisture from the carbon particles. The adsorption experiments using the mineral-free activated carbon were performed and the results indicate that the NO adsorption efficiency was substantially improved (Figure 6). A 100% NO removal efficiency was obtained with the mineral-free carbon for the entire 2 h experiment, using a gas mixture containing 250 ppm NO and 10% O₂ and at a W/F, the ratio of the amount of carbon (g) to the flow rate of gas (L/min), of 30 g·min/L. The contact time of flue gas with the carbon bed was 10.2 s. With the same contact time, however, the NO removal efficiency of carbon containing mineral exhibited a decrease from the initial 100% to 92 and 82% after 1 and 2 h adsorption, respectively. The improved NO removal efficiency by the activated carbon with mineral removed is attributed to the increase of the carbon surface area, which was otherwise covered by the minerals. The BET surface area of the activated carbon after the mineral was removed by water dissolution reached 300 m²/g. Because of this finding, the parametric study on the NO removal efficiency was performed mostly with the activated carbon after soaking in water for 2 h to remove soluble minerals and then drying at 150 °C for 1 h to remove the moisture, WS-2-600-650 (SD), where S and D stand for soaking and drying, respectively.

Parametric Study of the NO Removal Efficiency. *Effects of Oxygen on Adsorption.* Experiments on the effect of oxygen on the NO adsorption by WS-2-600-1-650 (SD) have been performed. The soluble minerals in the activated carbon have been removed. Oxygen concentrations were varied between 0 and 10%. Figure 8 shows that the NO adsorption on activated carbons increases with the increase of oxygen concentration in flue gas. A 100% NO removal efficiency was obtained at 20 °C with 10% oxygen and a *WF* of 30 g·min/L, which corresponds to a gas—solid contact time of 10.2 s, during the entire 2-h run. The NO removal efficiency decreased to 90%, 65%, and 10% after 1 h adsorption

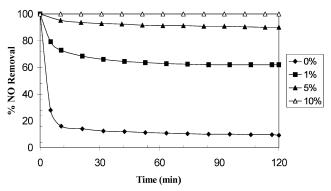


Figure 7. The effect of oxygen on NO removal efficiency by WS-2-600-1-650(SD). Flue gas composition: 250 ppm NO, 10% CO_2 with N_2 the balance and at a flow rate of 1 L/min; W/F =30 g·min L^{-1} with an empty bed contact time of 10.2 s.

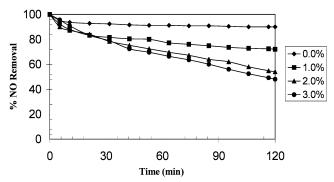


Figure 8. The effect of water vapor on NO removal efficiency by WS-2-600-1-650(SD). Flue gas composition: 250 ppm NO, 10% CO2, 5% O2 with N2 the balance and at a flow rate of 1 L/min; F/W = 30 g·min L⁻¹ with an empty bed contact time of 10.2 s; at 25 °C.

as the oxygen concentration decreased to 5%, 1%, and 0%, respectively. From Figure 7, the NO removal efficiency as a function of time (t in min) can be expressed as % NO removal efficiency = $ae^{-bt} + c$, where a, b, and c are constants and dependent on the oxygen concentration. The a, b, and c are, respectively 89, 0.3, and 10.9 for 0% oxygen; 36, 0.125, and 63 for 1% oxygen; 9, 0.048, and 90.5 for 5% oxygen; and 0, 0, and 100 for 10% oxygen.

It is obvious that the presence of oxygen is critical for NO adsorption by carbon to be effective. This phenomenon is attributed to the catalytic oxidation $^{25-29}$ of NO by O₂ on the carbon surface to form NO₂, which is more readily adsorbed by the activated carbon as described by eqs 1 and 2.

$$2C() + O_2 \rightarrow 2C(O) \tag{1}$$

$$C(O) + NO \rightarrow C - NO_2 \text{ or } C - ONO$$
 (2)

where C() represents the activated carbon with active surface sites. One class of active surface site was postulated to be the highly unsaturated carbon atoms,

while the second class of active site was postulated to be the unsaturated edge sites.³⁰ The adsorbed oxygen on the activated carbon is known to become a more effective oxidant than the molecular oxygen.^{25,31}

Effects of Moisture on Adsorption. It is expected that the high-temperature flue gas will be cooled before it passes into the carbon bed to avoid combustion of carbon due to the presence of flue gas oxygen. This cooling results in the condensation of water vapor. Flue gas can contain up to 3.0% v/v H₂O even after being cooled to room temperature; thus, it is important to study the effect of water vapor on the removal efficiency of NO by carbon. Figure 8 shows that moisture causes a significant decrease in the NO removal efficiency of the carbon, WS-2-600-1-650 (SD). The more water vapor present in the flue gas, the lower the NO removal efficiency. With a simulated flue gas containing 250 ppm NO, 5% O₂, using a W/F = 30 g·min/L, the NO removal efficiency reduced to 92%, 74%, 56%, and 48% after 2 h adsorption as the H₂O vapor concentration increased from 0%, 1%, 2%, to 3%, respectively. This is because water vapor competes effectively with NO for the adsorption sites on carbon particles. From Figure 8, the NO removal efficiency in the presence of water vapor as a function of time (t in min.) can be expressed as %NO removal = $de^{-t/f} + g$, where d, f, and g depend on the concentration of water vapor in the flue gas. The d, f, and g are, respectively, 8.6, 0.088, and 90.7 for 0% water; 24.6, 0.031, and 72.7 for 1% water; 58.2, 0.010, and 37.1 for 2% water; and 70.4, 0.010, and 28.2 for 3% water. The detrimental effect of water vapor on NO adsorption can be overcome by the removal of water vapor either by using drying agents or by cooling the flue gas to low temperatures prior to adsorption.

Reduction of NO by Activated Carbon. The adsorbed NO can be desorbed from the activated carbon if the temperature of the carbon bed is raised. Further increases in temperature result in the reduction of NO to N₂ by the activated carbon. Simultaneously, the activated carbon is regenerated as a result of the reaction. The kinetics and mechanism of the reduction of NO_x by the carbon has been extensively studied. $^{28,30,32-41}$ It has been found that not all carbons are equivalent; the origin, natural impurities, and heat treatments of a carbon affect its efficiency, both as an adsorbent and as a reducing agent. The reduction mechanism may be described as follows:

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$$2C() + NO \rightarrow C(N) + C(O)$$
 (3)

$$C(O) + NO \rightarrow C - NO_{2} \tag{4}$$

$$C() + NO2 \rightarrow C(N) + O2$$
 (5)

$$3C() + NO_2 \rightarrow C(N) + 2C(O)$$
 (6)

$$C(N) + C(N) \rightarrow 2C() + N_2$$
 (7)

$$C(N) + NO \rightarrow C(O) \text{ or } CO + N_2$$
 (8)

$$C(N) + NO_2 \rightarrow CO_2 + N_2 \tag{9}$$

The oxygen-containing and nitrogen-containing species, denoted as C(O) and C(N), respectively, are known to form on the carbon surface. ^{28,35–39}

Experiments on NO reduction were performed by heating the NO-saturated carbon under anaerobic conditions. To evaluate the behavior of the process over time, a N2 purge gas flow of 1.0 L/min was passed through the carbon bed and subsequently directed to the NOx analyzer. Desorption was conducted at a temperature ramp rate of 40 °C/min from room temperature to 600 °C. As the temperature of the carbon bed was increased, NO was desorbed from the surface of the activated carbon. Further increases in temperature resulted in the reduction of NO to N2 by the activated carbon. The fraction of adsorbed NO reduced to N2 can be calculated by subtracting the amount of NO desorbing from the carbon bed from the total amount of NO adsorbed. The fraction of adsorbed NO that is reduced depends on the temperature and the flow rate of N₂ gas.

Figure 9 shows the fraction of the desorbed NO integrated over the temperatures as the temperatures of the carbon bed was raised. As can be seen, NO started desorption at 300 °C and stopped desorption after 500 °C, and after integration we found that only 9.1% of the total NO originally adsorbed were desorbed as NO. The difference of which is attributed to the reaction of NO with the activated carbon to form N2. Thus, more than 90% of the adsorbed NO was reduced to N2 by wheat straw-derived carbon under the condition when the carbon bed was heated from 20 °C to 500 °C. Since the ramp rate was 40 °C per min, it is expected that all of the adsorbed NO would be reduced to N2 within the 12 min time under an isolated condition when there is no N₂ carrier gas passing through the bed during the heating process.

Another set of experiments were performed to study the reduction of NO by activated carbon as a function of temperature and WF. In this study, the temperature was varied between 300 and 450 °C and WF was raised from 10 to 40 g·min/L. Figure 10 shows that with a feed gas containing 250 ppm NO with the balance N₂, the fraction of NO reduced by activated carbon increases with the increase of temperature at a given WF, and the fraction also increases with the increase of WF at a given temperature. All inlet NO was reduced to N₂ at 450 °C with a WF above 15 g·min/L. At a lower temperature of the carbon bed, a larger WF is needed to ensure a 100% NO reduction. A WF of at least 30 and 40 g·min/L is needed to reduce all of NO to N₂ at 400 °C and 350 °C, respectively. The WF of 30 and 40

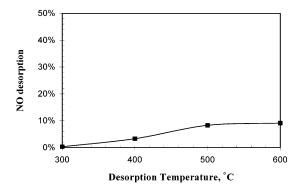


Figure 9. Fraction of NO desorbed when integrated over temperatures as the temperature of the wheat straw-derived carbon bed was raised at 40 °C/min. N_2 was used as a carrier gas at 1 L/min. The amount of carbon used was 15 g.

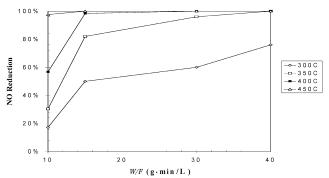


Figure 10. The effect of the ratio of carbon weight to flue gas flow rate (WF) on the reduction efficiency of NO by wheat straw-derived activated carbon at various temperatures. The flue gas contains 250 ppm NO with N_2 the balance and was at a flow rate of 0.5 L/min. The amount of the carbon used was 5, 7.5, 15, and 20 g, corresponding to an empty bed contact time of 3.4, 5.1, 10.2, and 13.6 s, respectively.

g·min/L corresponds to an empty bed contact time of 10.2 and 13.6 s, respectively. Higher temperatures and/ or larger WF ratios are more favorable for NO reduction. An equation describing the NO reduction to N_2 by the wheat straw-derived carbon as a function of WF at various temperatures can be obtained from the data of Figure 10 as % NO reduction = 100 h(WF)ⁱ, where h and h are 0.026 and 0.94 at 300 °C, 0.07 and 0.76 at 350 °C, 0.31 and 0.34 at 400 °C, and 0.96 and 0.012 at 450 °C.

The NO reduction efficiency also depends on the concentration of NO in the system. Figure 11 shows the NO reduction by activated carbons at 450 °C with two inlet NO concentrations, 250 and 1000 ppm. The results indicate that the higher the inlet NO concentrations, the smaller the fraction of the inlet NO that is reduced at a given WF. The entire inlet NO was reduced by the wheat straw-derived activated carbon with a WF of 15 and 30 g·min/L using 250 and 1000 ppm of NO, respectively. The WF of 15 and 30 g·min/L corresponds to an empty bed contact time of 5.1 and 10.2 s, respectively.

Assessment of the Amount of Inedible Biomass Required. Because of the length of the space travel, the sufficiency of the amount of inedible biomass in providing the activated carbon for life-support systems should be assessed. For a six-person crew, such as that planned for a mission to Mars, the average food con-



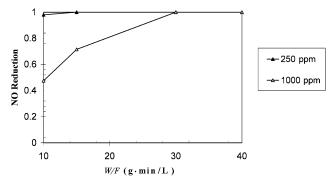


Figure 11. The effect of NO concentration on the NO reduction efficiency by wheat straw-derived activated carbons at 450 °C; N₂ is the carrier gas at a flow rate of 0.5 L/min; The amount of carbon used was 5, 7.5, 15, and 20 g, corresponding to an empty bed contact time of 3.4, 5.1, 10.2, and 13.6 s, respectively.

sumption is about 0.25 kg/day per capita. 42,43 Six people would need 1.5 kg of wheat per day. Wheat straw yield depends on the specific varieties harvested and is widely affected by agronomic and climatic factors. An average ratio of 1.3 kg-straw/kg-grain is found for most common varieties.44 Burnoff accounts for 66.7% at 600 °C in pyrolysis and 650 °C in activation, while the loss of carbon mass from soaking and drying was determined to be about 14.4%. Thus, 203 kg of wheat-straw-derived activated carbon can be produced per year.

By incinerating feces, inedible biomass, and trash, between 3 and 30 g of NO_x will be generated per day, depending mostly on the amount of nitrogen in the inedible biomass. The range in the amount of NO_x produced covers 90% pretreatment removal of nitrogen to no pretreatment. 45 (Calculations were made under the assumption of maximum NO emission.) About 10% of the nitrogen in the waste will be released as NO_x. 46

The assumption was made that the regeneration of activated carbon via the reduction reaction will take place once a week. The loss of carbon mass was determined to be about 0.99% at 600 °C per cycle of regeneration if the regeneration takes place when flue gas NO after the carbon bed reaches 4.8 ppm, the space maximum allowable concentration. After one year, all of the activated carbon should be incinerated and replaced. Calculations based on the above assumptions yield 210 g of NO emissions per week on a space shuttle, and the adsorption capacity of NO by the activated carbon was determined to be 5.46 mg-NO/g-carbon. Thus, about 38.5 kg of wheat-straw activated carbon will be required. This quantity of activated carbon can be supplied by one adsorption tank, which is loaded with

64.6 kg of wheat-derived activated carbon at the beginning of the year. Every week, the tank should be regenerated. After one year, the total loss of carbon would be 26.1 kg, taking into consideration 52 cycles of regeneration. At the end of the year, there will still be 38.5 kg of carbon to maintain high adsorption efficiency. Thus, the activated carbon produced from wheat straw is sufficient to control NO_x emission. In fact, NO_x adsorption was shown to improve after regeneration.⁴⁷

Conclusion

Commercial activated carbon, made mostly from materials such as coconut shells and coal, has been studied for the adsorption and/or reduction of NO_x.48-51 In this paper, we have demonstrated that wheat straw, an inedible byproduct of a crop that can be grown in space vehicles, can be converted to activated carbon for the adsorption and reduction of NO in an effective manner. No expendable material, such as binders, is needed to make an effective activated carbon.

The optimal carbonization temperature of wheat straw was found to be around 600 °C for a burnoff of 67%. The BET surface area of the hydroponically grown wheat straw-derived activated carbon with mineral content was determined to be 105.2 m²/g, while the surface area reached 300 m²/g after the mineral was removed from carbon by water dissolution. Higher carbonization temperatures caused larger portions of the biomass to burn off and turn to ash.

The presence of oxygen in the flue gas is necessary for the effective adsorption of NO by the activated carbon. Water vapor, however, inhibits the NO adsorption efficiency. Consequently, water vapor in the flue gas should be removed either by condensation at low temperatures or by drying agents before adsorption to ensure high NO adsorption efficiency. All of the NO in the flue gas was removed for more than 2 h when 10% oxygen was present and the carbon weight to flue gas flow rate ratio (*W/F*) was 30 g·min/L with an empty bed contact time of 10.2 s. When in equilibrium with a gas mixture containing 250 ppm of NO, the adsorption capacity of NO on the wheat straw-derived activated carbon containing mineral was found to be 1.42 mg-NO/ g-carbon. The NO adsorption capacity increases to 5.46 mg-NO/g-carbon after mineral was removed.

After the adsorption of NO_x, the activated carbon can be regenerated for reuse. The regeneration can be simply done by heating the carbon bed under anaerobic conditions to 600 °C, when all of the adsorbed NO_x is reduced to N2. The loss of carbon mass was determined to be about 0.99% for wheat straw-derived activated carbon per cycle of regeneration at 600 °C if the regeneration takes place when flue gas NO after the

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carbon bed reaches 4.8 ppm, the space maximum allowable concentration. The regenerated activated carbon exhibits improved NO adsorption efficiency.

It was determined that with a load of 64.6 kg of wheat straw-derived carbon at the beginning of the year, 38.5 kg of carbon remains after 52 cycles of regeneration. For a six-person crew, about 203 kg of wheat straw-derived carbon can be produced per year. Thus, the amount of activated carbon obtained from wheat straw is sufficient for the control of NO_x emissions. So taking all aspects into consideration, we have demonstrated that the use

of wheat straw to provide activated carbons for the control of NO_{x} emissions from the combustion in a space vehicle is sustainable and effective for deep space missions.

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