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Reactive Carbon from Life Support Wastes for Incinerator Flue Gas Cleanup

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ABSTRACT

This paper presents the results from a joint research initiative between NASA Ames Research Center and Lawrence Berkeley National lab. The objective of the research is to produce activated carbon from life support wastes and to use the activated carbon to adsorb and chemically reduce the NO_x and SO_2 contained in incinerator flue gas. Inedible biomass waste from food production is the primary waste considered for conversion to activated carbon. Results to date show adsorption of both NO_x and SO_2 in activated carbon made from biomass. Conversion of adsorbed NO_x to nitrogen has also been observed.

INTRODUCTION

Space travel by humans depends upon the operation of life support systems. Current life support systems such as the Shuttle life support system are effective and appropriate for small crews on relatively short missions. The waste handling system is largely a store and return to Earth system. Longer missions, however, will require much more from the waste treatment system than storage. For fully regenerative life support systems the waste treatment system must recover carbon and nutrients from the waste for recycle back to the food production system.

A number of solid waste reclamation technologies are under investigation for space applications. Technologies such as incineration, supercritical water oxidation, steam reformation, and electrochemical oxidation are at

various stages of development for use in space. Incineration is perhaps the most promising technology because it rapidly and completely converts the waste to carbon dioxide and water and minerals, it lends itself to experiment more affordably than most of the other technologies, and it is already the most thoroughly developed in a terrestrial environment. The major difficulty with the use of incineration, particularly in a closed environment, is the emission of pollutants that can build up, necessitating a flue gas cleanup system.

The objective of the proposed research effort is to research, design and build a novel regenerable flue gas cleanup system based on the ability of activated carbon to first adsorb and then chemically reduce contaminants. This system will operate without the need of expendables and it will remove contaminants from the incinerator flue gas. The system makes the activated carbon from wastes that are generated in space; an added bonus of this system is the potential to make activated carbon that could be used in other systems such as the trace contaminant control system and the water treatment system.

The following sections first address the character of the waste and the resulting flue gas contaminants that a waste incinerator produces. Next is a description of how the reactive activated carbon cleanup system works in a life support system. Last is a description of the experimental approach and the experimental results. The experimental results include the effects of temperature, oxygen composition, moisture, starting material, preparation method, and regeneration on the performance of activated carbon.

WASTE CHARACTERISTICS

Production rates and composition of solid wastes have been described in previous reports (Wydeven, et al., 1989,1990, Upadhye, et al., 1993). Some of the types of waste include feces, trash, and inedible biomass. In a bioregenerative system with full food production the inedible biomass is the largest component of waste. Inedible biomass is the most important waste stream to be processed in order to reclaim carbon dioxide and nutrients. Feces is an important waste to consider because it is hazardous. Table 1 shows the elemental composition of wheat straw (and for comparison, feces). Wheat straw is a significant and representative component of inedible biomass. Inedible biomass such as wheat straw can be used to make activated carbon.

Table 1. Characteristics of Wastes –Wheat Straw (Fisher, et al., 1998)

Parameter	Feces (elemental composition based on dry weight basis)	Dried Wheat Straw
Moisture Content	65-85%	0%
C	43%	42%
H	6.3%	5.6%
N	2.4%	1 %
O	n/a	42%
S	n/a	0.1%
Elemental Ash	10-15%	8-11%

Table 2. Ultimate and Ash Analysis of Wheat Straw (Fisher, et al., 1998)

ULTIMATE ANALYSIS	
CARBON (%)	36.32
HYDROGEN (%)	5.19
OXYGEN (%)	40.09
NITROGEN (%)	3.04
SULFUR (%)	0.67
ASH (%)	14.69
Total (%)	100
BTU/LB	6144
VOL. MATTER (%)	67.49
FIXED CARBON (%)	12.44
WATER (%)	5.38
ASH ANALYSIS	
Al ₂ O ₃ (%)	0.01
CaO (%)	9.13
Fe ₂ O ₃ (%)	0.52
MgO (%)	4.89
MnO ₂ (%)	0.1
P ₂ O ₅ (%)	8.87
K ₂ O (%)	54.14
SiO ₂ (%)	0.04
Na ₂ O (%)	0.02
SO ₃ (%)	10.11
TiO ₂ (%)	< 0.01
Total (%)	87.83
FORMS of SULFUR	
Sulfate	0.28
Pyritic	<0.01

Table 2 shows an analysis of a sample of wheat straw including a breakdown of the ash component of the wheat straw.

Table 3. Flue Gas Emissions from Combustion of Simulated Feces as a Function of Oxygen Stoichiometry (Fisher, et al., 1998)

FLUE GAS COMPOSITION

Combustion of the inedible portion of hydroponically grown crops and wastes such as human feces produces mostly carbon dioxide, water, and ash. However, flue gas typically also contains small quantities of uncombusted hydrocarbons, carbon monoxide, and other contaminants. Organically bound nitrogen and sulfur can produce the contaminants NO_x and SO₂ in the flue gas. Table 3 shows the production of contaminants from incineration of a life support waste. Note that even though sulfur is present in the waste being burned, sulfur dioxide is not observed in the flue gas. Alkali metals in the waste can cause sulfur to leave the system in the ash as sulfate (Nordin, 1995).

Sample	1	2	3	4
CONDITIONS				
Feed Rate (g/hr)	794	794	760	760
Air Flow (slpm)	62.8	51	41.5	40.1
Stoichiometric Ratio	1.51	1.13	1.01	0.92
Bed Temperature (K)	1071	1083	975	978
Pressure (atm.)	0.91	0.9	0.89	0.89
EMISSIONS				
O ₂ (%)	6.26	1.99	0	0
CO ₂ (%)	10.45	13.61	14.54	15.44
CO (3% O ₂) (ppm)	14506	17830	22613	26033
THC (3% O ₂) (ppm)	313	945	6310	6377
NO _x (3%O ₂) (ppm)	790	660	216	337
SO ₂ (ppm)	<0.5	<0.5	<0.5	<0.5

FLUE GAS CLEANUP

There are many technologies for flue gas cleanup. Catalytic oxidation processes are very good at removing trace hydrocarbons and carbon monoxide. Catalytic reduction is commonly used commercially for NO_x removal. Of all the technologies available, almost none of the technologies are capable of removal of all the contaminants in one process step. Adsorption on activated carbon comes close to being the technology that is able to remove all the contaminants. Because of the ability to remove many contaminants, activated carbon is frequently used as the final scavenger process after some other process removes the bulk of the contaminants. Activated carbon can be a primary contaminant removal process for contaminants such as NO_x and SO₂ if it can be supplied in sufficient quantities to remove the contaminants.

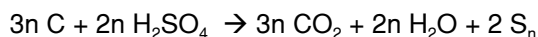
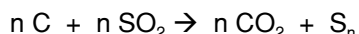
DESCRIPTION OF THE REACTIVE ACTIVATED CARBON PROCESS FOR LIFE SUPPORT APPLICATION

Following is a discussion of how the making and use of activated carbon would work in a life support system. Figure 1, Appendix 1, shows how the production and use of activated carbon integrates into an incineration system. Issues in such a system include the means for NO_x and SO₂ removal, the process for making activated carbon, and the ultimate fate of carbon, nitrogen, and sulfur in the system. Besides the process shown in Figure 1, Appendix 1, alternative processing schemes for activated carbon are discussed. Parameters such as weight and power that are important to space systems are estimated for an activated carbon process.

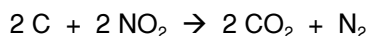
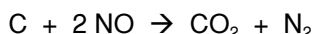
NO_x AND SO₂ REMOVAL ISSUES

Although not widely used commercially due to economic considerations, the technology of using activated carbon (or char) for the removal of SO₂ and/or NO_x has been successfully demonstrated (Neathery, 1997; Illan-Gomez, 1993; Tsuji, 1991,; Singoredjo, 1993; Kaneko, 1988). Note that activated carbon can serve both as an adsorbent and as a reductant. The primary redox reactions are as follows:

Sulfur:



Nitrogen:



Adsorption followed by chemical reduction of SO₂ has been commercialized as the Bergbau-Forschung/Foster Wheeler Process. In this process SO₂ from flue gas is adsorbed in a bed of char at 120–150°C. Subsequently, the saturated char is heated to regenerate the char and yield gaseous SO₂. The SO₂ stream is then reduced by coal at about 650°C to elemental sulfur (Bergbau, 1991).

Simultaneous adsorption followed by reduction of NO_x and SO₂ using a carbon bed was demonstrated by Cha. The Cha process employs carbon to adsorb NO_x and SO₂ in the presence of moisture and oxygen and then uses microwave energy to induce the reduction of the adsorbed NO_x and SO₂ by carbon to yield N₂, carbon oxides and elemental sulfur. Cha reports that this process achieves destruction of more than 95% of the NO_x and SO₂ (Cha, Yougen, et al., 1995,1996).

PRODUCTION OF ACTIVATED CARBON FROM BIOMASS

Commercially, activated carbon is made mostly from materials such as coconut shells and coal. A number of researchers have reported making activated carbon from inedible biomass type materials (Arriagada, et al., 1994; Balc,i et al., 1994; Reinoso-Rodriguez, et al., 1982; Rodriguez-Mirasol, et al., 1993; Usmani, et al., 1993; Gergova, 1994). The activated carbon made from the alternative biomass types of materials can sometimes approach the quality of commercial activated carbon. The availability of biomass on a space mission, and the need to avoid resupply of materials such as activated carbon makes the production of activated carbon on a space mission attractive.

THE PROCESS FOR MAKING ACTIVATED CARBON IN SPACE

Because activated carbon is useful as a flue gas contaminant cleanup material and because activated carbon can be made from available materials in space, it makes sense to investigate how the char could be made, used, and recycled in space. One process configuration, consisting of the preparation of char from inedible biomass, the adsorption of NO_x on a char bed, and the reduction of NO_x by carbon at high temperature to form N₂ is shown in Figure 1, Appendix 1. In this scheme sulfur leaves the system in the incinerator ash. The adsorption and reduction of NO_x are separate steps. Following is a detailed description of how various materials are handled in an incineration system as shown in Figure 1, Appendix 1.

FATE OF CARBON IN THE SYSTEM

Carbon enters the incineration system as waste or as carbon dioxide for activation or purge purpose. Purge CO₂ can come from the system that removes CO₂ from

the air such as the four-bed molecular sieve system. Most of the organic carbon is oxidized to CO_2 in the combustor. CO and trace hydrocarbons after the combustor are converted to CO_2 in an oxidation catalyst. All the CO_2 made or from purge either leaves the system in the exit gas or in the waste condensate from the incinerator.

Some of the waste biomass is used to make char (activated carbon). The char is used to treat flue gas leaving the incinerator. The char, once it is saturated with contaminants, will be treated to remove at least the NO_x as nitrogen. If the char is adequately regenerated by the treatment, then the char will be reused for removing flue gas contaminants. Otherwise the spent char is burned in the incinerator with the other wastes. Carbon in the char eventually leaves the incineration system as carbon dioxide. Carbon does not accumulate over time in this system. All carbon entering the incineration system will eventually be available to make its way back to the biomass production system as CO_2 .

FATE OF NITROGEN IN THE SYSTEM

Nitrogen enters the system as organic nitrogen in the biomass, as nitrogen gas in the air to the incinerator, and as nitrogen in various purge streams. Air nitrogen can come from the cabin. Purge nitrogen can come from whatever system provides nitrogen makeup to the cabin or, if necessary, there are devices that will concentrate nitrogen from air for use in the incineration system as a purge.

About 10% of the organic nitrogen (and nitrogen in other forms such as ammonia, if present) will oxidize to NO_x in the combustor. About 80% of the NO_x will be NO and 20% will be NO_2 . Only a very small portion of the gaseous nitrogen will convert to NO_x in the combustor (called thermal NO_x). The rest of the fuel nitrogen will convert to nitrogen gas in the combustor. NO will be adsorbed in the activated carbon bed at the end of the incineration system if sufficient oxygen is present. Some NO_2 may leave the system dissolved in the incinerator condensate. The rest of the NO_2 will also be adsorbed on the activated carbon bed. Gaseous nitrogen leaves the incineration system in the cleaned flue gas.

Adsorbed nitrogen on the char is converted to gaseous nitrogen in the treatment/regeneration step for the char. The NO_x is chemically reduced by the carbon of the char to form gaseous nitrogen and carbon dioxide. The gaseous nitrogen eventually leaves the system with the clean flue gas.

There is no accumulation of nitrogen in this system. A very small amount of the nitrogen may leave the system as NO_2 dissolved in the incinerator condensate. The vast majority of all the nitrogen that enters the incineration system will leave as gaseous nitrogen in the cleaned flue gas.

FATE OF SULFUR IN THE SYSTEM

Sulfur enters the incineration system with biomass. Sulfur is converted to SO_2 or SO_4^- in the combustor. Experience at NASA Ames and at the University of Utah with the combustion of biomass has shown that the sulfur mostly leaves the combustor in the ash as SO_4^- (Fisher, et al., 1998). Any sulfur not in the ash will leave the combustor as SO_2 and will adsorb on the activated carbon or dissolve in the incinerator condensate. Any SO_2 in the condensate will rapidly oxidize to SO_4^- . Any SO_2 adsorbed on the activated carbon will be returned to the combustor, where it will mostly leave the system with the ash as before in the first pass through the incinerator.

In summary, sulfur will leave the system mostly in the ash. A small amount of the sulfur may leave the system dissolved in the condensate. There is no accumulation of sulfur in the incineration system.

ALTERNATIVE PROCESSING SCHEMES

There are alternative processing schemes for making and using activated carbon. All of these schemes include NO_x removal. Some of these schemes are based on the conservative assumption that SO_2 is present in the flue gas. Although SO_2 is a common contaminant in incineration flue gas, studies of the combustion of biomass by NASA Ames and the University of Utah have shown that sulfur from biomass leaves the system in the ash rather than as SO_2 in the flue gas (Fisher, 1998).

One scheme includes removal of NO_x and SO_2 by adsorption on the activated carbon bed followed by a separate reduction step. In the separate reduction step the bed is heated to a high temperature in an inert atmosphere and the NO_x and SO_2 are reduced by reaction with the carbon of the carbon bed to nitrogen gas and elemental sulfur. Another scheme involves the reduction of NO_x by char at high temperature to N_2 followed by the dissolution of SO_2 to produce sulfuric acid. Based upon the experiments being conducted, the best scheme will be selected for testing in the later stages of the research.

SYSTEM PARAMETERS OF A REACTIVE CARBON PROCESS

A rough estimate of the weight, power, and volume was made for the production and use of activated carbon as the flue gas cleanup system. Assumptions:

- 1% loading of the activated carbon
- six person crew such as planned for a Mars mission
- incineration of feces, inedible biomass, and trash

- 3-30 g of NO_x produced per day based mostly on the amount of nitrogen in inedible biomass (NO_x is present in much higher concentrations than SO₂ based on ARC experience). The range in the amount of NO_x produced covers 90% pretreatment removal of nitrogen to no pretreatment (Finger, 1995).
- about 10% of nitrogen in the waste goes to NO_x (Pershing, et al., 1976)
- a regeneration of the adsorber activated carbon once a week via the reduction reaction.
- energy is based on the amount of energy needed to heat a 20 kg carbon bed to 600°C for the reduction reaction.

- The activated carbon must be characterized in terms of structure, surface area, and adsorptivity.

Issues that must be considered to develop the process for reduction of adsorbed species:

- Reaction rates of NO_x and SO₂ with activated carbon must be determined. The reaction rate will be a function of temperature, the characteristics of the activated carbon, and reactor conditions such as residual oxygen.
- Byproducts may form during the reaction. The reaction byproducts need to be characterized. The effect of temperature on byproduct formation needs to be understood.
- The activated carbon will be consumed during the reaction step and the carbon may also be physically degraded. This must be characterized in order to understand the lifetime of use for a batch of activated carbon.

Calculation from the above assumptions lead to a roughly 5 cubic foot processor weighing about 50 kg and using power at an average of about 5-50 Watt (instantaneous power during regeneration would of course be much higher). The range is due to the range in assumption of pretreatment (nitrogen can be extracted by a water wash and bio treatment) or no pretreatment to remove nitrogen before the incinerator. The energy usage of 5-50 Watts can be significantly reduced to almost zero by utilizing the heat of the incinerator, which runs at close to 600°C, to heat the reduction reactor.

GENERAL TASKS UNDERWAY

1. An investigation of methods of pyrolyzing and activating organic wastes to form the activated char
2. A determination of optimum conditions for the activated char to adsorb NO_x and SO₂ from combustion flue gas
3. Evaluation of the use of activated char to chemically reduce the adsorbed NO_x to N₂ and SO₂ to elemental sulfur

EXPERIMENTAL APPROACH

OBJECTIVES

The overall objective of the research project is to develop a process for removing NO_x and SO₂ from flue gas and converting those contaminants to N₂ and elemental sulfur using activated carbon made from waste biomass.

The research consists of two parts. First, a process must be developed to make good quality activated carbon from the available materials. Second, investigation and optimization must be conducted on the reduction reaction of the adsorbed NO_x and SO₂. The following issues must be addressed for the making of the activated carbon.

- Representative samples of material that would be available in space must be obtained and used. Hydroponically grown inedible biomass must be used because it differs from field grown plants in terms of inorganic content, and perhaps in other ways.
- The quality of activated carbon depends on many factors. It is necessary to consider the type of material to be used, the temperature and rate of heating during the carbonization step, the method of activation (CO₂ or steam), and any pretreatment such as water extraction to remove inorganics from the waste.

BIOMASS SOURCES

Biomass was acquired from various sources for making activated carbon. Because the biomass on a space mission would likely come from a hydroponic growth system, an effort was made to acquire biomass from hydroponic systems at Kennedy Space Center, Rutgers University, Utah University, and Tuskegee University. Rice husk and peanut shells were the first materials acquired.

Hydroponic biomass can differ significantly from field-grown biomass. Silica is present in field grown biomass, but it is generally absent in hydroponically grown biomass because silica is not usually an ingredient of hydroponic nutrient solutions. The total mineral content of hydroponic biomass can be much higher than field-grown biomass if nutrients are supplied luxuriantly to the hydroponic solution. Although field grown biomass generally has less than 10% mineral (ash) content, hydroponic biomass can have up to 30% mineral content.

Unfortunately biomass that is completely representative of what would be available on a space mission is not available. The various research facilities that produce hydroponic biomass do not produce large quantities. It is also not clear that the hydroponic biomass that is produced is the same as what would be produced on an actual space mission because mineral content of the biomass is so dependent on how the supply of hydroponic nutrients is controlled during plant growth. Some of the methods of activated carbon preparation include water extraction of the biomass before or during charring. The extraction tends to remove most of the inorganics from the biomass and thereby significantly reduced the amount of inorganics in the final carbon char. The approach for the present research is to use hydroponic biomass when available and to use field-grown biomass when hydroponic biomass is unavailable.

REACTOR SETUP

Carbonization reactors were setup for use in preparing and testing activated carbon. The reactor system used at ARC is shown in Figure 2, Appendix 1. The reactor system used at LBNL is shown in Figure 3, Appendix 1.

EXPERIMENTAL RESULTS

Experiments were conducted to evaluate the effects of temperature, oxygen composition, moisture, starting material, preparation method, and regeneration on the performance of activated carbon.

PERCENT BURNOFF

Experimental preparation of activated carbon was conducted using the hydroponic rice husk and peanut shells. Carbon dioxide was used as the activating gas. The time, temperature, and gas supply was varied during carbonization.

The gas flow rate for both activation and carbonization was one liter per minute. The amount of biomass was approximately 4.7–6.1 g for each sample. Once the time for activation was completed, nitrogen was supplied to the sample until it could be removed and sealed in a container.

Table 4 shows the percentage of dry biomass burned off for each sample for varying conditions. The activation conditions were always 500°C, 4 hours, and CO₂ activation gas.

TABLE 4. Burnoff from Activated Carbon Preparation

Sample Number	Material	Carbon-ization Temp [C]	Carbon-ization Time [hr]	Carbon-ization Gas	Percent Burnoff
1	RH	500	4	N ₂	48.7
2	RH	500	2	CO ₂	59.2
3	RH	600	2	CO ₂	48.4
4	RH	500	4	CO ₂	61.8
5	PS	500	2	CO ₂	72.5
6	PS	500	2	N ₂	66.7
7	PS	600	2	CO ₂	66.6

RH=Rice Hulls, PS=Peanut Shells

As can be seen, the amount of material burned off by the preparation can vary considerably depending on the material and process conditions. The range is about 45% to 75%. If oxygen is present during the carbonization, even higher burnoffs are possible.

PERFORMANCE OF COMMERCIAL ACTIVATED CARBON

A number of experiments were done with commercial activated carbon. These experiments demonstrated some of the adsorption behavior reported by other researchers and established a benchmark for comparison to the performance of the activated carbon made from biomass.

OXYGEN EFFECTS ON ADSORPTION

Room Temperature Experiments

Eighteen experiments were conducted at room temperature using commercial activated carbon. The principle variables manipulated were inlet concentrations of NO_x and Oxygen. Concentrations were controlled by varying the flow rates of the gases. Flowrates ranged from zero to seven liters per minute of air and one to four liters per minute of the gas containing NO_x. Figure 4 shows about 25% NO_x removal without oxygen present, about 80% removal at 4% oxygen, and about 90% removal at 18% oxygen.

The lowest NO_x outlet concentration was 6.98 ppm with an oxygen concentration of 17.75%. The space maximum allowable concentration (SMAC) in the human occupied cabin is 4.8 ppm.

Another series of experiments was conducted that evaluated the effect of moisture in the flue gas as well as the effect of oxygen concentration on NO_x adsorption. Figure 5 shows the NO removal efficiency with a commercial activated carbon (Calgon CTC-60, 560 m²/g) as a function of oxygen concentration. A gas mixture with 200 ppm of NO passed through a tubular reactor

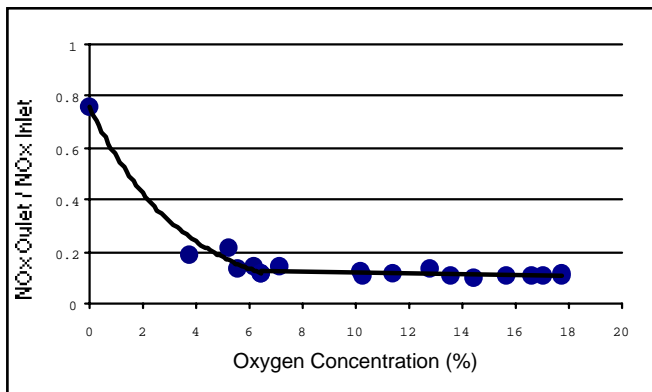


Fig. 4. NO_x outlet concentration/inlet concentration vs. oxygen concentration at 20°C. commercial activated carbon.

containing 15 g of carbon at a flow rate of 1,000 ml/min at 20°C. The NO removal efficiency increases asymptotically with increasing oxygen concentrations in the feed gas. The figure also shows that the NO removal efficiency does not change significantly when the feed gas is saturated with water vapor.

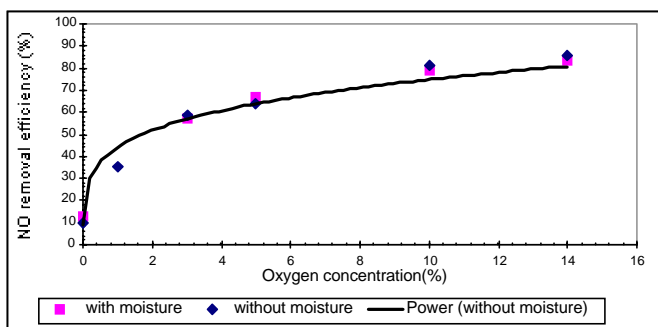
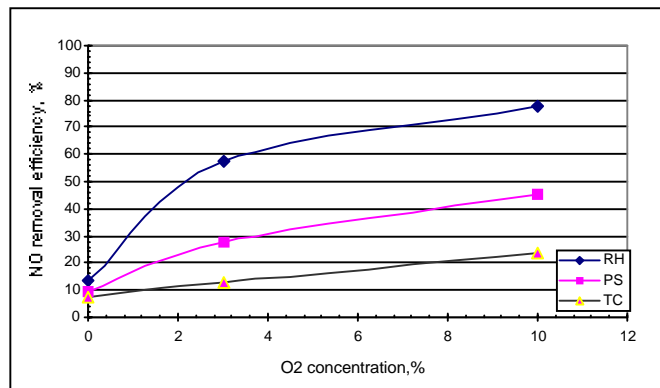


Fig. 5 Effect of oxygen and moisture on removal efficiency of NO with commercial activated carbon from coconut shell.

Experiments on the effect of oxygen on the NO_x adsorption using activated carbon made from biomass have also been done. Char from rice husks (RH) was prepared using a simulated flue gas at 300°C for 15 hours followed by half an hour activation by CO_2 at 600°C. Peanut shell char (PS) was prepared by using a simulated flue gas for one hour followed by CO_2 activation for 1 hour. The tomato cane char (TC) was prepared by using CO_2 at 600°C for 2 hours. Up to 79% NO removal was obtained for these samples. Figure 6 shows again that oxygen enhances the adsorption of NO. Note that generally 80% or more of the NO_x in flue gas is typically NO rather than NO_2 . Figure 6 also shows that different starting materials and/or the preparation method has a significant effect on the adsorptivity of the activated carbon.



TC-Tomato Cane, RH-Rice Hull, PS-Peanut Shell

Fig. 6. The Effect of oxygen on NO removal efficiency (3/4" reactor, 1000 cc/min. 10% CO , 230 ppm NO in, 250 ppm SO_2 in, balance N_2 , 18°C)

Low Temperature Experiments

Very encouraging results were obtained with experiments conducted at low temperatures. The reaction cylinder containing the activated carbon was placed into an ice bath and allowed to reach a temperature of 0°C. Adsorption was still very poor in the absence of oxygen. A NO_x outlet over inlet ratio of 0.66 was obtained when no oxygen was present. Adsorption was very high when in the presence of oxygen. A NO_x outlet over inlet ratio of 0.0011 (99.89% removal) was obtained with an oxygen concentration of 11.8%. Figure 7 shows a plot of the results. The lowest outlet concentration obtained was 0.16 NO_x ppm at 14.1% oxygen. This is much less than the SMAC limit of 4.8 ppm.

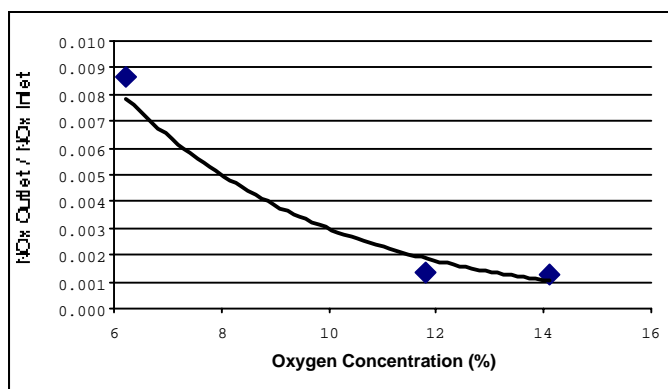


Fig. 7. NO_x Outlet concentration over NO_x inlet concentration vs. oxygen concentration at 0°C. commercial activated carbon.

TEMPERATURE EFFECTS ON ADSORPTION

The effect of temperature and water vapor on the removal of NO from feed gas at constant oxygen concentration was studied. Figure 8 shows that the adsorption of NO on commercial Calgon CTC-60 at 3% oxygen decreased with an increase of temperature when temperatures were less than 150°C. However the NO removal efficiency reverses course with further increases in temperature beyond 150°C. This is attributed to the reaction of NO with the activated carbon, resulting in the formation of nitrogen gas at high temperatures. When water vapor, at a 30% concentration in the feed gas, was introduced at high temperatures (above 350°C), a decrease in NO removal efficiency (up to 25%) was observed.

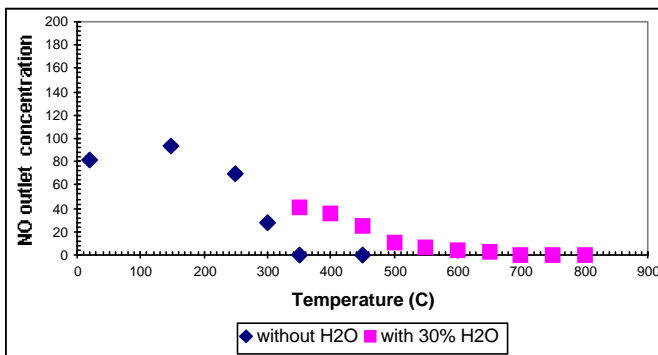


Fig. 8. The effect of temperature and water vapor on NO removal with commercial activated carbon from coconut shell.

Similar behavior is observed when there is more oxygen present, except the low temperature performance is better. Figure 9 shows the performance of commercial Calgon F-300 activated carbon as function of temperature. Again, NO removal is good at low and high temperatures, and removal is poor at an intermediate region – between 100°C and 400°C.

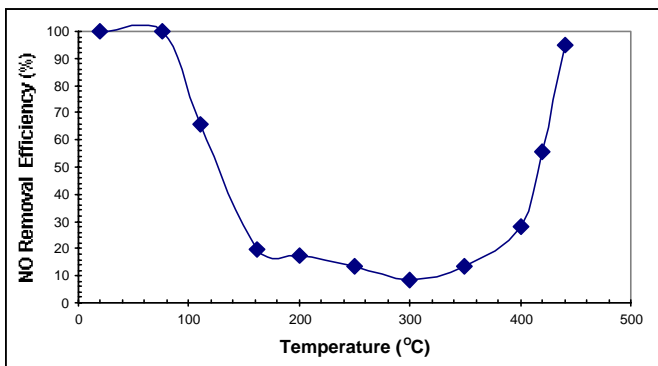


Fig. 9. Temperature effect on NO removal efficiency for commercial activated carbon at 21% oxygen, 490 ppm NO in, 79% nitrogen.

Figure 10 shows the results for simultaneous removal of NO and SO₂ using an activated carbon made from rice husk. The carbon was prepared by the carbonization of rice husk with a simulated flue gas at 450°C for half an hour. The feed gas contained 240 ppm SO₂, 204 ppm NO, 3% O₂, 10% CO₂, and the balance comprised of N₂ and water vapor. The flow rate of the simulated flue gas was 2,000 ml/min. 7 g of the rice husk carbon was used. The SO₂ removal efficiency reached 100% at 20°C and decreased with increased temperatures. The behavior was different for NO. There was no removal of NO at low temperatures (below 200°C, but this is due to low oxygen content of the gas in this experiment, 3%), however the NO removal efficiency increased drastically with increased temperatures. Above 300°C, the presence of 30% water in the gas resulted in about a 20% and 30% reduction in removal of NO.

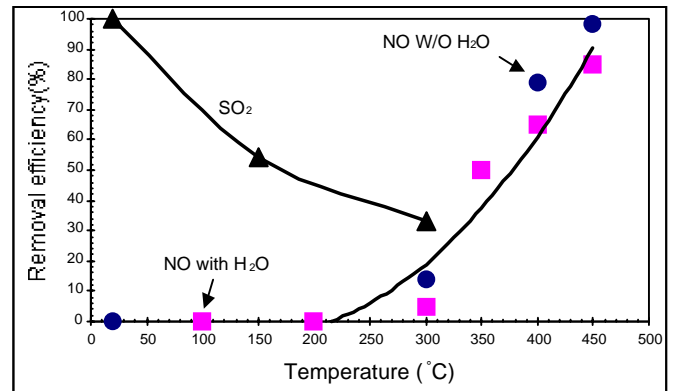


Fig. 10. Removal efficiency for NO and SO₂ using char from rice hulls at 3% oxygen.

The high temperature performance suggests that activated carbon could be used at high temperatures to adsorb and react with the NO simultaneously. Oxygen concentrations would likely have to be maintained at low concentrations in the flue gas for such a process in order to avoid rapid loss of the activated carbon.

MOISTURE EFFECTS ON ADSORPTION

Moisture in the flue gas generally caused a moderate decrease in NO removal efficiency. See Figures 8 and 10 above.

MATERIAL AND PREPARATION EFFECTS ON ADSORPTION

One way of evaluating the quality of activated carbon is to measure the surface area and average pore size. Various methods of measuring and calculating surface area and pore size are used with BET surface area and BJH average pore size being common. One series of experiments looked at rice hulls (RH) and peanut shells (PS) and wheat straw (WS) converted to char by different methods. Temperature, hold time, and

activating gas were varied. The results are shown in Table 5. A rice hull char had the highest surface area. The rice hull (RH) char was prepared using simulated flue gas (CO₂, 10%; O₂, 3%; N₂, 57%; H₂O, 30%) for activation. The rice hull data also shows that there are significant effects of preparation on the resulting char. Unfortunately rice hull is only a small part of the rice plant and may not be available in sufficient quantities to make activated carbon on a space mission. Another high surface area in this group was prepared from wheat straw using a wet carbonization method. The wet carbonized wheat straw had a surface area of 211 m²/g, which compares to about 1000 m²/g for typical commercial activated carbon. Preparation methods and materials continue to be evaluated to produce the most active material possible.

Table 5. Area and Pore Size Analysis of Activated Carbon Prepared from Hydroponically Grown Rice Husks, Peanut Shells, and Wheat Straw

	Activated Carbon	BET m ² /g	BJH A ⁺
1	RH, 350°C, 3hrs, flue gas, 700 cc/min	76.5	
2	RH, 0.5 hr, 600°C, CO ₂ , 500cc/min,	163.0	25.1
3	RH, 2 hr, 600°C, CO ₂ , 500cc/min	167.1	45.1
4	RH, 5hr, flue gas, 50-450°C, 2000cc/min	237.6	47.6
5	PS, 0.5 hr, flue gas, 450°C, 500cc/min	14.2	53.9
6	WS, wet carbonization	211	28.0

RH--Rice husks; PS--Peanut shells, WS--Wheat Straw

COMPARISON OF NO AND SO₂ ADSORPTION

Figure 10 above shows the result of the simultaneous removal of NO and SO₂ using an activated carbon made from rice husk. In this figure SO₂ removal decreases with temperature and NO removal increases with temperature. Both SO₂ and NO are less adsorbed as the temperature increases. For NO this loss of adsorption is counterbalanced by increased reaction of the NO with the carbon to form N₂. Although Figure 10 shows little removal of NO at low temperatures, this is a result of the low oxygen concentration used in that experiment (3% oxygen). At 21% oxygen (Figure 9) NO adsorption at low temperatures is high.

REGENERATION

Wheat straw is likely to be one of the more common constituents of available biomass, and a number of experiments were conducted to investigate the use of wheat straw as the source of char. Adsorption of NO followed by regeneration of the activated carbon has

tended to result in improvement of the performance of the activated carbon. Figure 11 shows the performance of the activated carbon after 7 regenerations (the 8th adsorption). Note that the concentration is below the SMAC limit of 4.8 ppm for about the first 30 minutes.

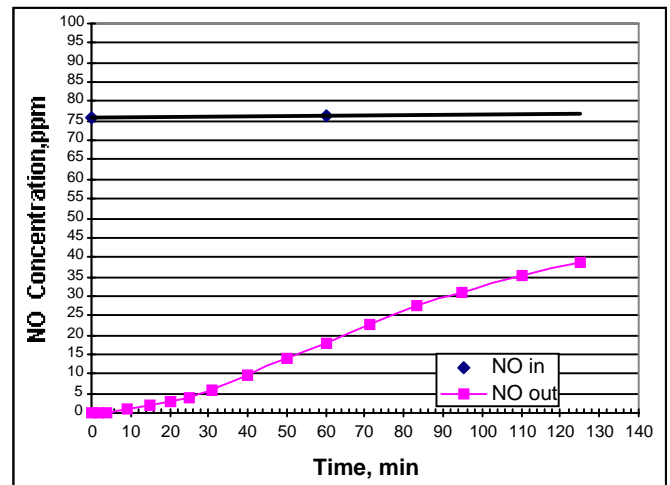


Fig. 11. NO adsorption by wheat straw char at room temperature. (8th cycle, 16.5g wheat straw, 2" reactor, 1 L/min flow of 10% CO₂, 10% O₂, balance N₂, NO in=75ppm, SO₂ in=201ppm, 20°C).

Regeneration of the char can be accomplished by heating the NO and SO₂ loaded char in the absence of oxygen. In order to evaluate the time behavior of the process, a purge gas flow of nitrogen was applied during experiments, and the outlet was directed to gas analyzers. Figure 12 shows a typical desorption curve for wheat straw stem on its 4th regeneration. The concentration of NO leaving the bed reached a maximum at 372°C and was near zero at 500°C. The amount of NO adsorbed and desorbed is shown in Table 6.

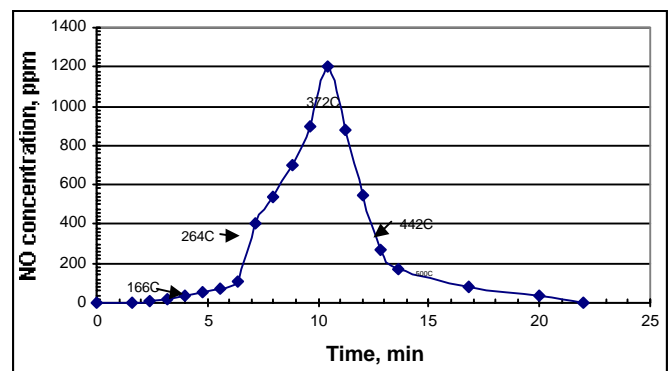


Fig. 12. NO desorption from wheat straw (stem) char by CO₂ gas (4th regeneration, 5.4 g char, heating ramp 40°C/min., 1 L/min. CO₂ purge)

Table 6. Quantities of NO Adsorbed and Desorbed

run	NO adsorbed mole	NO desorbed mole	NO desorption ratio (%)	NO adsorbed over char, (g/g)
3 rd cycle	2.606E-4	1.70 E-4	65.2	1.23 E-3
4 th cycle	2.794E-4	2.095 E-4	75.0	1.34 E-3

NO desorp. ratio = (NO desorbed)/(NO adsorbed)

Desorption ratios less than 100% are likely caused by the reaction of NO with the activated carbon to form N₂, which is the desired reaction. The reaction yield can be greatly improved by eliminating the gas purge, which was used only for analytical reasons.

The amount of NO adsorbed per g of activated carbon is low in the Table 6 runs. The BET surface areas for these samples of wheat straw char were as low as 10 m²/g, and it is expected that that samples of char with the higher surface areas will show better adsorption capacity. Some of the most recent experiments have shown adsorptive capacity as high as 0.008 g NO adsorbed per g of char made by the 211 m²/g wet carbonization char (see Table 5).

Figure 13 shows the desorption of both SO₂ and NO from peanut shell char. The peanut shell char was prepared by a simulated flue gas for an hour followed using CO₂ activation for one hour. The desorption was conducted at several different temperatures with a temperature ramp rate of 40°C/min. before or between. NO shows one significant desorption peak at 300°C. Higher temperatures are necessary to desorb SO₂ rapidly as can be seen by the second SO₂ peak at 500°C.

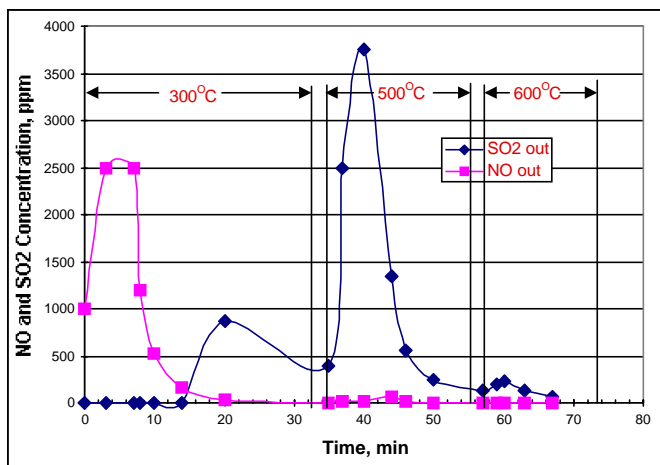


Fig. 13. Desorption of NO and SO₂ by peanut shell char after 20°C adsorption.

SUMMARY OF RESULTS

Experiments were conducted to evaluate the effects of temperature, oxygen composition, moisture, starting material, preparation method, and regeneration on the

performance of activated carbon. Some of these experiments were conducted with commercial activated carbon.

Adsorption experiments with commercial activated carbon were conducted in order to establish standard performance to which to compare the biomass-produced char could attain. Commercial activated carbon can reduce NO to below SMAC concentrations (Figure 7). Commercial char was also used to establish other general trends for activated carbon (Figures 4,5,7,8,9)

Material burnoff data enables estimates of the amount of char that can be produced from a material. Samples of biomass were obtained and processed to produce activated carbon. Burnoff of material was 45% to 75% depending on the temperatures, hold times, purge gas, and starting material (Table 4).

Low temperatures such as 0°C and oxygen concentrations above 10% improve the adsorption of NO on activated carbon (Figures 7,9). Enhancement of adsorption by lower temperatures is normal for most adsorption processes. Enhancement of adsorption by oxygen is unique to NO adsorption. This phenomenon has been previously reported (Degroot, et al., 1991). NO complexes with oxygen on the surface of the activated carbon and may react to form NO₂. NO removal has a non-linear relation to temperature (Figure 9). NO removal is good at low temperatures when adsorption on the carbon is high. As the temperature increases adsorption and removal decreases. At some point as the temperature increases, the NO removal begins to improve as reaction with the carbon begins to dominate and removal of NO increases. SO₂ shows the decrease of adsorption with temperature (Figure 10).

Regeneration of the activated carbon has improved its adsorptive performance in subsequent runs. Low adsorptive capacity has been observed on samples with low surface area (Table 6). Regeneration experiments show evidence of partial reaction of the NO with the carbon bed (Table 6).

It is expected that adsorptive capacity will improve as samples with higher surface area are prepared and tested (see wheat straw Table 5). Some of the most recent experiments have shown adsorptive capacity as high as 0.008 g NO adsorbed per g of char made by the wet carbonization method.

CONCLUSION

Activated carbon is well known for its ability to adsorb hydrocarbon species. It can also be used to adsorb species such as NO, NO₂, and SO₂. The species NO, NO₂, and SO₂ can react to form N₂ and elemental sulfur. The adsorption-reaction phenomenon can be utilized to make activated carbon a primary processor in flue gas cleanup system.

A major advantage of the activated carbon flue gas cleanup process is that the activated carbon can be made from biomass on hand in a regenerative life support system. Research to date has demonstrated most of the fundamental aspects of the proposed process including production of activated carbon from biomass and the adsorption-reaction of NO. Although reaction of SO₂ with the char was not yet demonstrated, this may not be necessary because the alkali metals in biomass scrub out sulfur as sulfate in the incinerator ash.

More research is necessary to optimize the process for making activated carbon and regenerating the activated carbon before the process will be ready for application. This optimization is the goal of the ongoing research effort.

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COMMERCIAL NOTE

The discussion of research results from the use of commercial activated carbon products in this paper does not constitute an endorsement of these products by NASA.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CELSS: controlled ecological life support system

WS: wheat straw

PS: peanut shell

TC: tomato cane

RH: rice hull

JSC: Johnson Space Center

LBNL: Lawrence Berkeley National Lab

ARC: Ames Research Center

SMAC: Space Maximum Allowable Concentration

KSC: Kennedy Space Center

Appendix 1 Figures:

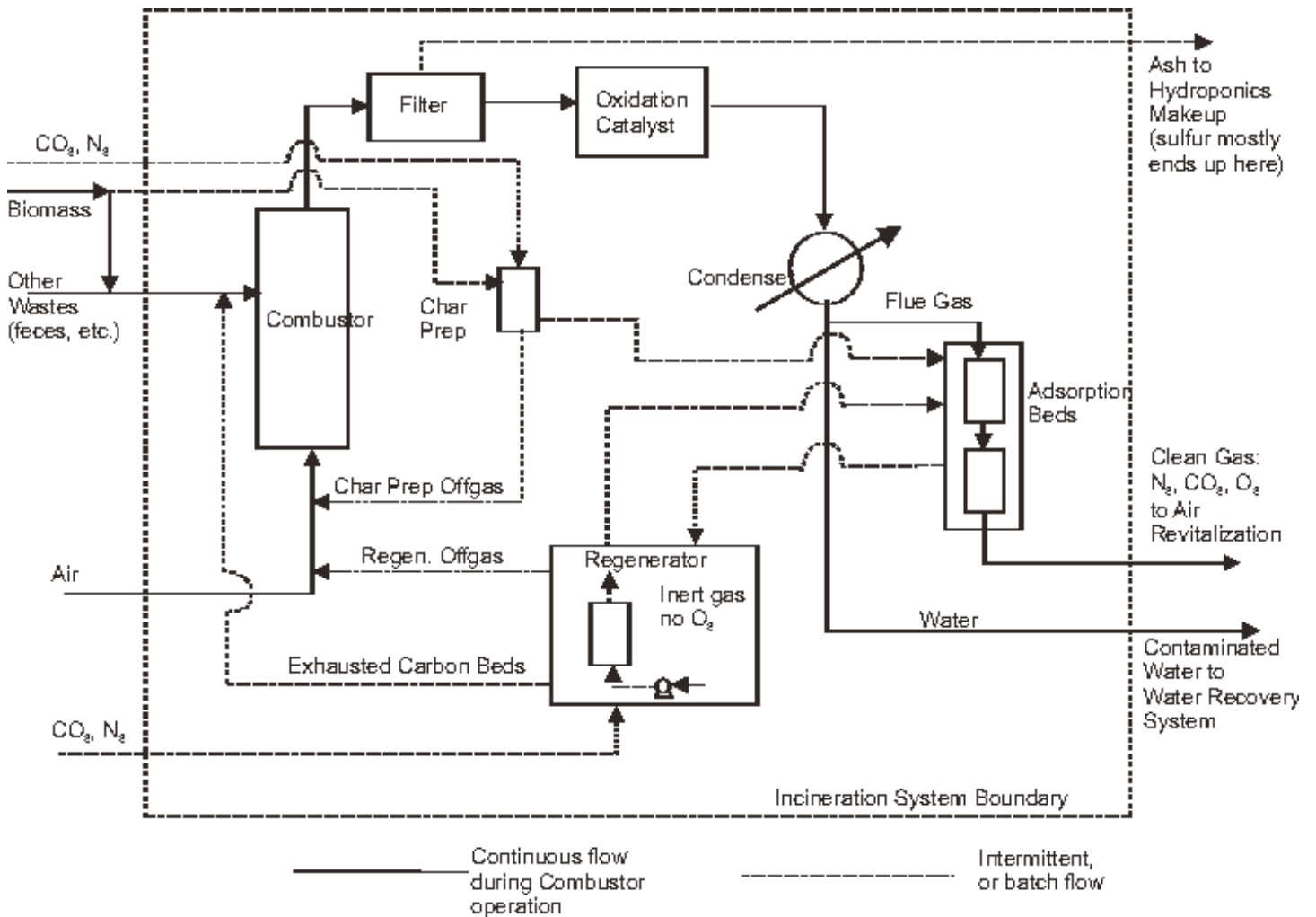


Fig. 1. Example flow diagram of reactive carbon for flue gas cleanup.

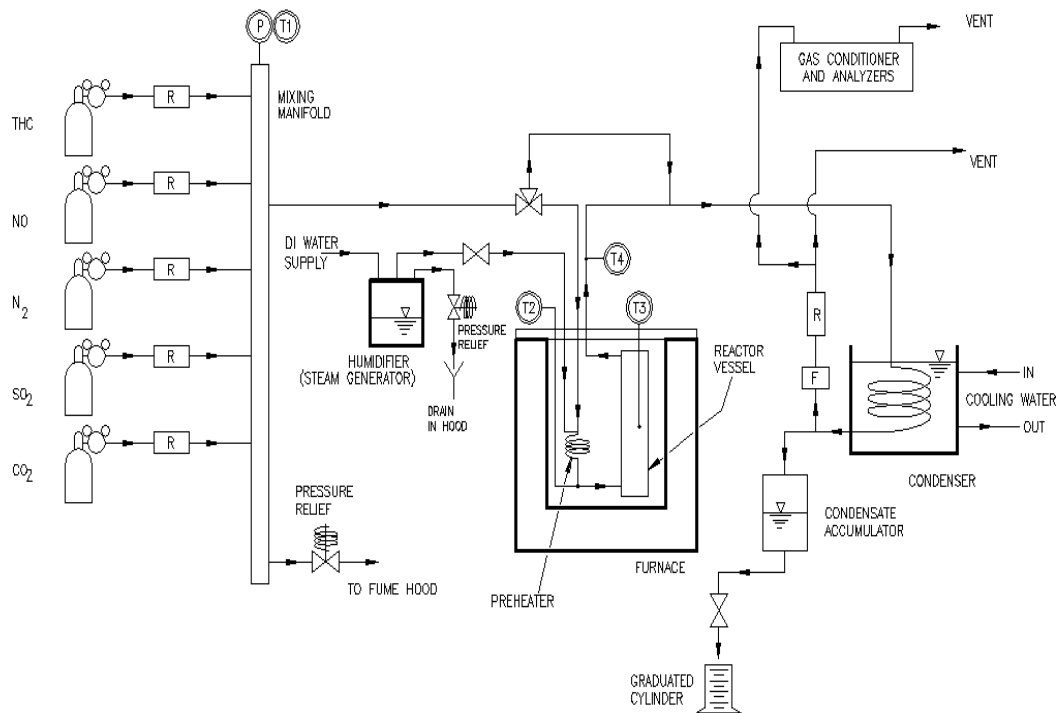


Fig. 2. Experimental setup at Ames Research Center for char preparation and adsorption experiments.

Fig. 3. Experimental setup at Lawrence Berkeley National Laboratory for char preparation and adsorption experiments.