Purifying Casino Air with Optimal Temperature and Carbon Source Choice

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Summary

The goal of this experiment was influenced by the need to assist a casino purify their air by removing the CO₂ from it. A recommendation for the better performing carbon source desired as well as a desired operating temperature.

The system's uncertainties were accounted for in temperatures of the gas and inlet column and the flow rates of the feed flows of air and CO₂. The thermocouples and flow meters in the unit were also found to provide confidence in choosing the best recommendations at the end of the experiment.

It was determined that Carbon A would provide the highest saturation capacity when it's operated at ambient temperature (26°C) when compared to Carbon D. Operating at lower temperatures provides a higher efficiency from the carbon source to adsorb the most gas.

Introduction

In industry, adsorption can be used to remove components of flue gas when the gas components are attached to the surface of a solid phase as it is passed over it. The experiment is focused on this solid/gas adsorption using CO₂ for the gas and two different activated carbons (Carbon A and D) as the solid. We were asked by Casino Barriere Ruhl (CBR) to examine two carbon sources at 10% vol CO₂ at five temperatures chosen to be ambient temperature, 30°C, 35°C, 40°C, and 45°C. The experiment was performed at the five temperatures using the two activated carbons to determine the best operating temperature and carbon source for this adsorption of CO₂. The recommended carbon source and temperature were determined statistically as well as confidentially when compared to literature.

Literature Review/ Theory

According to Zulkurnai et al. (2017), CO₂ emissions into the atmosphere have been increasing over the past several decades primarily due to the combustion of hydrocarbons in fossil fuels. Due to CO₂ being a greenhouse gas, these emissions are the leading cause of global warming and represent a dire concern amongst the scientific community. CO₂ separation methods such as membrane separation and cryogenics are encouraging, but solid-gas adsorption is of particular interest to CBR. Adsorption, simply put, is the "sticking" of molecules to another smooth or porous solid surface. Not to be mistaken for absorption, where molecules enter some bulk phase. The reduction in operating cost when using adsorption is its main advantage when compared to other separation methods. CO_2 separation and storage using adsorption involves a gas feed containing CO_2 and a solid adsorbent. When the gas feed flows through a packed bed of the solid adsorbent, CO_2 adsorbs to the surface of the porous bed thus decreasing the concentration of CO_2 in the gas exiting the bed. Unfortunately, there is a point that every adsorbent becomes saturated with the adsorbate and cannot hold any more adsorbate. If the concentration of CO_2 in the exiting gas is plotted versus time up to when the concentration no longer changes after saturation, we obtain a breakthrough curve seen in figure 1 below.



Figure 1. Breakthrough curve for adsorption.

Notice that initially, the adsorbent can adsorb all of the adsorbate in the feed of initial concentration C_0 up to when the packed bed approaches saturation. After this point, the concentration of adsorbate in the feed increases to its initial value where it reaches steady state. According to Dudukovic (2014), the following equation can be used to calculate the adsorption capacity of the adsorbent.

$$\int_0^\infty \left(1 - \frac{C_A}{C_{A0}}\right) dt = \frac{\epsilon_b V}{Q_f} + \frac{(1 - \epsilon_b) V \rho_p w_{A\infty}}{Q_f C_{A0} \rho_A}$$
 Eqn. (1)

Where the left-hand side of the equation is the integral of the initial concentration minus the exit gas concentration until steady state, C_A is the concentration of Adsorbate exiting the packed bed, C_{A0} is the initial feed concentration of the adsorbate, ϵ_b is the porosity of the packed bed, Q_f is the flow rate of the feed, V is the volume of the packed bed, ρ_p is the density of the particles, ρ_A is the density of the adsorbate, and $w_{A\infty}$ is the saturation capacity of the adsorbent.

The porosity of the bed may be estimated using the following equation from Pushnov (2006):

$$\epsilon_b = \frac{A}{\left(\frac{D}{d}\right)^n} + B \qquad \qquad Eqn. (2)$$

Where A, B, and n are parameters dependent on the shape category of the particle, D is the diameter of the packed bed, and d is the diameter of the particles. Of particular interest, particles fitting the 'lumps of irregular shape' category use the parameters A = 1.5, B = 0.35, and n = 1.

$$\rho_p = \frac{\rho_b}{1 - \epsilon_b} \qquad \qquad Eqn. (3)$$

The equation above relates density of the particle to the bed porosity and density.

In a 2020 study by Dr. Lapham, published by Micromeritics Instrument Corporation, it was found that the enthalpy of adsorption of CO₂ onto activated carbon was exothermic.



Figure 2. Quantity adsorbed vs relative pressure at various temperatures by Dr. Lapham (2020)

From the above figure, it can be seen that the quantity adsorbed decreases when temperature increases at constant relative pressure, indicating an exothermic (negative) enthalpy of adsorption. CO₂ adsorption is an exothermic process; therefore, the rate of adsorption decreases whenever temperature increases. Alternatively, CO₂ desorption is an endothermic process. Each are demonstrated with sudden spikes and drops in temperature when CO₂ is introduced and removed into the feed respectively. Additionally, Rashidi et al. (2016) found that saturation capacity decreases when temperature increases. Rashidi et al. (2016) also state that this particular sorption process is physical adsorption, not chemical adsorption; the key difference being that

the adsorption process is facilitated by weak van der Waals forces which tend to be broken at higher temperatures. Additionally, the reduction in saturation capacity can be explained by Le Chatelier's principle such that endothermic desorption is more favorable at elevated temperatures (Rashidi et al. 2016).

CBR would like to confirm whether the temperature dependance of Henry's constant demonstrates behavior that follows the Arrhenius law below:

$$K' = \frac{W_{A\infty}}{C_0} = K'_0 e^{\frac{-\Delta H_0}{R_g T}} \qquad Eqn. (4)$$

Where K' is Henry's constant, K'_0 is the pre-exponential factor, ΔH_0 is the enthalpy of adsorption, R_g is the gas constant, and T is temperature. It is assumed that Henry's law applies at concentrations of CO₂ less than or equal to 10% by volume. After obtaining Henry's constant for the various temperatures studied, a semi-log plot of K' vs. T⁻¹ will produce a line with slope of $-\Delta H_0/R_g$ and a y-intercept of pre-exponential factor K'_0 .

Experimental

Introduction

The engineers with Salton Sea Sorption, Inc. examined the temperature effects on saturation capacities for different activated carbons at five temperatures– ambient temperature, 30°C, 35°C, 40°C, and 45°C. The beginning of the cycle will be using Carbon A, while the end of our cycle will be using Carbon D. Carbon A has a larger grain size than Carbon D averaging around 0.6-2.4mm. A calibration cycle was performed to get the values for our air and CO₂ flowrates as well as the values of their concentrations and calibration curve data to use when we gather the CO₂ vol% from the meter during the different temperature runs. Using these allows us to get the correct CO₂ vol% using Eqn 1.

Plotting the CO₂ breakthrough values from the 10-minute cycle and integrating it over the adsorption cycle provided information necessary to solve for the saturation capacity at that temperature.

Conditions/ system studied

The equipment used in our experiment uses physical devices such as pumps, heaters, and valves as well as electronic devices such as the ADSG programmable logic controller (PLC) and the Honeywell Station application. The column has a usable volume of roughly 0.3 L with an inside diameter of 25mm and height of 0.6m. The PLC on the system is used to control flowrates of air and CO₂ as well as some temperatures.

The Honeywell Station application reads the concentration of CO₂ in our column during the time of the runs. Figure 3 shows the unit system of the adsorption process in this report.





Two activated carbons are being used in the unit at different times during the experiment. The first four days, the unit had Carbon A while Carbon D was in the unit for the last three days. To calculate the bulk density, the porosity needs to be determined by using the Pushnov equation (Eqn 2) which calls for the diameters of the grains of activated carbons. The diameter of each carbon source was averaged using a caliper on 30 particles, coming out to be about 2.06mm for Carbon A and 1.266mm for Carbon D. An illustration for measuring the diameter of Carbon A is shown below in Figure 4 along with visuals of the different sizes of the carbon particles in Figure 5.



Figure 4. Caliper used to find diameter of Carbon A particles

Figure 5. Carbon A and D particle samples



Uncertainty/ Statistics

Uncertainty is found with Monte Carlo Latin Hypercube sampling which requires both random uncertainty and combined fixed uncertainty. Random uncertainties were accounted for with the temperatures of the column and gas flowing through the system, as well as the air and CO₂ feed flowrates. The diameters of each carbon source also had random uncertainties to account for. The thermocouple in the unit is factory calibrated ($\pm 2^{\circ}$ C accuracy) that works along with a thermal flow meter ($\pm 0.9\%$ accuracy). The expanded uncertainties were found and are displayed in Table 1.

Expanded Uncertainties (U _{95%})				
Measurement	Source A	Source D		
Gas Phase Temperature	$\textbf{2.0}\pm\textbf{7.3\%}$	$\textbf{1.9}\pm\textbf{8.2\%}$		
Internal Column Temperature	$\textbf{2.0} \pm \textbf{4.8\%}$	$\textbf{2.4} \pm \textbf{5.7\%}$		
Air Feed Flow Rate	$\textbf{0.86} \pm \textbf{0.36\%}$	$\textbf{2.2}\pm\textbf{0.01\%}$		
CO ₂ Feed Flow Rate	$\textbf{2.1} \pm \textbf{5.6\%}$	$0.57 \pm 1.5\%$		

 Table 1. Carbon A and D particle sample

The law of propagation was used to find the uncertainty of the bed porosity since D was known to be 25mm and posed no uncertainty, however, d does have uncertainty. The standard deviation of Carbon A was 0.46 and for Carbon D was 0.262. The uncertainty for the integral in (Eqn 1) was performed with after taking multiple runs with one temperature– this was done at ambient temperature and 45°C. The volume of the bed is dependent on the bed diameter, which doesn't pose an uncertainty, and the bed height, which has a random uncertainty. The density of the bed depends on the mass of the bed which is assumed to have no uncertainty since it was not able to be estimated as well as the bed volume. The uncertainty for the density of the bed is used alongside the density of the particles to assume an uncertainty there as well.

Experimental Plan

The beginning of our experimental plan was set to calibrate the Honeywell CO₂ meter using air and carbon dioxide sources to get our calibration curve that's going to be used for the rest of the experiment. We also calculate the flowrates of air and CO₂ that we're going to be using each day to get the desired 10%vol CO₂ concentration using the calibration values. The experiment will be running at the five temperatures using the two activated carbons to determine the best operating temperature and carbon source for this adsorption of CO₂. Since achieving steady state is optimum, a test run was performed at ambient temperature for 20 minutes with each carbon sources to decide on an efficient time to perform the remaining runs at. Ambient was the temperature chosen to do this since it should, theoretically, take the longest time to reach steady state. The test runs achieved steady state in about 7 minutes for each

carbon source, therefore, 10 minutes was the decided run time for all operations throughout the experiment. The Honeywell application was also set to track the CO₂ concentration in 1 second increments. After each 10-minute run, a desorption cycle is ran using only air in the column until the air concentration reaches the desired 0.04% volume known value on the pump since this was determined during our calibration cycle. After the desorption cycle is completed, the system is either ran again at the same temperature or heated to a higher temperature depending on the experimental outline.

The CO₂ values obtained from the meter are graphed and integrated over the adsorption cycle to achieve, with the information of porosity and packed bed values, the saturation capacity of each temperature.

Day	Plan	Notes
Day 1 3/7/22	 Learning the equipment Complete JSA form CO₂ Calibration Data 	
Day 2 3/9/22	 Ambient temperature 3 runs operating for 10 minutes each 	Carbon A
Day 3 3/21/22	 30°C 1 run operating for 10 minutes	Carbon A Meeting with Dr. Toups
Day 4 3/23/22	 35°C and 40°C: one 10 minute run each 45°C: three 10 minute runs 	Carbon A Carbon sources get switched in unit next lab day
Day 5 3/28/22	Ambient temperature3 runs for 10 minutes each	Carbon D
Day 6 4/04/22	 30°C, 35°C, 40°C: one run each for 10 minutes 45°C: 3 runs for 10 minutes each 	Carbon D

Table 1: Experiment outline

Day	Plan	Notes
Day 7	All data was collected by Day 6 and no experiment was performed	
Day 8	Presentation	

Results

The first results calculated was temperature's effect on saturation capacity for both carbon sources. By comparing the saturation curves obtained at both ambient temperature (26°C) and 45°C, a statistically significant difference between the two is observed. In figure 6 the saturation curves for both carbon sources are plotted. A clear difference can be observed just from looking at the graphs, but to quantify this difference, t-tests were used to compare the saturation capacity at each temperature. The actual calculations were done in the submitted excel sheet, but using an alpha value of 0.01, a 99% confident difference in saturation capacities for carbon source A is obtained and using an alpha value of 0.05, a 95% confident difference in saturation capacity is observed for carbon source D. This proves that for this adsorber, the saturation capacity is, in fact, a function of temperature, consistently being higher at lower temperatures.



Figure 6. Saturation curves for carbon source A and D at ambient temperature and 45°C.

The next step in the results was to compare all saturation curves obtained at both carbon sources. Ambient temperature and 45°C was used the calculate the results

shown above in figure 6 since these two temperatures share the largest difference and tests were run three separate times for each making it able to do statistical analysis on them. These two saturation curves are included in figure 7 along with the curves for runs at 30°C, 35°C, and 40°C which were all run once. For carbon source A, the data retrieved for runs at 35°C and 40°C ended up pasting into excel incorrect so data from those temperatures are included in Appendix 1, but not below in figure 7



Figure 7. Saturation curves for Carbon source A and D at ambient temperature (26°C), 30°C, 35°C, 40°C, and 45°C.

Regardless of the missing data for 35°C and 40°C, further results are still able to be calculated and used in the decision making for this experiment. Now that the effects of temperature has been looked at for each individual carbon source, our team can begin to compare the advantages and disadvantages of each carbon source relative to each other. First, Since a higher saturation capacities is preferred for carbon adsorption, these values at ambient temperature and 45°C will be compared. In table 2, the saturation capacities for three runs at ambient temperature and 45°C are displayed for both carbon sources.

Run	Capacity A at 26°C	Capacity A at 45°C	Capacity D at 26°C	Capacity D at 45°C
1	10.67	9.00	3.47	8.20
2	10.99	8.07	5.66	8.72
3	10.99	7.91	8.79	8.66

Table 2. Tabulates the saturation capacity for three separate runs at 26°C and45°C for carbon source A and D.

Again, using a t-test, a difference between the saturation capacity for each carbon source at 26°C is quantified. For both sources at 26°C, using an alpha value of 0.05, a 95% confident observation of carbon source A's saturation capacity is

calculated. The opposite is found comparing the saturation capacities at 45°C. These values are statistically equal. These saturation capacities graphed can be found below in figure 8.



Saturation Capacity

Figure 8. Bar graph displaying saturation capacities of carbon sources A and D at 26°C and 45°C.

The last results calculates are the Henry's constants correlated with each carbon source at ambient temperature and 45°C. These constants are tabulated below in table 3 for all three runs done.

Run	Capacity A at 26°C	Capacity A at 45°C	Capacity D at 26°C	Capacity D at 45°C
1	1.13	0.89	0.35	0.82
2	1.16	0.78	0.58	0.87
3	1.16	0.78	0.89	0.86

Table 3. Tabulates Henry's constants for three separate runs at 26°C and 45°C for carbon source A and D.

Like the t-tests done for the saturation curve, the same results are found for the Henry's constants when comparing the different sources at the same temperature. With 95% confidence, the 26°C Henry's constant for carbon source A is greater than that of

carbon source D's. The Henry's constants at 45°C for each carbon source are statistically equal. Below in figure 9, these results are graphed.



Henry's Constant

Figure 9. Bar graph displaying Henry's Constants of carbon sources A and D at 26°C and 45°C.

Discussion

Using a carbon source with a large specific area is necessary to have an optimal adsorption. Depending on the material that's needing to be adsorbed, more information about the carbon source (such as porosity) is necessary when the material's molecular size is needing to be considered. Measuring the diameters of the different carbon sources had low standard deviations, considering there was a possibility of human error when measuring the 30 different samples of each carbon source. Carbon A was decided as the recommended carbon source to Casino Barriere Ruhl to work towards purifying their air. Looking at Figure 7 Carbon A had higher saturation capacities compared to Carbon D. This could have to do with Carbon A having a higher surface area compared to Carbon D. It was expected with calculations following the literature that Carbon A would have a higher saturation capacity (Figure 1A).

The adsorption efficiency decreases while temperature increases. This is because the adsorption of CO_2 using activated carbon is exothermic. This can be seen in Table 2 where the ambient temperature for each carbon source is showing a higher saturation capacity compared to the 45°C data. The statement can be tied back to

literature where Rashidi et al. (2016) found that saturation capacity decreases when temperature increases. Because of this, the recommended operating temperature is at ambient temperature.

Nomenclature

AC – Activated Carbon

- Casino Barriere Ruhl CBR
- Q_f Total feed flowrate
- ϵ_b Porosity of the bed
- ρ_b Density of the bed
- ρ_p Density of the bed
- u_0 Superficial velocity of feed
- L height of the bed
- V Volume of the bed
- D Diameter of the bed
- $C_A CO_2$ concentration at any time (Vol%)
- $C_{A0} CO_2$ concentration of the feed (Vol%)
- $w_{A\infty}$ Saturation Capacity
- K Henry's Constant

Literature Cited

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- N Z Zulkurnai1, U F Md. Ali1*, N Ibrahim1, N S Abdul Manan2 1 School of Environmental Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia 2 Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
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Reporting Responsibilities

Final Report	Deliverable	Lead Author
	Summary	Mason Phelps
	Results	Nicholas Gonsoulin
	Discussion	Kaitlynn Graffeo

Appendix

Job Safety Analysis Form

Complete all basic information and all other fields that are appropriate as part of the pre-experimental safety review. Revision Date: 7/1/2019

Basic Information

 Experiment
 ADSG

 Date
 3/7/2022

 JSA Authors
 Nicholas Gonsoulin, Kaitlynn Graffeo, Mason Phelps

 Instructor
 Dr. Toups

 Experimental Torman Description
 Measuring CO2 adsorption while it's passing through activated carbon at various temperatures

Personal Protective Equipment

Check all additional PPE to be worn during any part of the experimental program.

Lab coat
Chemical resistant gloves
Chemical apron
Chemical goggles
Full face shield
Particle mask
Cartridge respirator
Other

Hazards Summary

Check all the general hazards that are likely to be encountered during this experimental program and list a) the major sources of each hazard, b) exposure means for each hazard, and c) the precaution to take to avoid exposure.

Toxicity	a) large CO2 leak b) breathing in air c) constantly metering atmosphere
Fire/Flammability	
Reactivity	
⊠Pressure Hazard	a) HP gas cylinder b) glass projectile c) always run at 1 bar.
⊠Temperature Hazard	a) reactor vessel at high temperature b) physical contact with reactor vessel c) do not
touch vessel, if necessary wear	heat resistent gloves.
Hot Surfaces (>150°F)	
Electrical Hazard	
Mechanical Hazard	a) column explodes due to under/overpressure b) glass projectile c) always run at 1 bar.
Biohazard	
Laser/Ionizing Radiation	
Other	
Other	

Available Safety Equipment

Provide the location of each item shown below. If not available, type NA in the field

Fire extinguisher	Above the cabinets by the windows
Safety shower	At entrance of the lab
Eyewash	At entrance of the lab
First-aid kit	In front of shower
Telephone	Where Thomas sits
Other safety equipment	

Chemical Information

Fill in as much of the data below as possible. List all chemicals used of produced.

Chemical name	Carbon Dioxic	le			
NFPA ratings	H3 F0	R 0			
Airborne exposure	PEL 5000 ppm	n TLV 5	000 ppm	TWA 8-hour	
Disposal method	Return empty	gas cylinder to	manufacturer.		
Chemical name	Activated Car	bon			
NFPA ratings	H1 F3	R 0			
Airborne exposure	PEL not estab	lished	TLV not estab	lished	TWA not established
Disposal method	Appropriate la	andfill			
Chemical name					
NFPA ratings	H Pick one	F Pick one	R Pick one		
Airborne exposure	PEL	TLV		TWA	
Disposal method					
Chemical name					
NFPA ratings	H Pick one	F Pick one	R Pick one		
Airborne exposure	PEL	TLV		TWA	
Disposal method					
Chemical name					
NFPA ratings	H Pick one	F Pick one	R Pick one		
Airborne exposure	PEL	TLV		TWA	
Disposal method					

Emergency Shutdown

Minimum required procedure to leave the experiment in a safe condition prior to evacuation. Such procedures should not put operations personnel in harm's way and must be necessary in order to avoid creating a seriously unsafe situation.



Figure 1A. Predicted Saturation Capacities from Literature

Table 1A: Predicted Saturation Capacities from Literature Calculations

Mean Saturation Capacity, g CO_2 / g AC			
т, °С	Source A	Source D	
26	0.005179	0.004685	
30	0.005096	0.004516	
35	0.004830	0.004354	
40	0.004508	0.004110	
45	0.004200	0.003843	





Carbon Source A Saturation Curve