

Volatile Organic Compound Recovery Using Activated-Carbon Fiber-Cloth with Rapid Electrothermal Desorption

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ABSTRACT

Activated-carbon fiber-cloth (ACFC) has been investigated as an alternative adsorbent to remove volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) from gas streams when compared to conventional granular activated carbons (GACs). ACFC has up to twice the adsorption capacity of GAC and is more suited to electrothermal regeneration.

An automated bench-scale ACFC system was developed to capture and recover a continuous 1000 ppmv air stream of methyl ethyl ketone (MEK) while evaluating the use of electrothermal regeneration technology. The adsorption system operated at 25 lpm and each bed contained 24 g of ACFC. Five percent breakthrough times were approximately 1.3 hr. Throughput ratios of ~80% were achieved.

Each bed was desorbed by applying an alternating electrical current for 3 min. The desorbed MEK condensed onto the inner walls of the adsorber and was collected via a drain at the bottom. Seventy percent of the MEK in each adsorption cycle is collected as condensate, with the balance being recycled to the alternate adsorber. The preliminary estimated cost to recover MEK for a 50 m³/min system is \$0.38/kg.

INTRODUCTION

The Clean Air Act Amendments of 1990 have mandated that Maximum Available Control Technology (MACT) be applied to control the emissions of Hazardous Air Pollutants (HAPs) from numerous industrial sources [1]. MACT can consist of the installation of new pollution control equipment or of process modifications such as the use of low-emission chemical substitutes. Many of these MACT standards were promulgated in the mid to late 1990's, leading to implementation of these standards within the past five years.

This recent change in regulations has fostered interest in the development of new air pollution control technologies for many HAPs and volatile organic compounds (VOCs). Some emitters of VOCs and HAPs are not completely satisfied with chemical substitutes, as they often provide inferior process performance to the products they have replaced. The installation of air pollution control equipment allows the continued use of higher performance chemicals and also can often

result in lower total emission of VOCs and HAPs to the environment. In any instance, the installation of new air pollution control equipment leads to scrutiny of the cost and efficiency of the state of the art of these controls.

Activated-carbon fiber-cloth (ACFC) has been investigated recently as an alternative adsorbent to conventional granular activated carbon (GAC) for capture and recovery of VOCs from gas streams. ACFC has up to twice the adsorption capacity of typical GAC and is more suited to electrothermal regeneration. [2],[3] Direct heating of the activated carbon with electrical energy can be more rapid and energy efficient than indirect heating of the activated carbon with steam or inert gas. [4] Electrothermal desorption also allows desorption and condensation of a VOC without mixing the resulting condensate with water. Electrothermal desorption does not require an adsorbent drying step, as required with conventional steam regeneration technology. Inert gas heating can provide some of these advantages, but requires a larger volume of inert gas to regenerate the adsorbent when compared to electrothermal desorption.

This paper documents recent developments in ACFC adsorption technology to capture and recover dilute VOCs and HAPs from air streams. Previous research [5] indicated that electrothermal desorption of MEK was so rapid that condensation occurred within the adsorber vessel, thus causing lower cycle times, and taking advantage of energy-efficient passive condensation. Based on these results, a bench-scale system was retrofitted to further evaluate electrothermal regeneration of the ACFC, to evaluate the efficacy of passive condensation to capture and recover MEK, and to operate at higher inlet gas flow rates into the adsorber.

EXPERIMENTAL SYSTEM

Overall System Design

The bench-scale system that was retrofitted consisted of a gas generation system, two parallel adsorbers containing ACFC adsorbent, an electrothermal power supply, a cryogenic condenser, a data acquisition and control system, and gas detection devices. Detailed descriptions of the experimental apparatus and methods used to conduct the research described herein are documented by Rood et al. [5], and Sullivan et al. [6] The same system was used for this research except for the following modifications:

- The outlets of both ACFC adsorbers were modified to allow for rapid drainage of condensed MEK from the adsorbers during electrothermal regeneration.
- The cryogenic condenser was eliminated and the adsorber vessel acted as a passive heat exchanger, allowing the MEK to condense on the vessel's inner walls.
- A separate electrical power circuit was added to the data acquisition and control system to allow more electrical power to be applied to the ACFC during electrothermal regeneration.

The revised system is described in Figure 1.

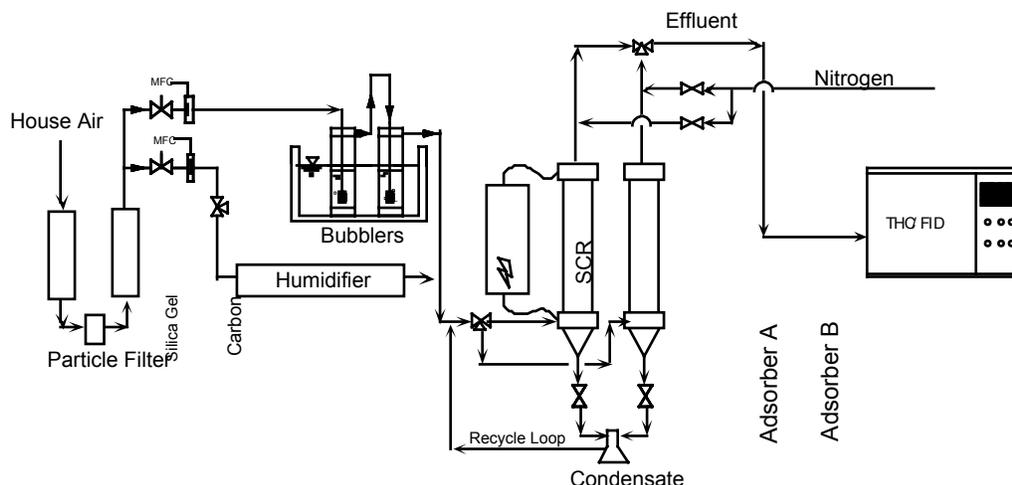


Figure 1. Overall Schematic of the Modified ACFC Adsorption-Passive Condensation System.

Adsorber

The annular ACFC filter cartridges remained unaltered from the previous design [6]. Each adsorber bed consisted of two 14.6 cm by 67.3 cm sheets of ACFC. Each sheet formed a cylindrical roll with eight layers and an effective annular length of ~ 11.4 cm. The mass of ACFC/sheet was 24.0 g to 30.5 g, depending on the lot of ACFC used. The filter cartridges were transferred to the new adsorption vessels to evaluate adsorption-desorption cycling of the adsorbers with the same configuration of adsorbent. Pyrex™ glass tubes with 75 mm outer diameter and 4 mm wall thickness were used in place of the existing aluminum tubes that housed the filter cartridges. Such modification allowed visual observation of the in-vessel condensation during electrothermal condensation and reduced the rate of heat transfer through the walls of the adsorber. The original outlets of the adsorber that were used during regeneration of the adsorbent were replaced with conical outlets. The revised outlets allowed rapid drainage of the MEK condensate that formed on the adsorber’s walls during electrothermal desorption (Figure 2). Gas flows described in Figure 2 occur when the adsorption bed is adsorbing MEK from the gas stream with a closed outlet for the condensate. Operating conditions for the inlet and outlets of the adsorber are changed during electrothermal regeneration such that the gas inlet is closed, the condensate outlet is opened, and the gas outlet becomes the gas inlet.

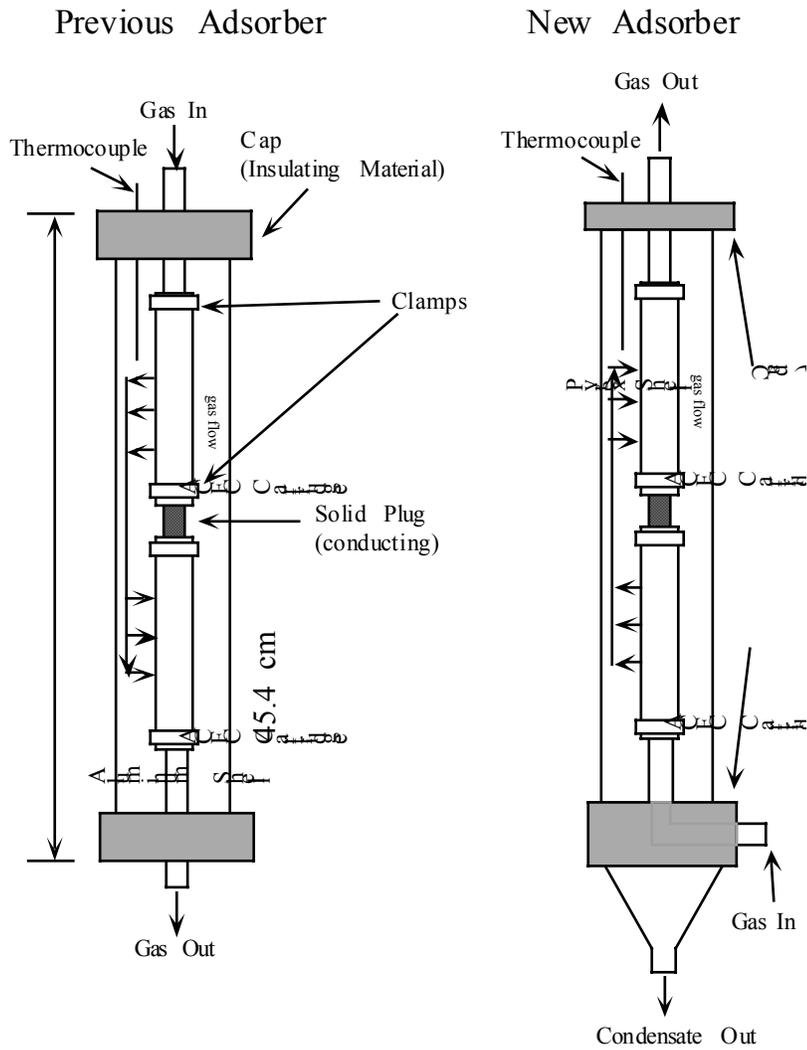


Figure 2. Previous and New Adsorption Beds

Interpretation of Results

Analysis of the breakthrough curves provide the total mass of MEK adsorbed (M_{sat}), the adsorption capacity of the ACFC, the throughput ratio (TPR), and length of unused bed (LUB). The total mass of MEK adsorbed by the ACFC was determined with equation (1):

$$(M_{\text{sat}}) = \frac{P (MW) Q_{\text{air}}}{R T} \int_0^{t_{\text{sat}}} \left(\frac{C_{\text{in}}}{1 - C_{\text{in}}} - \frac{C_{\text{out}}}{1 - C_{\text{out}}} \right) dt \quad (1)$$

where P is the total pressure of the inlet gas stream, MW is the molecular weight of the adsorbate, Q_{air} is low rate of carrier gas, R is the ideal gas constant, T is absolute temperature of the inlet carrier gas (K), C_{in} is the concentration of adsorbate in the inlet gas stream (mole fraction), C_{out} is the concentration of adsorbate in the exhaust gas stream (mole fraction), and t_{sat} is the time at which C_{out} has reached its final, steady-state value because the adsorbent is saturated with respect to the adsorbate.

Adsorption capacity of MEK achievable by the ACFC in the adsorption bed is the ratio of M_{sat} to the mass of ACFC in the adsorption bed. TPR is defined in equation 2.

$$\text{TPR} = \left(\frac{t_{5\%}}{t_{50\%}} \right) (100) \quad (2)$$

Where $t_{5\%}$ and $t_{50\%}$, are the durations required for the effluent concentration to achieve 5% and 50% of the influent concentration, respectively. As TPR approaches unity, the time required to develop the mass transfer zone in the adsorber becomes insignificant compared to the time required to saturate the adsorbent.

The dimensionless adsorber outlet concentration is defined as the adsorber's effluent gas phase MEK concentration (C_{out}) divided by its inlet gas phase MEK concentration (C_{in}). The dimensionless adsorption time (t/t_{50}) is defined as the ratio of time the bed is online (t) divided by the amount of time required to achieve $C_{\text{out}}/C_{\text{in}} = 0.5$. The time required to achieve $C_{\text{out}}/C_{\text{in}} = 0.5$ is defined as the stoichiometric time (t_{50}).

The LUB describes the percent of adsorption bed that is not utilized due to the length of the adsorption zone within the bed (equation 3).

$$\text{LUB} = \left(1 - \frac{M_{5\%}}{M_{\text{sat}}} \right) (100) \quad (3)$$

where $M_{5\%}$ is the mass of the adsorbate in the bed at 5% breakthrough time and M_{sat} is the mass of the adsorbate in the bed when the adsorbent is saturated.

The mass of desorbed MEK is described by equation 4.

$$(M_{\text{desorb}}) = \frac{P (MW) Q_{\text{N}_2}}{R T} \int_0^{t_{\text{in}}} \left(\frac{C_{\text{out}}}{1 - C_{\text{out}}} \right) dt \quad (4)$$

where, Q_{N_2} is the carrier gas flow rate, C_{out} is the concentration of adsorbate in the gas stream

exiting the bed (mole fraction), and t_{fin} is the duration of the desorption cycle.

The equilibrium vapor pressure of MEK was determined using the Wagner equation [7].

$$\ln \left(\frac{P_{vp}}{P_c} \right) = \left(\frac{VP_A x + VP_B x^{1.5} + VP_C x^3 + VP_D x^6}{1 - x} \right) \quad (5)$$

where,

$$x = 1 - \left(\frac{T}{T_c} \right)$$

P_{vp} = vapor pressure, Bar

P_c = critical pressure; for MEK = 42.1 Bar

T_c = critical temperature; for MEK = 536.8 K

T = temperature, K

VP_A, VP_B, VP_C & VP_D = Constants; for MEK = -7.71476, 1.71061, -3.6877, -0.75169

RESULTS AND DISCUSSION

Adsorption Results

The breakthrough curves that describe the dependence of the dimensionless adsorber outlet concentration on the dimensionless adsorption time are presented in Figure 3. Breakthrough curves from the previous adsorber and the new adsorber are represented in Figure 3. These results demonstrate that the slope of the breakthrough curve is essentially constant over the range of process conditions tested, allowing prediction of adsorption parameters such as breakthrough time and thickness of the mass transfer zone.

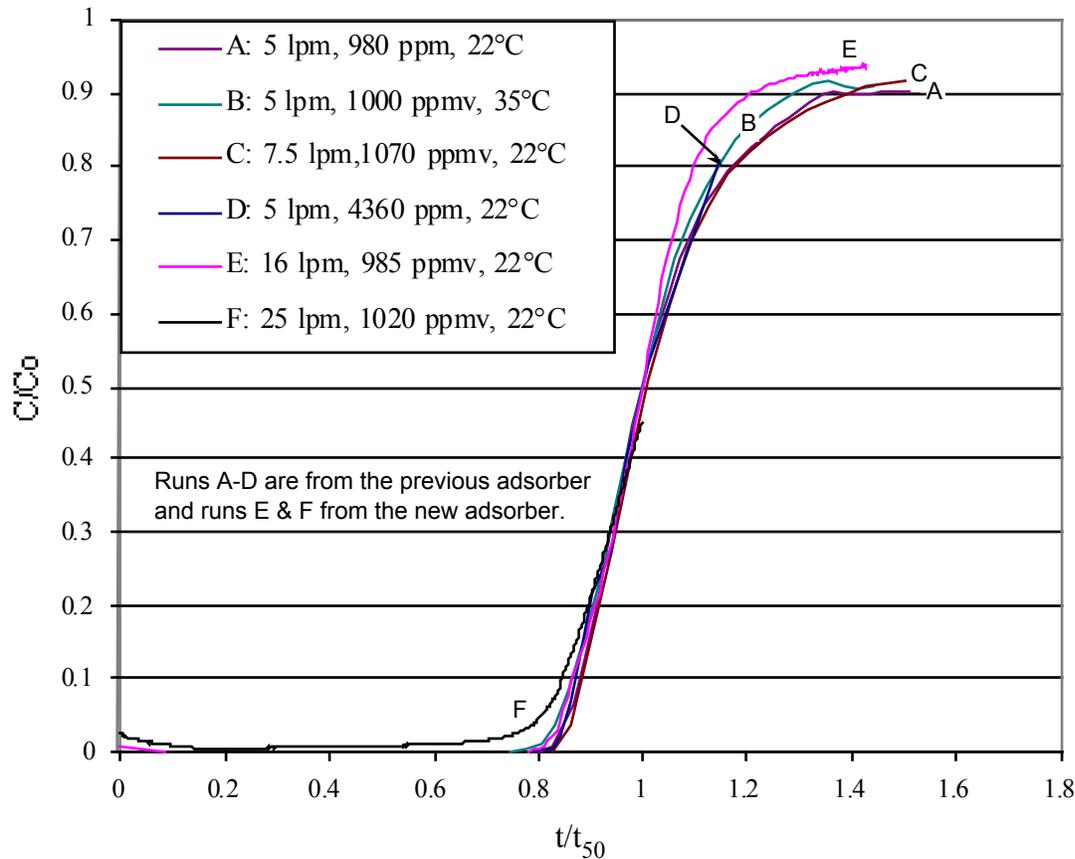


Figure 3. Dimensionless Breakthrough Curves.

Desorption Test Results

Once the adsorption bed was saturated, it was regenerated electrothermally with 0.5 lpm N₂ purge gas, 28 V AC power and amperage controlled between 6 and 11 amps. Results describing liquid MEK generation rate versus the amount of time the bed experienced electrothermal desorption are provided in Figure 4. The amount of time that power was applied to the bed during regeneration was reduced from 30 to 45 min in the previously designed system to ~ 3 min [5]. The desorbed MEK rapidly condensed onto the inside walls of the Pyrex™ adsorber and drained through the outlet of the bed with the N₂ gas stream that was saturated with MEK. Subsequent desorption tests yielded similar results with 0.2 lpm N₂ flow. The mass of liquid MEK collected is ~ 70% of the total adsorbed MEK based on material balances of MEK vapor entering the adsorber during the adsorption cycles and liquid MEK emitted from the adsorber during desorption cycles. MEK vapor in the regeneration stream is 10% to 15% of the adsorbed MEK, based on the calculated saturation vapor pressure. This leaves a balance of 10% to 15%, which is retained in the bed, or unaccounted for based on material balance measurements and calculations.

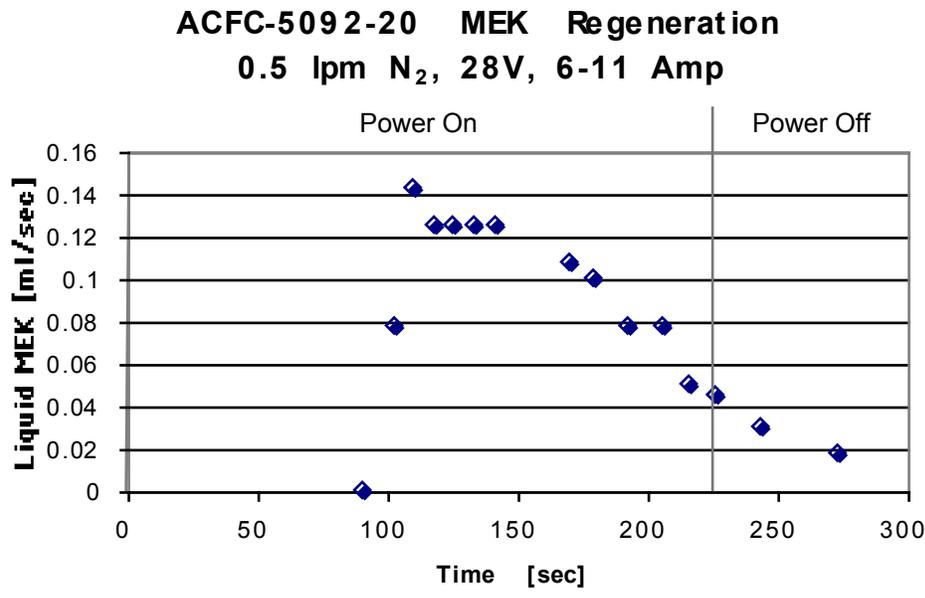


Figure 4. Desorption Rate of liquid MEK during desorption vs. Time.

(add units to vertical axis)

Automated ACFC System Operation

The revised system was then operated in an automated mode with continuous adsorption-desorption cycling. The N₂ gas stream flow rate during regeneration was 2% of the 25 lpm flow rate that passed into the adsorber that was online to adsorb MEK from the air stream. The system was operated with and without recycling of the N₂ gas stream that was saturated in MEK (Figure 5). These two recycling scenarios are equivalent to a condenser operating at ambient temperature (recycling gaseous effluent from the condenser to the adsorber), and a condenser operating at an infinitely cold temperature (not recycling gaseous effluent from a condenser to the adsorber). The difference between these scenarios is the maximum benefit that can be achieved by cryogenically cooling the recycled gas stream to reduce the mass feed rate of recycled MEK back into the adsorber that is online adsorbing MEK. No recycling was utilized for the first 25,000 sec while recycling occurred for the next 25,000 sec (Figure 5). The top panel in Figure 5 describes the temporal dependence of the ACFC’s temperature in each adsorber. Temperatures increased rapidly from 22°C to 160°C with the application of electrical power. The ACFC then experienced an exponential decay in temperature after termination of the electrical power. A desorption cycle consisted of ~ 3 min of electrothermal desorption and then 20 to 30 min of cooling. The lower panel in Figure 5 describes the MEK’s outlet concentration for the adsorber that is online. The adsorbers were online until t = t₅₀ to compare the response of the system to both recycling scenarios. Recycling of the effluent from the condenser resulted in breakthrough times of ~1.3 hr, and a 20.2% reduction in t₅₀ compared to the case with no recycling of the MEK vapor. TPR changed from 87% to 80%. LUB changed from 21% to 30%. Approximately 60% (12.2% of 20.2%) of the reduction in t₅₀ is due to the mass of MEK that is in the recycle stream, assuming saturated MEK vapor in the recycle stream at ambient temperature. These results

demonstrate that the system can operate with recycling of the gas stream generated during electrothermal regeneration and not require a cryogenic condenser. Such results support using a less complicated heat exchanger downstream of the adsorbers and no liquid N₂ in the condenser.

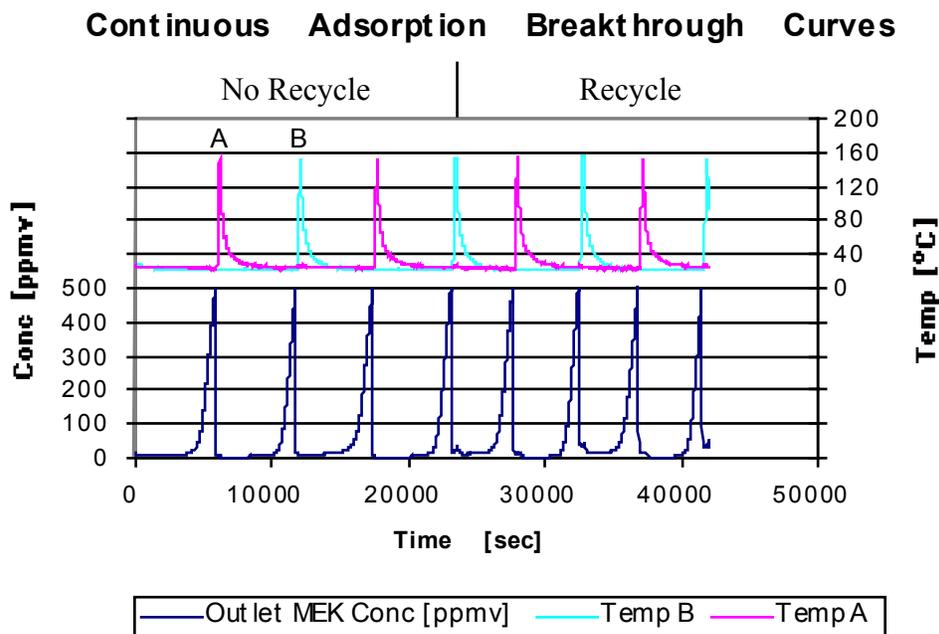


Figure 5. Adsorber temperature and effluent MEK concentration vs. time during continuous operation of the system

Cost Estimates

Reduction in consumption of liquid N₂ due to elimination of the cryogenic condensation resulted in a reduction of 20% of the operating cost of the previous system. [5] Elimination of the cryogenic condenser, reduction in N₂ consumption (0.2 lpm compared to 1 lpm of N₂ during regeneration, and elimination of liquid N₂ requirements), and increasing the inlet gas flow rate into the adsorber from 5 to 25 lpm, resulted in an estimated reduction in cost to capture and recover MEK for a 50 m³/min system from \$2.01/kg to \$0.38/kg.

SUMMARY & CONCLUSIONS

An automated bench-scale activated-carbon fiber-cloth (ACFC) adsorption system was retrofitted and operated to capture and recover dilute volatile organic compounds (VOCs) hazardous air pollutants (HAPs) from air streams. The new design allows for:

- 500% increase in air flow rate into the adsorber that was online adsorbing methyl ethyl ketone (MEK)

- More rapid electrothermal regeneration of the ACFC and condensation of the desorbed MEK to the inside walls of the vessel
- Elimination of the cryogenic condenser and decrease in N₂ consumption by a factor of five. Elimination of the cryogenic condenser resulted in a 20% reduction in adsorber run time. TPR is ~ 80% and LUB is ~30% for the system.
- Reduction in the amount of time the adsorbent was electrothermally regenerated by a factor of ten, but cool-down time remained ~ constant. The overall decrease in duration of regeneration is 67%.
- N₂ gas flow rate during regeneration is now determined only by explosion prevention considerations. N₂ flow rate during regeneration is now 1% of the air flow rate passing through the adsorber during adsorption. Modification of the system resulted in a cost savings of 81% for cost to capture and recover the MEK when considering the cost per unit mass of MEK captured and recovered.
- Continuous adsorption, desorption, condensation, and recovery of MEK has been demonstrated to be possible with a much simpler system. When capturing many commonly used HAPs, an ACFC adsorber bed and condenser can be constructed without any moving parts beyond the exhaust gas blower and valves that control fluid flows.
- Elimination of the need for equipment such as steam generators or inert gas heaters allows an ACFC unit to be constructed as a smaller unit than conventional adsorption/recovery systems. The elimination of any utility requirements beyond electrical power facilitates operation in non-industrial or remote locations.
- The ACFC adsorber with electrothermal desorption technology herein will extend the application of carbon adsorption systems to situations which were previously economically and physically impractical.

ACKNOWLEDGMENTS

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Key Words

Adsorption

Electrothermal Desorption

VOC Solvent Recovery

Activated Carbon Fiber Cloth

Passive Condensation