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Project Summary

Supercritical Fluid Regeneration of Activated Carbon Used for Volatile-Organic-Compound Vapor Adsorption

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The report gives results of a program to develop a sound fundamental technical base for supercritical-fluid regeneration of activated carbon applied to adsorption of volatile organic compounds. The process is based on using a supercritical fluid to desorb granular activated carbon containing adsorbed vapor contaminants. The desorption is at high pressure, and is followed by distillation of the fluid/adsorbate mixture at subcritical conditions for removing contaminants and recovering fluid solvent for recycle. Key unit operations characterized were (1) desorption from the carbon bed, and (2) distillation of the solvent/adsorbate solution. The process was characterized for both leaded and unleaded gasoline vapors, representing contaminants from gasoline storage and distribution facilities; and for ethanol and methyl ethyl ketone (MEK) vapors, representing many solvent finishing operations. Commercial vapor-phase activated carbon loaded with gasoline vapor components, ethanol, or MEK vapor could be completely regenerated with supercritical CO_2 at 1500 psia and 50°C. A carbon adsorption/supercritical CO_2 regeneration system to purify 10,000 scfm of air containing a quarter of the lower explosive limit of MEK was estimated to have a price of $530,000 (December 1980), a yearly operating cost of $285,000, and a MEK recovery value (pure MEK is recovered) of $1,386,000.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Activated carbon has been shown to be effective for atmosphere contamination control because of its ability to adsorb a wide range of organic compounds. The principal drawback of existing processes using carbon for the control of organic vapor emissions has been the requirement for a large carbon inventory to compensate for the inability of the regeneration technique to keep the carbon working capacity from declining over the course of multiple adsorption/regeneration cycles. However, process studies have shown that supercritical fluids (fluids in the region above their critical temperatures and pressures) can rapidly and effectively

regenerate activated carbon loaded with a broad range of organic compounds. The use of this regeneration method could favorably influence the economics of carbon used in emission control.

The essential features of the supercritical fluid process are set forth in a simplified process flowsheet, Figure 1. In the adsorption cycle, air contaminated with organic vapor flows through the granular activated carbon bed until breakthrough. Loaded carbon is then transferred to the pressure desorption vessel, and the desorption cycle begins. Supercritical fluid at conditions which favor the desorption of the component adsorbed on the carbon flows through the carbon bed. The effluent regenerant stream is rendered subcritical by alterations of its pressure and/or temperature, and a vapor/liquid separation (distillation) of this stream is effected to recover the solvent fluid for recycle. The regeneration system is efficient because the supercritical fluid has high solubility for the carbon adsorbates, favorable mass transfer properties for rapid desorption, and high volatility for subsequent separation of solutes. CO_2 is particularly suitable as the solvent; its critical temperature and pressure (31.0°C and 72.8 atm) are economically attainable, it has high solubilities for organic compounds, it is fairly dense at process conditions (therefore power requirements for compression are reasonable), and it is non-flammable and non-toxic. Where desirable, adsorbate can be recovered in reasonably pure form without a water/adsorbate separation process.

The objective of this program was to develop process information and economic estimates for this emission control system. The two key unit operations characterized were:

(1) The desorption of the carbon bed with the supercritical fluid.

(2) Distillation of the solvent/adsorbate mixture.

The program involved combination of an analytical and experimental approach to obtain proper characterization of parameters for the design of each unit operation. Specifically, the desorption operation was characterized for four test adsorbates. Two of these were volatile organic compounds (VOCs) representing important industrial solvents: ethanol and methyl ethyl ketone. The two other adsorbates were vapors from leaded and unleaded gasoline. For each, a range of regeneration conditions were evaluated using CO_2 as the regenerating solvent.

The process analysis and design phase included evaluation and selection of CO_2/adsorbate separation processes. Efficiency, low-cost, and component purities were criteria used in the evaluation.

Calgon type BPL granular activated carbon (GAC) was chosen as the carbon for the experimental work of this investigation. This GAC was chosen because it is in widespread use in commercial vapor-phase applications.

Gasoline and Industrial Volatile Organic Compound (IVOC) Adsorption/ Desorption Studies

The experimental adsorption/desorption studies included a series of screening runs, followed by evaluation

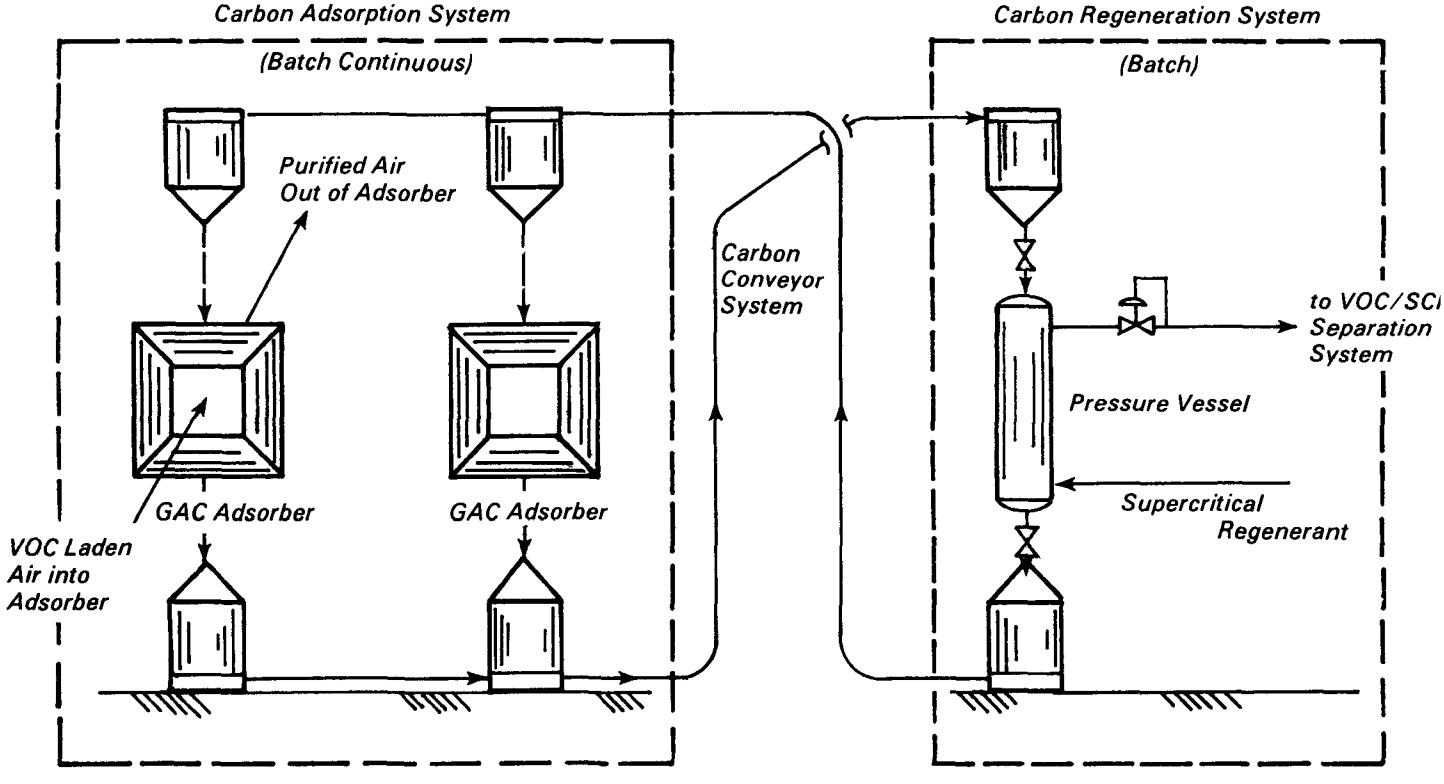


Figure 1. Simplified process flow sheet for supercritical-fluid regeneration of GAC used for VOC adsorption.

of the effects of regeneration process parameters. This was followed by a series of multi-cycle runs to establish regenerability in a bench-scale simulation of realistic operation of the adsorption/desorption process.

Screening Studies

A six-cycle adsorption/regeneration test on Calgon BPL 12x30 mesh GAC was carried out. A British Petroleum Company 89-octane no-lead gasoline (purchased at a local service station) was used as the vapor source. Air saturated with the gasoline at temperatures of 22-24°C flowed at approximately 500 cc/min through a 0.95-cm-diameter 23-cm-long high-pressure pipe packed with 7.5 g carbon. The adsorptions were not terminated at a particular breakthrough point, but rather after 30 minutes of adsorption. Regenerations were run immediately after adsorption. The tests occurred over a 6-day period, with the column open to the atmosphere when it was not adsorbing or being regenerated; the humidity of the air was not controlled. The carbon loadings, regeneration conditions, and residual weights for each cycle are presented in Table 1.

The first three regenerations were run with liquid CO_2, but above the critical pressure. The 53 standard liters (SL) of CO_2 used in the third run left more residual on the carbon than did the 96 and 85 SL of CO_2 used in the first and second regenerations, respectively. The fourth regeneration was run with supercritical CO_2 and had the lowest residual, 0.013 g/g carbon. The working capacity for this cycle was 26.1 g/100 g carbon.

The fifth and sixth regenerations were run with Freon-13 (chlorotrifluoromethane; T_C = 28.9°C, P_C = 38.2 atm). The fifth regeneration with 92 SL of liquid Freon-13 at 24°C had a greater residual, 0.036 g/g carbon, than did the first cycle (96 SL of liquid CO_2 at 24°C, residual of 0.018 g/g carbon). The residual left by 108 SL of supercritical Freon-13, 0.015 g/g carbon, was very close to the 0.013 g/g carbon residual left by the supercritical CO_2.

These preliminary data showed that both liquid CO_2 and Freon-13 can effectively regenerate GAC which had adsorbed gasoline vapors, with CO_2 leaving a lower residual than Freon when approximately 100 SL is used. Supercritical CO_2 and Freon left very low residuals when about 100 SL was used; supercritical CO_2 reduced the residual of 0.043 g/g, left after three cycles with liquid CO_2, to 0.013 g/g.

Table 1. Six-Cycle Adsorption/Regeneration Carbon Calgon BPL 12 x 30 Mesh Gasoline = B.P. No-Lead, 89 Octane (7.15 g GAC in Column)

Cycle	Loading & Residual		Regeneration Conditions	
1	Loading 1.98 g	0.277 g/g carbon	T = 24°C P = 1500 psi 96 SL @ 10 SL/min	Liquid CO_2
	Residual 0.13 g	0.018 g/g		
2	Loading 1.99 g	0.278 g/g	T = 26°C P = 1600 psi 85 SL @ 10 SL/min	Liquid CO_2
	Residual 0.20 g	0.028 g/g		
3	Loading 1.96 g	0.274 g/g	T = 24° C P = 1600 for 20 SL P ~ 1000 for 33 SL 53 SL@ 10 SL/min	Liquid CO_2
	Residual 0.31 g	0.043 g/g		
4	Loading 1.96 g	0.274 g/g	T ~ 50°C P = 1600 psi 102 SL @ 10 SL/min	Supercritical CO_2
	Residual 0.09 g	0.013 g/g		
5	Loading 1.84 g	0.257 g/g carbon	T = 24°C P = 1200 psi 92 SL @ 10 SL/min	
	Residual 0.26 g	0.036 g/g		
6	Loading 1.93 g	0.270 g/g	T ~ 50°C P = 1200 psi 108 SL @ 10 SL/min	Supercritical CF_3Cl
	Residual 0.11 g	0.015 g/g		

Preliminary testing was also done with an experimental GAC from Amoco, GX-31. Air saturated at 23°C with the BP no-lead gasoline flowed for 30 minutes through a 1.7-cm diameter 26-cm-long high-pressure pipe packed with 7 72 g of Amoco GX-31 pelletized 16-32 mesh carbon. The regeneration was run with 110 SL of supercritical CO_2 at 50°C and 1400 psi.

The working capacity was 0.60 g/g carbon. On the basis of g gasoline/cc carbon, the capacity of the Amoco carbon was 0.6 g/g carbon x 0.248 g carbon/cc = 0.15 g/cc, whereas the Calgon carbon was 0.25 g/g carbon x 0.455 g carbon/cc = 0.11 g/cc, a factor of 1.4 difference. Results for the adsorption/SCF regeneration on GX-31 were:

Loading and Residual	Regeneration Conditions
Loading: 5 02 g; 0.650 g/g carbon Residual. 0.39 g; 0.051 g/g	T ~ 50°C P = 1400 psi Supercritical CO_2 110 SL @ 10 SL/min

When the activated carbon column was removed from the high-pressure desorption apparatus after regeneration, the glass fiber plug at the desorption-effluent end of the column was blackened with fines from the carbon. Work was terminated with the GX-31 carbon at that time.

Toluene comprised up to 19 wt percent of the heel formed during a 1000-cycle test reported in the literature (Manos and Kelly (1977)). Thus, it was felt that the ability to desorb it from GAC would be a good indication of the ability of the near-critical fluid regeneration technique to maintain high carbon working capacity. Additionally, toluene is widely used as an industrial solvent, in paper-coating operations, for instance. Thus, toluene was selected for a preliminary pure component VOC study.

Air saturated at 23°C with toluene flowed through the 0.9-cm-diameter column packed with 7.47 g GAC. Three regenerations were run at the conditions given below:

Cycle	Loading & Residual		Regeneration Conditions	
1	Loading: 1.78 g;	0.238 g/g carbon	T = 24°C P = 1300 psi 150 SL @ 10 SL/min	Liquid CO_2
	Residual: 0.07 g;	0 g/g		
2	Loading: 1.64 g;	0.220 g/g	T = 24°C P = 500 psi 101 SL @ 10 SL/min	Gaseous CO_2
	Residual: 1.66 g;	0.222 g/g		
3	Loading: 1.66 g;	0.222 g/g	T = 24°C P = 1200 psi 138 SL @ 10 SL/min	Liquid CO_2
	Residual: 0.22 g;	0.029 g/g		

The first and third regenerations with liquid CO_2 were effective in removing toluene from the GAC. The gaseous CO_2 was totally ineffective for desorbing toluene.

The following grid generalizes these results with those for the gasoline vapor desorptions:

Fluid	State	Hydrocarbon Desorption from Activated Carbon
CO_2	gaseous T = 24°C P = 500 psi	totally ineffective
CO_2, Freon-13	near critical T = 24°C	very good
CO_2 Freon-13	supercritical T = 50°C	excellent

Thus, preliminary results indicated that CO_2 and Freon in the near-critical or supercritical states were effective in regenerating activated carbon loaded with hydrocarbons, while gaseous CO_2 was totally ineffective.

Process Studies with Gasoline

Additional experiments were done to determine what conditions of temperature and pressure were suitable to use as regeneration conditions for the multicycle adsorption/regeneration cycles. Four of the 7-g capacity columns, packed with the BPL 12x30 mesh GAC, were loaded with BP 89-octane no-lead gasoline vapors. Loading was allowed to continue until column effluent hydrocarbon concentration was 80 percent of that in the column influent. The columns were then regenerated with supercritical CO_2 at different conditions.

Column	Regeneration Conditions Pressure, atm	Temperature, °C
1	103	25
2	103	50
3	207	50
4	207	25

Approximately 180 SL of CO_2 was used for each regeneration; the flow rate was 15 SL/min. Three adsorption/regeneration cycles were run; results are shown in Table 2. After cycle 1, columns 1 and 4 had residuals of 0.05 g; whereas columns 2 and 3 had residuals of -0.01 and -0.04 g, respectively. The negative residuals suggest that the virgin carbon was initially slightly contaminated with volatile species, or that the water loading baseline varied slightly. After cycle 2, columns 1 and 4 had residuals of 0.07 g, and columns 2 and 3 had residuals of -0.01 and -0.03 g, respectively. After cycle 3, columns 1 and 4 had residuals of 0.11 and 0.06 g, respectively, and columns 2 and 3 had residuals of 0.03 and 0.02 g, respectively.

These data indicate that over three cycles, regenerations run at 207 atm are not significantly different than those run at 103 atm, and that regenerations run at 50°C are more complete than those run at 25°C.

Based on these results, regeneration conditions of P = 103 atm and T = 50°C were selected for the multicycle adsorption/regeneration experiments.

Process Studies with Industrial VOCs

After the selection of ethanol (EtOH) and methyl ethyl ketone (MEK) as the two industrial volatile organic compounds (IVOCs) for study, preliminary experiments were done to show that GAC loaded with these compounds could be regenerated by liquid CO_2. The procedure employed in the gasoline adsorption/regeneration cycles was used.

Air saturated with the VOC at 24°C flowed at approximately 800 cc/min through a 1.7-cm diameter, 16-cm long high-pressure pipe packed with 15.46 g of Calgon 12x30 mesh BPL carbon. The adsorptions were not terminated at a particular breakthrough point, but rather after 30 minutes of adsorption for the MEK, or after 60 minutes for the EtOH. Regenerations were run immediately after adsorption, with the column open to the atmosphere when it was being transferred between the adsorption and regeneration equipment; the humidity of the VOC carrier air was not controlled.

The MEK was Union Carbide commercial grade (99+ percent) from a 55 gal. drum; the EtOH was Publicker Industries Company 200 proof "Pharmco" brand. The carbon loadings, regeneration conditions, and residual weights for each cycle are given in Table 3.

All four regenerations were run with liquid CO_2 at 109 atm. In each cycle, the VOC was completely removed from the column; over four cycles there was no indication of residual buildup. The working capacity at 24°C of 0.21 g MEK/g carbon was approximately 80 percent of the capacity for no-lead gasoline vapors (0.26 g BP 89-octane no-lead/g carbon); the 0.16 g EtOH/g carbon working capacity was about 60 percent of the capacity for the no-lead gasoline vapors. Thus, preliminary studies indicated that liquid CO_2 was very effective as a regenerant for GAC loaded with MEK or EtOH.

Process studies and multicycle regenerations were run using at least 100 SL CO_2 for the 8-g carbon bed (about 22.5 lb CO_2/lb GAC). Because it is desirable to operate with minimum solvent usage, two tests were run with MEK at lower CO_2 usages to determine if lesser quantities would give adequate regeneration. The results are given in Table 4: 14 SL (3.4 lb CO_2/lb GAC) gave essentially the same capacity recovery as the larger CO_2 volumes.

Multicycle Tests

Multiple-cycle adsorption/regenerations were run on a 0.9-cm-diameter by 23.5-cm-long column packed with Calgon BPL 12x30 mesh GAC. Equilibrium vapor of a BP 89-octane unleaded gasoline in air was loaded at 200 cc/min onto the GAC column; loading was terminated when the hydrocarbon content of the column effluent reached

Table 2. *Three-Cycle Adsorption/Regeneration*

Column	Weight Carbon	Gasoline Loading 1	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 1
1	7.41 g	1.80g	0.243	1500 psi/25°C	0.05 g
2	7.66	1.93	0.252	1500/50	-0.01
3	7.39	1.86	0.252	3000/50	-0.04
4	7.20	1.76	0.244	3000/25	0.05

Column	Gasoline Loading 2	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 2
1	1.86 g	0.251	1500 psi/25°C	0.07 g
2	1.97	0.257	1500/50	-0.01
3	1.86	0.252	3000/50	-0.03
4	1.81	0.251	3000/25	0.07

Column	Gasoline Loading 3	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 3
1	1.88 g	0.254	1500 psi/25°C	0.11 g
2	1.91	0.249	1500/50	0.03
3	1.82	0.246	3000/50	0.02
4	1.80	0.250	3000/25	0.06

Carbon = Calgon BPL 12 x 30 mesh
Gasoline = B.P. no-lead 87-octane
Adsorption column influent flow rate = 180 ml/min
Adsorption termination when effluent hydrocarbon concentration = 80% of influent concentration
Desorption CO_2 flow rate = 15 SL/min
Desorption CO_2 volume = 180 SL

Table 3. *Four-Cycle Absorption/Regeneration (carbon = 15.46 g Calgon BPL 12 x 30 Mesh)*

Cycle	VOC	Loading and Residual		Regeneration Conditions[a]	
1	MEK	Loading 3.28 g	0.212 g/g carbon	T = 23°C P = 1600 psi	Liquid CO_2
		Residual-0.05 g	0 g/g	127 SL @ 10 SL/min	
2	MEK	Loading 3.33 g	0.215 g/g	T = 25°C P = 1600 psi	Liquid CO_2
		Residual-0.05g	0 g/g	137 SL @ 10 SL/min	
3	EtOH	Loading 2.43g	0.157 g/g	T = 24°C P = 1600 psi	Liquid CO_2
		Residual -0.09 g	0 g/g	124 SL @ 20 SL/min	
4	EtOH	Loading 2.44 g	0.158 g/g	T = 24°C P = 1600 psi	Liquid CO_2
		Residual -0 06 g	0 g/g	122 SL @ 20 SL/min	

[a] *For all regenerations, the last approximately 30 SL are $P_{sat} \approx 900$ psi.*

Table 4. *Reduced CO_2 Usage Regeneration Tests*

	After MEK Loading				After Regeneration		
Cycle	Column Mass	MEK mass	g/g Carbon	SL CO_2	Column Mass	MEK Residual	Residual g/g Carbon
1	438.41g	2.84g	0.376	20	435.83g	0.26g	0.034
2	438.35	2.78	0.368	14	436.06	0.49	0.065

Mass Carbon (Calgon BPL 12x30 Mesh): 7.56 g
Mass Carbon and Column : 435.57g
Column Loaded with Equilibrium MEK vapor in Air at 23°C (~ 1 x 10^5 ppmv)
Regeneration Conditions: T = 50°C
P = 100 atm

30 percent of the column influent, as determined with the FID. After loading, the column was regenerated with CO_2 at 103 atm and about 50°C; approximately 100 SL of CO_2 was used at a flow rate of 15-20 SL/min. After regeneration, constant humidity air flowed through the column at 2.5 L/min for about 1 min to desorb residual CO_2.

In the 25-adsorption/regeneration-cycle test for unleaded gasoline, the initial mass of the column and the virgin GAC (equilibrated with constant humidity air) was 435.42 g After 25 cycles, the mass was 435.42 g, i e., the carbon was 100 percent regenerated. The working capacity of the carbon was 0.24 g/g carbon; using as little as 89 SL CO_2 appeared to completely regenerate the carbon.

Another series of multiple-cycle adsorption/regenerations were run using BP 89-octane leaded gasoline. The same adsorption procedures as with the unleaded gasoline were employed. The air/leaded gasoline stream had a smaller flow rate: about 150 vs 200 cc/min for unleaded. Similar regeneration conditions were used to desorb the leaded gasoline as for unleaded.

In the 25-adsorption/regeneration-cycle test for leaded gasoline, the initial mass of the column and the virgin GAC was 436.30 g. After 25 cycles, the mass was 436.28 g; i.e., the carbon was 100 percent regenerated (the experimental precision is ±0.02 g). There were gasoline residuals on the carbon after regenerations 6 and 11; cycles 6 and 11 had relatively high initial gasoline loadings, 0.249 and 0.254 g/g, respectively. The working capacity of the carbon was 0.25 g/g carbon.

After the 25th cycle of the leaded gasoline vapor testing, additional adsorption/regeneration cycles were carried out with ethanol vapor. Equilibrium vapor of 200 proof ethanol in air, about $6x10^4$ vol. ppm at 23°C, flowed at 1.5 SL/min through the GAC column. The loading was terminated when the ethanol content of the column effluent reached 80 percent of the column influent, as determined with the FID. After loading, the column was regenerated with CO_2 at 103 atm, and temperatures slightly lower than used for the gasoline vapor regeneration, 41 to 51°C. The carbon was 100 percent regenerated after each cycle; the working capacity was about 0.32 g/g.

Thus, after 50 adsorption/regeneration cycles, 25 cycles with leaded gasoline vapor adsorbate and 25 cycles with ethanol vapor adsorbate, the carbon retained 100 percent of its virgin working capacity.

Further testing on this carbon bed included multicycle tests with MEK. Equilibrium vapor of Doe and Ingalls Industries Co. industrial grade MEK in air, about 1.13×10^5 vol. ppm at 22°C, flowed at 0.8 SL/min through the GAC column. The loading was terminated when the MEK content of the column effluent reached about 80 percent of the column influent. After loading, the column was regenerated with CO_2 at 103 atm, and temperatures of 40-64°C.

A residual of 0.02 g, which could not be removed with up to 235 SL CO_2 (at 50°C and 103 atm), was left on the carbon. After the first four cycles, it was discovered that the MEK had attacked the rubber gaskets in the flowmeter upstream of the carbon bed; some of the rubber was probably adsorbed on the carbon and caused its 0.02 g increase in mass.

While 100-110 SL CO_2 at 50°C and 103 atm could completely regenerate carbon loaded with gasoline vapors or EtOH, approximately 150 SL CO_2 was necessary to regenerate the MEK-loaded carbon. With 120 SL CO_2 regeneration, or about a 0.07 g residual, the carbon working capacity was about 0.33 g MEK/g carbon; with 150 SL of regeneration, or a 0.02 g residual, the carbon working capacity was approximately 0.34g MEK/g carbon.

Figure 2 shows the working capacity as a function of cycle number over the entire 75-cycle test.

Adsorbate/Regenerant Separation

The effluent stream from a carbon column undergoing regeneration with a supercritical fluid must have nearly complete separation of the adsorbate from the regenerant so that the regenerant may be recycled. These paragraphs discuss separation of CO_2 regenerant by distillation from the different test adsorbates: gasoline vapor components (GVCs), EtOH, and MEK.

CO_2/GVC Separation

The feed stream to a CO_2/GVC separation system would be at typical carbon regeneration temperature and pressure: 100 atm and 50°C. The stream would be between 1 and 10 mole percent hydrocarbon in CO_2 (most likely at the low end of that range). The GVCs would be approximately 50 mole percent n-butane, 30 mole percent isopentane, 2 mole percent n-hexane, with the remainder being light paraffins, olefins, and aromatics (C_5-C_8). The heavy key component is n-butane, and design calculations were done on this basis.

Vapor/liquid equilibrium data for the CO_2-n-butane system at 34 atm* are available (Olds et al., 1949; Poettman and Katz, 1945).

To achieve a separation with

$^{x}CO_2$ bottoms < 0.01

$^{x}CO_2$ distillate > 0.99,

a graphical calculation using the McCabe-Thiele method indicated that the minimum number of theoretical stages is seven.

A column design with a low reflux ratio is feasible because of the high CO_2

*Slightly below the maximum pressure at which CO_2-n-butane separation can be effected -- 37 atm, the critical pressure of n-butane

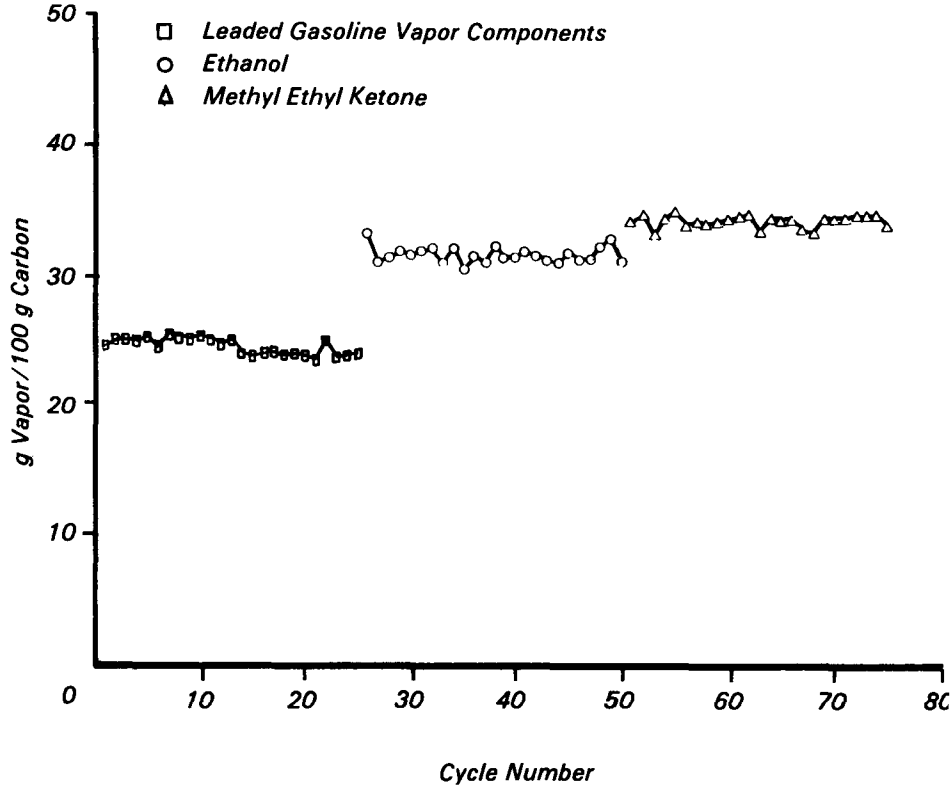


Figure 2. *Carbon working capacity vs. cycle number for 75-cycle test with supercritical CO_2 regeneration.*

feed concentration ($^{x}CO_2 \geq 0.9$) and high relative CO_2-n-butane volatility. The feed stream at 100 atm and 50°C is flashed to 34 atm, and in so doing is about 75 percent vaporized, if the mixture's thermodynamic properties are assumed to be equal to those of pure CO_2. A D/V (= total overhead product rate/CO_2 phase rate) = 0.6, or L/V (= slope of upper operating line) = 0.4 when $^{x}CO_2$ distillate $\simeq$ 1.0 gives nine theoretical stages. The external reflux ratio at the top of the column is 0.67.

The column has the feed introduced between stages 7 and 8 and has a partial condenser. The distillate (vapor at 0°C and 34 atm) is compressed to 100 atm and 50°C in a two-stage compressor. Figure 3 is a flowsheet for this distillation system.

The column design cannot be optimized with respect to reflux ratio versus total number of stages (column height) until the height equivalent to a theoretical plate (HETP) is known. The HETP is preferably obtained by experiment; although there are correlations in the literature (e.g., Murch, 1953), that can be used for preliminary design estimates. One would expect low mass transfer resistances between the liquid and vapor phases at the temperatures and pressures under consideration, and hence relatively small HETPs.

The energy requirement of the sample nine-stage system shown in Figure 3 was estimated to be 4000 Btu/lb-mol feed including the recycle compressor. This assumes that the compressor and cooler are run electrically and that the reboiler is steam heated; the conversion factor between electrical and steam energy is 0.8/0.34.

Alternatively, a vapor-recompression distillation system can be used for a more energy-efficient CO_2/butane separation. Figure 4 is a flowsheet for this system. In this scheme, the entire overhead vapor stream V is fed to compressor CI where it is compressed to the recycle pressure (100 atm). A portion of the heat of compression of compressor discharge stream 1 is used to heat stream 1 in partial reboiler PRBI. The compression ratio, compressor efficiency, and heat exchanger flow rates and efficiency determine the maximum temperature which can be obtained in the reboiler. If this reboiler temperature is insufficient to achieve the desired bottoms purity, stream B would have to be flashed to a lower pressure and fed to another separation system.

Reflux at the top of the column is provided by splitting stream 2, cooling split-stream 2a in reflux exchanger RE and flashing back to column pressure by means of valve X. For instance, if stream 2 were at 100 atm and 50°C, 2a could be cooled to about 30°C with cooling water in RE, and upon flashing to 34 atm, would be about 70 percent liquefied.

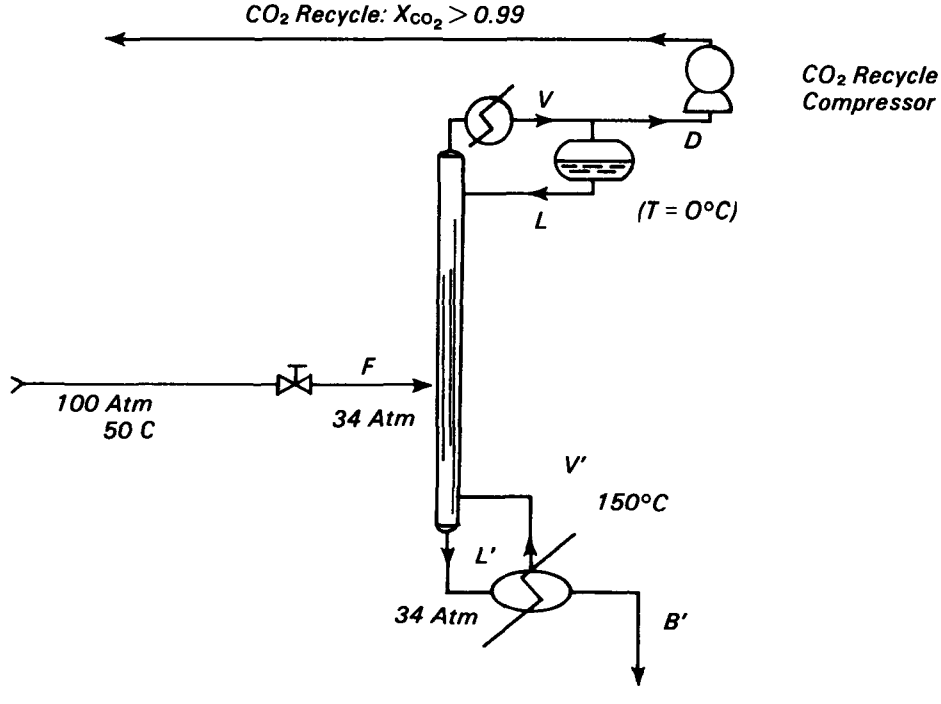
The recycle compressor cost would likely be a sizable fraction of the fixed capital investment for this vapor-recompression system, and this an optimal design would tend toward a relatively small reflux ratio and more theoretical stages.

CO_2/IVOC Separation

To carry out the design calculations for a system for removal and recovery of MEK or EtOH, performance of vapor/liquid separations for the binaries CO_2/MEK and CO_2/EtOH are required. Detailed design calculations were done for an MEK adsorption/regeneration process. In these paragraphs, the bases for the CO_2/MEK separation design are given, plus the fundamental information needed for a CO_2/EtOH vapor/liquid separation design.

No experimental data for the CO_2/MEK system are available, and only fragmentary information has been published for CO_2/EtOH. Thus, two-component phase-equilibrium relationships had to be used to predict the required data from thermodynamic properties of the pure components. A common method, the Lewis and Randall rule, failed to give reasonable agreement with the published CO_2/EtOH data.

The Peng-Robinson modification of the Redlich-Kwong equation of state was shown recently to predict vapor-liquid equilibria successfully near the critical point. This approach was tried for both CO_2/EtOH and CO_2/MEK, and



D/V = 0.6
L/V = 0.4
L'/V' = 1.15

D = 0.89 F mols
B x 0.11 F mols
V = 1.48 F mols
L = 0.59 F mols
V' = 0.73F
L' = 0.84 F

Figure 3. CO_2-butane separation flow sheet.

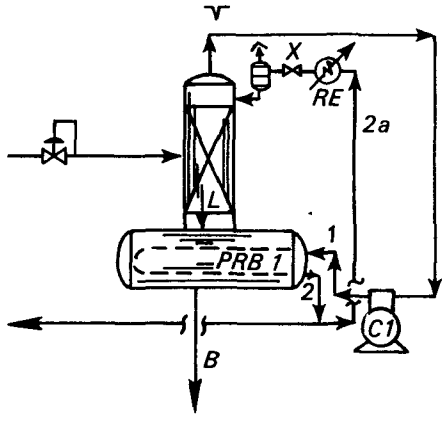


Figure 4. *Vapor-recompression distillation for CO_2-butane separation.*

it was found to adequately model the known CO_2/EtOH data. Thus, it was used for the CO_2/MEK predictions. Calculations for CO_2/MEK were done at both 800 and 300 psia, in preparation for the design case.

The CO_2/MEK vapor/liquid equilibrium data were then used to fix the separation system design. The results show:

(1) feed composition (desorber effluent) of 0.95 CO_2 mol fraction (0.05 MEK mol fraction), at a pressure of 102 atm (1500 psia) and a temperature of 50°C (122°F), a CO_2 purity of 0.999995 can be achieved at a distillation pressure of 54.4 atm (800 psia), representing 90.6 mol percent of the feed. The bottoms composition is 0.49 CO_2 mol fraction. Five rectifying stages and one stripping stage are needed, and the reflux ratio is 0.06.

(2) feed composition of 0.49 CO_2 mol fraction, at 54.4 atm (800 psia) and 50°C (122°F), an overhead product of 0.991 CO_2 mol fraction is obtained at 20.4 (300 psia), representing 38 mol percent of the feed. The bottoms composition is 0.18 CO_2 mol fraction. Two stripping stages are needed, with no reflux requirement.

Process Design

These paragraphs describe the process design of a full-scale system to treat 10,000 scfm of air with 4500 ppmv MEK vapors. System operation is described first; the design of important components, such as adsorption and desorption vessels, is then presented, followed by the capital and operating costs for the system.

System Operation

The adsorption/desorption system described here is based on the use of supercritical CO_2 to remove adsorbed MEK vapors from GAC. The adsorption and desorption vessels are separate because of significant differences in design criteria; thus, the carbon is transported from one to the other. The desorption cycle includes separation of MEK dissolved in the CO_2 effluent by distillation and flash units at several pressure levels, to minimize the loss of CO_2, to recover the maximum amount of MEK adsorbate, and to maximize the purity of CO_2 return to the desorption vessel.

The adsorption cycle operation is shown schematically in Figures 5A-D. Carbon adsorption vessels CA1 and CA2 and ancillary carbon hoppers H1-H4 are connected to carbon regeneration vessel CRV and hoppers H5 and H6 by tubular conveyor TC. The MEK-containing air stream, flowing at 10,000 scfm with a head of 8 in. water, is alternately cycled over a 15-minute adsorption period between CA1 and CA2.

Figure 5A shows a 10-min phase in the adsorption cycle. Air flows through carbon bed CA1, regenerated carbon from H6 is transferred by TC to H1, and MEK-loaded carbon in H4 (previously in CA2) is moved through TC to H5. At the end of 10-minutes, the system is as shown in Figure 5B: H1, H3, and CRV contain regenerated carbon. In the next 2½ minutes, CRV is depressurized, the carbon is transferred to H6 and the carbon from H3 is moved into CA2. In the following 2½ minutes, CRV is filled with the carbon in H5 and repressurized. The system is then as shown in Figure 5C. The air flow is then switched to CA2, and the cycle begins again, as shown in Figure 5D.

Figure 6 is a flow schematic of the desorption and solvent recovery portion of the system. The CRV shown in Figure 6 is the same as that shown in Figure 5.

The desorption cycle operates as follows. Desorption at 100 atm and 50°C is carried out with continuous CO_2 flow for 10 minutes. At the completion of regeneration, CRV is first depressurized into FV-1, the primary distillation unit, until CRV pressure falls to 54 atm. At that point, depressurization continues with CO_2 flow into FV-2, the secondary flash vessel, until CRV pressure falls to 20 atm. Finally, CRV is depressurized to 2 atm with CO_2 flow directed to low-pressure accumulator LPA. Following this, the remaining CO_2 is vented, and the carbon is discharged to hopper H-6.

CRV is then charged with carbon from hopper H-5. During the CRW downtime, high-pressure accumulator HPA is recharged from about 50 atm to 100 atm by continuing operation of compressor C-1. After the carbon charge is received by CRV, the valve between HPA and the CRV is opened, the pressure equalizes at about 50 atm, and the valve is closed. At that point, the CO_2 flow from compressor C-1 is redirected to pressurize the CRV to 100 atm as the desorption cycle is initiated.

During the desorption cycle, the desorber effluent, stream No. 1, leaves CRV at 100 atm and 59°C. It is flashed through a valve to 54 atm and 20°C (stream No. 2) to still FV-1, a small packed column with the equivalent of five theoretical plates in the rectifying section, and one theoretical plate in the stripping section. The overhead from FV-1 is fed to the suction side of compressor C-1 to increase the pressure to 100 atm, with a concomitant temperature rise to 65°C. The C-1 discharge is then fed to reboiler FV-1 to provide the heat of vaporization, in a standard vapor recompression cycle. Approximately 6 mole percent of this stream is fed back to the still as reflux by being cooled to 27°C, and being flashed to 54 atm where its quality becomes about 95 percent liquid, 5 percent vapor. At this point, a bleed of noncondensable gases may be taken, if necessary (FV-4), and stream No. 15, the column reflux, is reintroduced into FV-1. The remainder of the recompressed CO_2 (stream No. 5) returns to the column, undergoing slight cooling from 57°C to 50°C, where it is reintroduced to CRV as clean makeup solvent.

The still bottoms from FV-1 leaves at 54 atm and 50°C, containing about 49 mole percent CO_2. It is directed to flash vessel FV-2, maintained at 20 atm and 21°C. The overhead from FV-2 is fed to compressor C-2, along with the required CO_2 makeup (available at 20 atm) and the discharge from compressor C-3, which empties low-pressure accumulator LPA from a pressure of 2 atm to atmospheric pressure. The C-2 discharge (stream No. 8), at 54 atm and 82°C, provides the heat of vaporization for the flash in FV-2. The cooled 54-atm effluent (stream No. 9) is then added to the

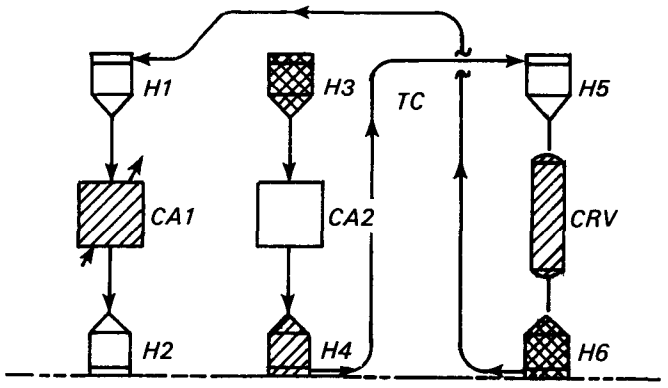


Figure 5A

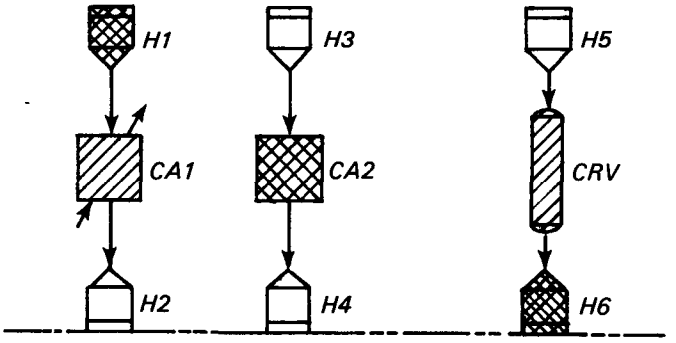


Figure 5C

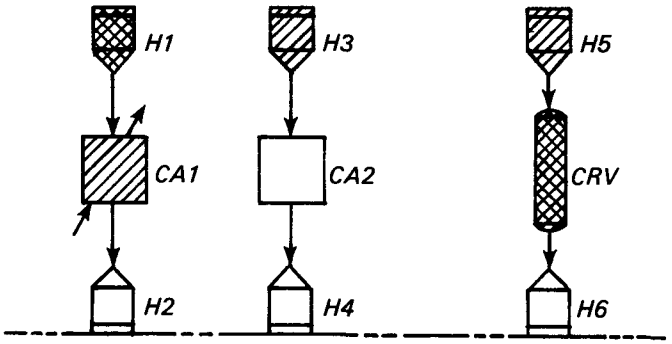


Figure 5B

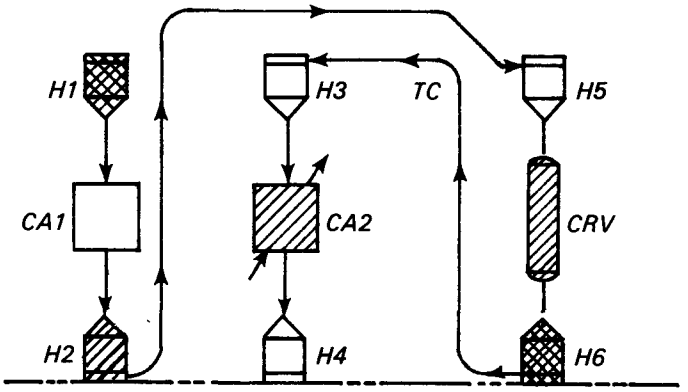


Figure 5D

Denoted MEK-loaded Carbon Denotes Regenerated Carbon

Figure 5. *Adsorption cycle operation schematic.*

FV-1 feed to ensure maximum removal of MEK from the CO_2.

The bottoms liquid from flash vessel FV-2 is discharged into small flash vessel FV-3, which operates at the pressure of LPA, cycling between 2 atm and atmospheric pressure. Heat is added to provide essentially complete stripping of CO_2 from the final MEK discharge, using an electric heater. Thus, the MEK discharge is essentially free of CO_2. The FV-3 overhead is directed to LPA.

System Design

The system is designed to handle 10,000 cfm containing 25 percent of the lower explosive limit (LEL) of MEK, giving a feed concentration of 4,500 ppm. The capacity of GAC for MEK at 1.1 x 10^5 ppm feed was measured experimentally as 0.34 lb/lb.

For design purposes, it was assumed that the carbon would adsorb 75 percent of this level (0.26 lb/lb carbon), since the MEK adsorption isotherm is relatively concentration independent at these concentration levels.

A 15-minute adsorption/desorption cycle was chosen by running optimization calculations with regard to vessel costs.

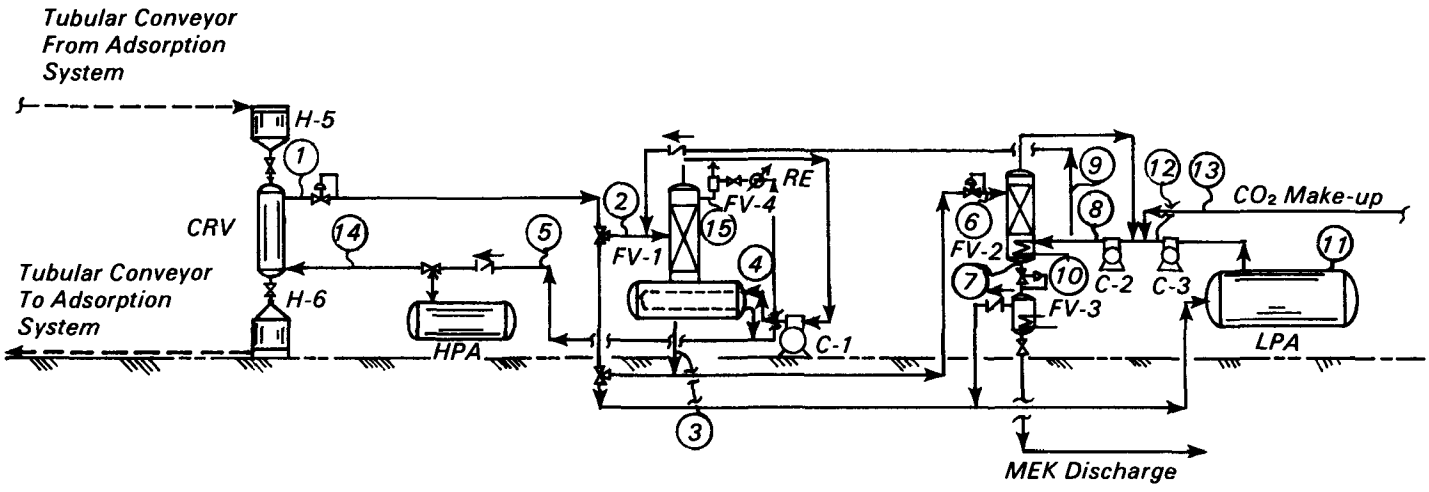
The above parameters fix the carbon bed size at 480 lb GAC, or about 18 ft^3. A figure of 20 ft^3 was used to fix the bed dimensions of both the adsorption and desorption vessel. In the adsorber, it was assumed that the bed depth would be about 4 in., utilizing a square vessel with a dimension of about 7 ft on the side. The desorber was dimensioned to give reasonable pressure-vessel parameters, and was taken as a 2 ft diameter, 7 ft long vessel.

Sizing of the flash vessels was based on established capacity correlations for packed or open vessels. Sizing of the high-and low-pressure accumulators was based on the gas volumes involved.

Figure 7 shows the material balance on CO_2 flow around the CO_2 recovery system.

Process Economics

Vendor's estimates or estimates based on standard correlations were used to obtain costs of the individual equipment items. Following the cost-estimating practice described by Guthrie (1969), installation factors were used to



	Stream No.														
Process Conditions	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Pressure PSIA	1500	900	800	1500	1500	300	300	800	800	14.7 to 30	14.7 to 30	300	300	1500	800
Temperature °C	50	20	50	66	57	21	47	82	60	16	16	82	-18	50	18
Temperature °F	122	68	122	150	135	70	117	180	140	60	60	180	0	122	65

Legend

C-1 - Compressor
C-2 - Compressor
C-3 - Compressor
CAV - Carbon Regeneration Vessel
FV-1 - Flash Vessel
FV-2 - Flash Vessel
FV-3 - Flash Vessel
H-5 - Carbon Feed Hopper
H-6 - Carbon Discharge Hopper
HPA - High Pressure Accumulator
LPA - Low Pressure Accumulator
FV-4 - Flash Vessel
RE - Reflux Exchanger

Figure 6. *Supercritical CO_2 VOC carbon regeneration system.*

give so-called module costs for each item; these were summed to give the installed costs for the system. As recommended by Guthrie, a 10 percent contingency and a 3 percent contractor's fee were added, for a system cost of $530,000. These costs were for December 1980.

System operating costs are shown in Table 5. These total about 2¢/lb of GAC regenerated.

Capital costs may be compared with those published for other carbon regeneration systems. The highest-cost system among competitive processes is about $450,000. That system, which involves steam regeneration, produces a mixture of MEK and water, which has a low value as solvent to be recycled to the industrial operation. The MEK discharge from the CO_2 system is essentially free of water, and thus may be valued at close to makeup MEK prices.

On this basis, it is possible to calculate an approximate payout for the system, assuming full value for recovery of MEK. The calculation shows that the annual MEK value, reduced by the annual operating costs of the entire carbon regeneration system, comes to $1,100,900/year. Dividing this into the capital cost of $530,000 gives a rough payout time of approximately 0.48 years. Thus, if good-purity MEK can be recovered from the system, the carbon regeneration process provides an opportunity for a rapid payout source of makeup industrial solvent.

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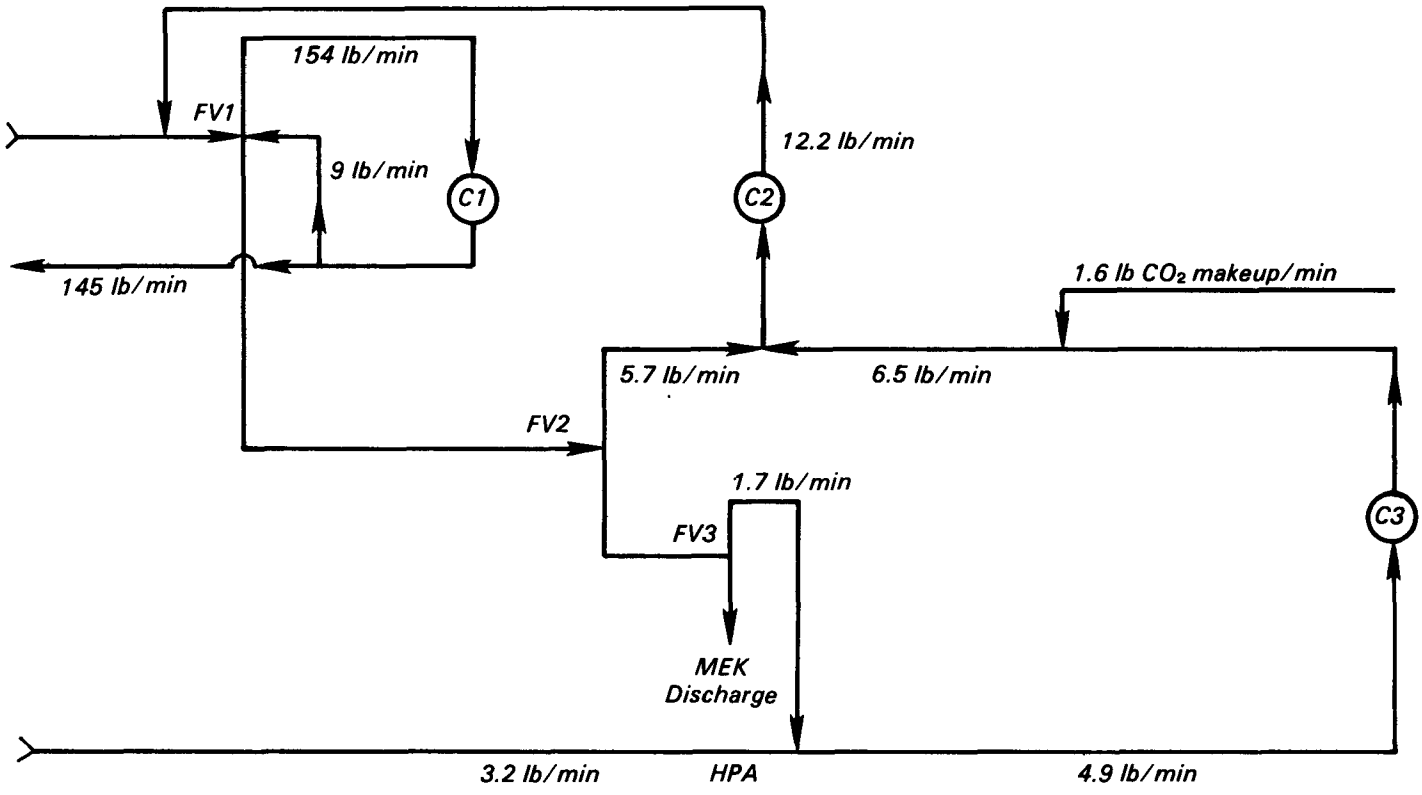

Figure 7. *CO_2 flow rates for MEK/CO_2 separation system.*

Table 5. *Process Cost Estimate*

Case: Supercritical CO_2 Regeneration of Activated Carbon Used for MEK Vapor Adsorption
Capacity: 10,000 scfm air laden with 0.25 LEL MEK = 12,000 lb MEK/day; 46,100 lb GAC regenerated/day
Capital Investment: $532,000 (Basis: December 1980)
Operation: 330 days/yr

Variable Costs	Unit/Day	$/Unit	$/day	¢/lb MEK Recovered
Electricity :	2208 kWh	0.05	110.40	0.920
Make-up CO_2 :	2304 lb	0.08	184.32	1.536
Cooling H_2O :	2.448 Mgal.	0 15	0.37	0.003
Make-up Carbon:	10% Carbon Inventory [a]/yr		1.45	0.012
	Total Variable Costs:		296.54	2 471
Semivariable Costs				
Operating Labor :	½ man/shift, 3 shift/ day @ $11.00/hr		132.00	1.100
Supervision :	¼ man/yr @ $30,000/yr		22.73	0.189
Labor Overhead :	60% of Labor & Supervision		92.84	0.774
Maintenance .	4% of Capital Investment/yr		64.48	0.537
	Total Semivariables:		312.05	2.600
Fixed Costs				
Plant Overhead :	40% of Labor & Supervision		61.89	0.516
Depreciation :	10% of Capital Investment/yr		161.21	1.343
Taxes & Insurance :	2% of Capital Investment/yr		32.24	0.269
	Total Fixed Costs:		255.34	2.128
	Total Operating Cost:		$863.93/ day 7.199 ¢/lb MEK recovered 1.87 ¢/lb GAC regenerated	

[a] For fixed-bed adsorber system.

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The complete report, entitled "Supercritical Fluid Regeneration of Activated Carbon Used for Volatile-Organic-Compound Vapor Adsorption," (Order No. PB 82-228 974; Cost: $12.00, subject to change) will be available only from:
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