

ACTIVATED CHAR FROM ILLINOIS COAL FOR VOC CONTROL

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Introduction

Volatile organic compound (VOC) emissions are of concern due to their negative effects on human health and contribution to photochemical smog formation. A variety of industrial processes utilize solvents and contribute to VOC emissions. Paint spraying and stripping applications are also an important VOC source. According to the U.S. Environmental Protection Agency, 137 million pounds of VOC compounds from industrial solvents are discharged into the atmosphere each year. Six industrial solvents are considered to be VOCs as well as hazardous air pollutants (HAPs): methyl ethyl ketone (MEK), trichloroethylene (TCE), toluene (TOL), methyl isobutyl ketone, xylene and acetone. These six solvents have a total release of 62.5 million pounds per year. Title III of the U.S. Clean Air Act Amendments of 1990 requires regulation of 189 chemicals which are referred to as HAPs. Those VOCs defined as HAPs are becoming strictly regulated as to their use and emissions.¹ Adsorption is one of several approaches to remove VOCs from contaminated air.^{1,2} For compatible applications, the factors that determine the technology of choice are economics and safety. The purpose of this study was to evaluate activated char produced from bituminous coal as a low cost replacement for activated carbon now used in regenerable adsorption VOC control systems. Activated chars were prepared by various methods and their MEK capacities measured and compared to commercial VOC control carbons and other types of carbons, e.g., activated carbon fiber (ACF).

Experimental

Activated chars were prepared from Illinois bituminous coal (IBC-102). Samples of IBC-102 coal (200 g, 48x100 mesh) were pyrolyzed in a 5 cm ID batch fluidized-bed reactor (N₂, 900°C, 0.5 h). The resulting chars were activated using steam (50%, 825°C, 2-5 h) or KOH (KOH/coal = 2, N₂, 800°C, 1 h). Selected H₂O activated chars were treated with nitric acid at 100°C for 2 h and thermally desorbed at 925°C. Other treatments are briefly summarized in Table 1.

VOC adsorption capacities of activated chars were measured by NOXSO (25°C, 400 ppmv MEK, 2.3% H₂O, balance N₂, 250 cm³/min) and the Illinois State Geological Survey (ISGS) (25°C, 800 ppmv MEK, 0% H₂O, balance N₂, 500 cm³/min) using different methods. NOXSO used a down-flow, fixed-bed microreactor (vertically mounted Pyrex tube, 1.9 cm ID x 19 cm) and a GC to monitor the concentration of MEK in the exit gas. Adsorption only (Table 1) and adsorption/regeneration (Table 2) experiments were run until 100% and 10% breakthrough, respectively. During regeneration the sorbent was heated to about 180°C under flowing N₂ (2.3% H₂O, 250 cm³/min). Adsorption runs were also performed using TCE and TOL. ISGS determined MEK capacities of activated chars using a thermogravimetric analyzer (Cahn 2000). Single-point N₂ BET surface areas were measured using a Monosorb flow apparatus (Quantachrome Corporation).

Results and Discussion

Table 1 lists MEK adsorption capacities of activated chars (A-H) under dry and/or humid conditions. Under dry

conditions, Char E adsorbed the most MEK (260 mg/g). Chars A-G, however, achieved essentially the same MEK surface loading (mg MEK/m²) regardless of preparation conditions. The MEK capacities of Chars A-G normalized with respect to their N₂ BET surface areas varied by only a factor of 1.2 (0.260/0.216) indicating an excellent correlation between MEK capacity and N₂ BET surface area. For comparison, the MEK capacities of three ACFs³ (inlet [MEK] = 1000 ppmv), four Ambersorb carbons⁴ (inlet [MEK] = 327 ppmv) and a commercial coconut shell based carbon are also listed. The VOC capacity of activated char appears to depend mostly on available surface area; however, Table 1 also shows that MEK surface loadings for Ambersorb 563 (0.36) and ACF-15 (0.30) are quite high, suggesting a more efficient utilization of surface area by these carbons. Other properties, such as pore size distribution and surface chemistry, may also play a role in MEK adsorption. For example, although ACF-25 has 800 m²/g of additional surface area, its capacity for MEK is about 10% lower than that of ACF-20. The micropore size distributions of ACFs 15, 20 and 25 are centered at 10, 12 and 14 Å, respectively.³

Under humid conditions (62% relative humidity), the MEK surface loadings of Chars F and G were reduced by about one half even though MEK readily dissolves in water (0.24 g MEK/g H₂O). A recent study⁶ showed that at RH < 90% and for soluble VOCs such as acetone, adsorbed H₂O had little or no effect on the VOC adsorption capacity of ACF. The study also showed that at RH > 65%, H₂O will begin to compete with insoluble VOCs such as benzene for adsorption sites.

Char C was subjected to a 10-cycle MEK adsorption/desorption experiment. Table 2 shows that while there was some variation in MEK capacity after each cycle, activity remained essentially constant over the 10 cycles. As expected, the surface area of the char was unaffected by the 10-cycle test. The absence of water in adsorption cycle 8 may have increased the MEK capacity of the char slightly. A typical MEK desorption curve is shown in Figure 1 (cycle 1). A large spike of MEK was observed at about 110°C in each cycle. Precise mass balances for MEK adsorption/desorption cycles were not possible because desorption peak concentrations saturated the detector. Table 2 shows an estimate of the MEK evolved during regeneration (cycles 1, 5 and 10) based on GC data.

Char C was also tested for its capacity to adsorb TOL and TCE (Table 3). Two cycles were carried out for each VOC. TOL (second cycle only), TCE, and MEK adsorption curves are shown in Figure 2. Char C exhibited a greater affinity for TOL and TCE than for MEK (Table 3). The order of affinity was TOL > TCE > MEK. This affinity trend is typical of most activated carbons, and reflects the strength of the interaction of the organic molecule with the carbon surface as well as the size of the organic molecule.⁴ The results obtained for TOL at the different feed concentrations indicated that a higher feed concentration results in a higher sorbent loading at breakthrough.

The mineral matter content of Char C, determined by a low temperature oxidation procedure, was 27% by weight. XRD results indicated that this material consisted of nearly amorphous carbon with a large amount of other crystalline material (SiO₂, Fe₃O₄, FeO); other materials present at lower concentrations were not identified. The mineral content of Char C and especially the high proportion of iron-based impurity phases could result in adverse effects for halogenated

VOC control applications. Regeneration would typically be carried out in the presence of moisture, either from steam regeneration or simply the water adsorbed during use. Transition metal impurities, iron in this case, are known to catalyze the decomposition of some halogenated solvents at elevated temperature in the presence of water resulting in corrosive byproducts such as hydrochloric acid or chloroalcohols.⁴ It is interesting to note that the MEK capacity of Char C, corrected for mineral matter content, was less than 10% that of the coconut shell based carbon used in commercial VOC removal applications and that physical coal cleaning methods⁸ can be used to remove more than 80% of the discrete mineral matter in Illinois coal.

Conclusions

Activated chars prepared from Illinois coal had MEK adsorption capacities approaching those of high-surface-area activated carbon fibers and commercial activated carbons. Under dry conditions, MEK surface loadings for activated chars were relatively constant and ranged between 0.22 and 0.26 mg MEK/m². Some commercial carbons and ACFs achieved higher surface loadings; these carbons utilized their surface area more efficiently to adsorb MEK, suggesting that pore size and surface chemistry also play a role in the adsorption process. Under humid conditions, the MEK removal performance (adsorption capacity and regenerability) of one steam activated IBC-102 char was comparable to that of a commercial VOC control carbon. These results show that activated chars have potential as low-cost VOC control sorbents; however, further research is necessary to optimize performance and characterize the effect of impurities.

Acknowledgments

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References

- Freeman, H.M., *Industrial Pollution Prevention Handbook*, McGraw-Hill, New York, NY, 1995, p. 384.
- Pennington, R.L., *Environmental Protection* 7, 32 (1996).
- Cal, M.P., Ph.D. Thesis, University of Illinois, Urbana, IL, 1995.
- Vandersall, M.T., McMurtrie, J.L. and Maroldo, S.G., AIChE Meeting, Miami Beach, FL, November, 1992.
- DeBarr, J.A., Lizzio, A.A. and Daley, M.A., *Energy and Fuels* 11, 267 (1997).
- Cal, M.P., Rood, M.J. and Larson, S.M., *Gas Sep. Purif.* 10, 117 (1996).
- Kenson, R. E., *Environmental Progress* 4, 161 (1985).

- Honaker, R.Q., Reed, S., Mohanty, M.K. and Ho, K.K., "In-Plant Testing of a Novel Coal Cleaning Circuit Using Advanced Technologies," Final Technical Report to the Illinois Clean Coal Institute, 1996.
- Lizzio, A.A., DeBarr, J.A. and Kruse, C.W., 22nd Biennial Conference on Carbon, 1995, p. 744.

Table 1. Summary of MEK capacity results under dry and humid conditions (100% breakthrough).

Sample	Surface area (m ² /g)	Dry		2.3% H ₂ O	
		Capacity (mg/g)	Surface loading (mg/m ²)	Capacity (mg/g)	Surface loading (mg/m ²)
ACF 15	900	270	0.300	---	---
ACF 20	1610	360	0.224	---	---
ACF 25	2420	330	0.136	---	---
Ambersorb 563	550	198	0.360	---	---
Ambersorb 564	550	171	0.311	---	---
Ambersorb 572	1100	304	0.276	---	---
Ambersorb 575	800	218	0.272	---	---
Char A - IBC-102; N ₂ , 700°C; 10% O ₂ , 440°C	320	75	0.234	---	---
Char B - IBC-102; H ₂ O, 825°C, 5 h	560	121	0.216	---	---
Char C - IBC-102; H ₂ O, 825°C, 8 h	710	---	---	88	0.124
Char D - Char B; 20% O ₂ , 350°C, 1 h; 925°C	498	112	0.225	---	---
Char E - IBC-102; KOH, 2:1, 800°C, 1 h	1130	260	0.230	---	---
Char F - Char B; HNO ₃	614	160	0.260	80	0.130
Char G - Char F, 925°C	755	181	0.240	68	0.090
Char H - low surface area char ^a	110	---	---	10	0.091
Commercial carbon for VOC control	1025	---	---	132*	0.129*
Char C - corrected for ash content	959	---	---	121	0.126

* = Full capacity value extrapolated from value at 50% breakthrough.

Table 2. Summary of 10 cycle experiment for Char C (10% breakthrough).

Cycle	MEK feed conc. (ppmv)	Sorbent weight after reaction (g)	Sorbent weight after regeneration (g)	adsorbed mg MEK / g sorbent	desorbed mg MEK / g sorbent
1	438	1.222	1.042	65	52
2	385	1.224	1.013	64	---
3	392	1.222	1.006	63	---
4	400	1.228	1.013	69	---
5	432	1.221	1.005	71	49
6	365	1.223	1.017	66	---
7	389	1.221	1.014	62	---
8	396	1.105	1.009	76 ^a	---
9	368	1.237	1.007	65	---
10	430	1.24	1.024	70	42

a = Same procedure used for all 10 cycles except cycle 8 where adsorption was dry and desorption was humid.

Table 3. Results of VOC removal by Char C.

VOC	TOL		TCE		MEK	
	1	2	1	2	1	2
Cycle						
Feed concentration (ppmv)	155	337	350	365	438	385
VOC collected ^a (mg/g sorbent)	138	211	141	160	65	64
VOC collected ^a (mmole/g sorbent)	1.50	2.24	1.07	1.22	0.90	0.89

a = MEK breakthrough at 10% of feed concentration.

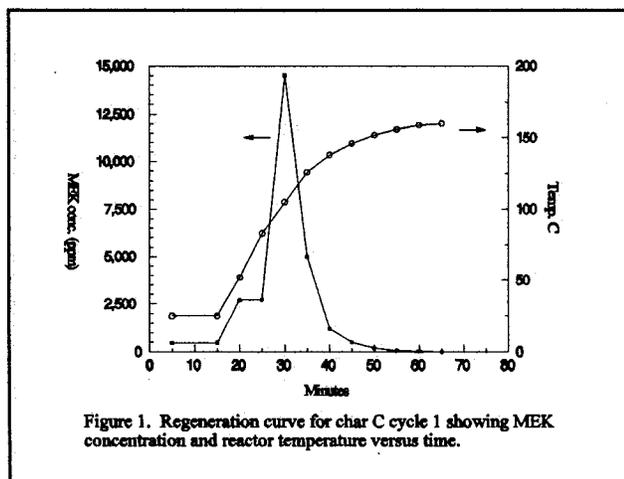


Figure 1. Regeneration curve for char C cycle 1 showing MEK concentration and reactor temperature versus time.

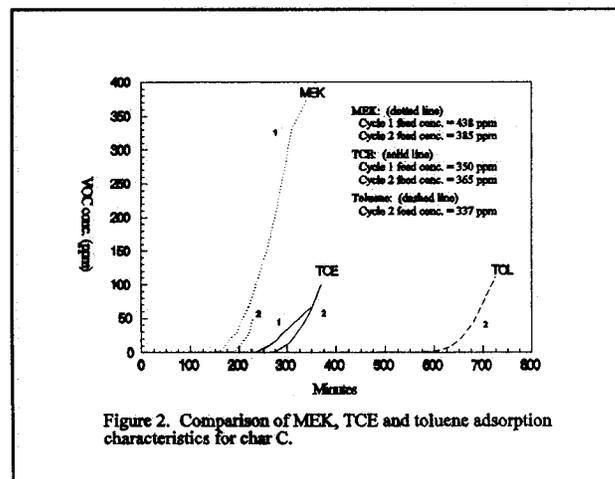


Figure 2. Comparison of MEK, TCE and toluene adsorption characteristics for char C.