

Chapter 1

Introduction



Volatile organic compounds (VOCs) are among the most common pollutants emitted from chemical process industries. Accordingly, VOC emission control is a major portion of the industry's environmental activities.

VOCs are hydrocarbon compounds that may react with nitrogen oxides and other airborne chemicals, in the presence of sunlight (photochemically), which is a primary component of smog. VOCs include most general purpose solvents, thinners, degreaser, and liquid fuels. The common VOCs of organic chemicals encompassing thousands of individual compounds, e.g. toluene, xylenes, ethers, ketones, acetone, petroleum distillates, naphthas, and mineral spirits [1].

The following technologies are identified as existing VOC abatement controls: thermal oxidizers or thermal incinerators, catalytic oxidizers or catalytic incinerators, flares, condensers, adsorbers, absorbers, boilers, biofilters, membrane separators, ultraviolet oxidizers, corona destruction reactors and plasma technology devices as summarized in Table 1.1. Because of their broad applicability to a wide variety of VOC emission streams, thermal and catalytic oxidizers, flares, condensers, and adsorbers are the most popular VOC controls in use today. Oxidizers and flares are equipments, in which VOCs are reduced, or are combusted to produce less hazardous compounds instead. Adsorbers and condensers, on the other hand, are recovering equipment, in which VOCs may be recovered and may be reused. The selection of such equipments is usually based on the economic benefit of recovering the VOCs from the waste gas stream.

Table 1.1: Summary of VOC control technologies

<i>Technology</i>	<i>Emission Source[†]</i>	<i>VOC Category[‡]</i>	<i>Emission Stream Flow Rate, scfm</i>	<i>VOC Concentration, ppm</i>
Thermal Oxidation	PV, ST, TO, WW	AHC, HHC, A, K	<20,000 without heat recovery ≥20,000 with heat recovery	20-1,000 without heat recovery ≥ 1,000 with heat recovery
Catalytic Oxidation	PV, ST, TO, WW	AHC, HHC*, A, K	Unlimited	50-10,000
Flaring	F, PV, ST, TO, WW	AHC, A, K		
Condensation	PV, ST, TO	AHC, HHC*, A, K	≤2,000	5,000-12,000
Adsorption	PV, ST	AHC, HHC, A	≥300	20-20,000
Absorption	PV, ST, TO	A, K	≥1,000	1,000-20,000
Boiler	PV	AHC, A, K		
Biofiltration	PV, WW	AHC, HHC*, A, K	Unlimited	500-2,000
Membrane Separation	PV, TO	AHC, HHC, A, K		0-1,000
Ultraviolet Oxidation	PV	AHC, HHC, A, K		

[†] F= Fugitive; PV= Process Vent; ST=Storage Tank; TO= Transfer Operation; WW= Wastewater Operations

[‡] AHC= Aliphatic and Aromatic Hydrocarbons; HHC= Halogenated Hydrocarbons(* = Limited Applicability); A= Alcohols, Glycols, Ethers, Epoxides, and Phenols; K= Ketones and Aldehydes

Absorbers and boilers are rarely used often for VOC control. In general, absorbers are less effective processes than other abatement technologies and are more commonly used to recover inorganic compounds. Boilers and process heaters are not used solely for VOC abatements; however existing boilers or process heaters may be used to convert VOCs less hazardous compounds as long as the safety and reliability of the primary process is not adversely affected.

Three of the technologies identified by survey participants-biofiltration, membrane separation, and ultraviolet (UV) oxidation have only recently become commercially available for VOC controls. Biofiltration involves the use of soil or compost beds containing microorganisms to convert VOCs into carbon dioxide, water, and mineral salts [2]. Membrane separation refers to the use of a semi-permeable polymeric membrane to separate VOCs from an exhaust gas stream. UV oxidation uses oxygen based oxidants, such as ozone, peroxide, or OH^- and O^- radicles, to convert VOCs into carbon dioxide and water in the presence of UV light.

Two of the technologies identified corona destruction and plasma technology are not yet commercially available. In corona destruction, energetic electrons are generated in a high-intensity reactor, where they collide with VOCs to produce reactiveless compounds such as carbon dioxide and water. The exact mechanism by which the excited electrons react with VOCs is not well known at this time. Early results indicate that corona destruction appears to be effective for dilute VOC streams. It does not appear to produce intermediate hazardous compounds that would require disposal as hazardous wastes. It can be operated at ambient temperature, does not require auxilliary fuel, and can be employed to treat halogenated and nonhalogenated compounds.

Plasma technology is not yet well known as a VOC abatement technology, although research and development are proceeding in the United States and Europe [3, 4]. The evaluation and selection of an appropriate VOC abatement technology depends upon several factors such as the environmental, economic, energy utilization and operability.

To study the adsorption and heats of adsorption of benzene and n-hexane on

graphitized carbon blacks. Furthermore, we have obtained and compared isotherm of the absolute magnitudes of adsorption, and different heats and entropies of adsorption. A description of the adsorption isotherm of benzene, hexane and nitrogen is discussed in terms of various equations, where the BET equation is only first approximation [5].

Originally the H-K method are used for nitrogen and molecular-sieve carbon. A very popular adsorbate in adsorption studies is benzene vapor, proposed by Dubinin (1966) as the standard. The benzene vapor adsorption-desorption isotherms are determined by the gravimetric method using a McBain-Bakr vacuum balance [6].

Diffusivities in the micropores and adsorption equilibrium constants are determined for neon, argon, krypton, xenon, nitrogen, methane, ethylene, ethane, propylene, n-butane and benzene on molecular sieve carbons by chromatographic measurement and moment analysis. Isothermic heat of adsorption are found to be 2.6 times heat of vaporization for gases examined here [7].

Chromatographic measurements were made for nitrogen adsorption on molecular sieve carbons for several different nitrogen surface coverages, Apparent adsorption equilibrium constants are determined from the retention volumes of the peaks for different concentrations, and the adsorption equilibrium isotherms are then determined [8].

The adsorption isotherms of benzene and toluene vapors on activated carbon are obtained by a static volumetric apparatus. The measurements are done at pressures up to 7 kPa for benzene and 2 kPa for toluene, respectively. The experimental data obtained are correlated by the UNILAN equation, which is generally used for heterogeneous adsorbents such as activated carbon [9].

A comparative study is conducted on the adsorption/desorption of organic vapors (toluene and p-xylene) on a synthetic resin and activated carbon using a gravimetric method involving the use of a quartz spring expansion. While the two sorbents can effectively remove the organic vapors, it was observed that activated carbon adsorbs more organic vapor than synthetic resin at low concentrations.

The rate of adsorption is higher than that of desorption for the two organic vapors regardless of the sorbent. However, the resin showed higher reversible adsorption [10].

A study has been made of simultaneous axial dispersion and solid-fluid mass exchange in a packed-bed adsorber. Four different and mutually exclusive controlling mechanisms for the solid-fluid mass exchange rate are considered. A dimensionless parameter K characterizes this interphase mass transfer. The Peclet number characterizes axial dispersion.

An impulse-response technique was used to obtain simultaneously values of the axial Peclet number obtained under conditions of interphase column. Values of the Peclet number obtained under conditions of interphase mass transfer were found to be significantly smaller than the values measured under pure mixing (no activity) conditions [11].

Longitudinal and lateral dispersion coefficient were measured at various axial positions in a packed bed in the Peclet number range from 102 to 104. Three different types of packings were used: uniform size particles, a narrow distribution, and a wide size distribution. For the case of uniform particles the longitudinal dispersivities were found to be strong functions of position in the bed unless the dispersion length satisfies a constraint dependent on the value of Peclet number. Generally, the larger the Peclet number, the larger the required length for constant axial dispersivities to be achieved. For the case of the wide size distribution, longitudinal dispersivities were larger than in the uniform particle case, and they required a larger dispersion length to achieve a constant value [12].

Binary diffusion coefficients of 15 organic vapors in nitrogen carrier gas were measured by using the peak arrest technique on a Hewlett-Packard 5840 A gas chromatograph with a flame ionization detector. The experiments were conducted at atmospheric pressure, above the n.b.p. of the organic vapors. The experimentally obtained values were compared with those predicted by using various correlations and reported in literature [13].

Axial dispersion coefficients in beds of small particles(0.1-1 mm.) are often

needed to interpret reaction rate data. A chromatographic technique was used to evaluate such coefficients for beds of porous catalyst particles and beds of non-porous glass beads over a wide range of velocities ($Re_p = 0.00237$ to 11.9). Two gaseous systems (He in H_2 and O_2 in N_2) were used to provide differential molecular diffusivities.

The results can be correlated by adding two terms: one due to molecular diffusion, which is dominant at low velocities, and a second term due to convective, which is dominant at high velocities. The unusually high values of axial dispersion for porous particles at low velocities could be explained by including a contribution due to intraparticle diffusion. At high velocities Peclet no. approached constant value which were proportion to particle diameter. Channeling in the bed due to shrinking of catalyst particles as a result of reduction, or to movement of particles, can cause a large increase in axial dispersion [14].

The objective of this research are to prepared carbon adsorbents from corncobs for increasing valuable, to study the effect of chemical reagent used for prepared carbon adsorbents, to study equilibrium adsorption constant and rate constant of aromatic hydrocarbons: benzene, toluene and o-xylene on prepared carbon adsorbents using chromatographic technique, and to study heat of adsorption. The equilibrium adsorption constant and adsorption rate constants from chromatogram will be evaluated by moment analysis [7, 8, 15, 16, 17, 18] to determine the adsorption equilibrium constant and rate of diffusion of aromatic hydrocarbons on various prepared activated carbons.