

THE USE OF MACRORETICULAR RESIN FOR SEPARATION OF COAL CONVERSION PROCESS WASTEWATER

James I. S. Tang, F. K. Kawahara* and T. F. Yen

School of Engineering
University of Southern California
Los Angeles, CA 90007
and
Environmental Protection Agency
Environmental Support Laboratory
Cincinnati, Ohio 45268*

INTRODUCTION

A three-dimensional co-polymer resin possessing macroreticular or macroporous structure is considered to be the most effective means of preliminary separation of organics in aqueous sample. These porous polymeric resins will function as the sorbing agent for organics. The full line of macroreticular adsorbent resins includes a spectrum of surfaces from the least polar to the most polar for adsorbing compounds with different polarities.

Gasification and liquefaction of coal will generate at least hundreds of organic species which will contaminate the water associated with the conversion processes, and thereafter pose a possible threat to the environment. A majority of coal plant waste streams released to the environment are process wastewaters from coal conversion process steps (Oak Ridge National Laboratory, 1977). This includes wastewater originating as moisture in the coal, water of constitution or decomposition, water added for stoichiometric process requirements, and water introduced for by-product recovery gas scrubbing. This type of wastewater contains most of the soluble and suspended organics and is produced in both the coal gasification and liquefaction processes. This wastewater is formed under the following conditions:

1. When gases are scrubbed to remove soluble contaminants, quenched to control operating temperature, compressed, or dehydrated;
2. When steam is used in the unit process cools and condenses or is reformed during methanation or hydrotreating;
3. When the product oil is formed by hydrogenation or pyrolysis and is allowed to settle for product recovery; or
4. When slags and ash are water-quenched for slurry removal.

The chemical species in waste effluents are considered varied and numerous because they represent practically all the organic compounds found in coal. The structure of coal, can be visualized as consisting of islands of aromatic and heterocyclic clusters connected by weak linkages, such as hydrogen bonding, quaternization, or donor-acceptor complexation. The coal conversion processes involve a variety of reactions with pressure, heat, catalysts, and/or water. These reactions produce many classes of organic species, such as polynuclear aromatic hydrocarbons (PAH), phenolics, nitrogenous compounds, other oxygen-functional compounds, and organometallics. Most of these species fall under the classification of potentially hazardous materials.

We are developing methods to separate the organics in coal-derived wastewater into a few major classes. One of the approaches is the pre-separation of hydrophobic and hydrophilic nature by macroreticular resin such as XAD-8 (1). The subsequent use of ion-exchange resin can again subclassify the hydrophobic or hydrophilic fractions into acidic, neutral or basic (Fig. 1).

EXPERIMENTAL

The following two wastewater samples, representative of coal gasification and liquefaction processes, were obtained:

1. Scrubber water from a coal hydrocarbonization process, derived from a gasification plant fluidized bed operation at 300 psi and 1035°F. Oak Ridge Division of Union Carbide Corporation.
2. Recycle process water No. 1511, from a coal liquefaction plant. PAMCO at DuPont, Washington.

The first classification step was the separation of the organic into hydrophobic (H0) and hydrophilic (HI) compounds on Amberlite XAD-8 macroreticular resin. Further classification was based upon acid-base characteristics (Fig. 2)

Hydrophobic acids and bases were desorbed by aqueous alkali (0.5 N NH_4OH) and acid (0.1 N HCl), respectively. Hydrophobic neutrals were eluted with methanol. Hydrophilic acids and bases were adsorbed on cation and anion exchange resins. The bases were concentrated on H^+ -form AG MP-50 cation exchange resin and eluted in 0.5 N NH_4OH . Hydrophilic acids were concentrated on OH^- -form AG MP-1 anion exchange resin and eluted with 0.5 N HCl . Hydrophilic neutrals passed through all columns and were collected.

The XAD-8 resin was supplied as an industrial grade product (20-40 mesh) which was purified by first rinsing with 0.1 N NaOH , 0.1 N HCl , and then by Soxhlet extracting for 24 hours successively in acetonitrile, ethyl ether, and methanol. The resin was then packed in a column and rinsed with distilled water for testing of organic compounds background.

The AG MP-50 and AG MP-1 resins were washed successively by 1 N HCl , 1 N NaOH , and then Soxhlet extracted for 24 hours in methanol, methylene

chloride, and n-pentane successively for column packing. Test samples of model compounds were made and tested for the extent of the separation.

One liter of water sample No. 1 was diluted to 3:1 volume with distilled water and passed through a 300 ml bed (3 bed volume) XAD-8 resin column. The flow rate of the sample was 10 ml/min. The column was then eluted with 500 ml 0.1 N HCl, 0.5 N NH₄OH, and CH₃OH to collect HO base, acid, and neutral compounds, respectively. The aqueous effluents were passed through a column of H⁺ form cation exchange resin (BioRad AG MP-1) to separate HI components. HI bases were collected by eluting with 500 ml 0.5 NH₄OH. Acids were recovered by eluting with 2.0 HCl. HI neutrals remained in the aqueous effluent. The water sample No. 2 was also separated via the same procedures. However, it was diluted with distilled water by the ratio of 1:1. This is because the total organic carbon concentration of water sample No. 2 is about one half of No. 1. The purpose of dilution is to reduce solute-solute interactions at high solute concentrations.

RESULTS

There are six separated fractions for each sample from the column absorption separation process. The organic components in these fractions are classified as HI acid, base, neutral and HO acid, base, and neutral compounds.

Total organic carbon (TOC) concentration of these fractions was detected by using a Dohrmann Envirotech DC-50 Model TOC analyzer. Preliminary data of TOC distribution among these fractions are shown in Table 1.

The separate organic fractions from coal process wastewater were subjected to GC-MS analysis. All the fractions are in aqueous solution except the HO neutral fraction which was eluted with CH₃OH through the column. Benzene was used to recover the pure organic component in HO neutral fraction. Samples of HO neutral fraction then were diluted to 1 ml in benzene for GC-MS analysis. All the other fractions were extracted by dichloromethane (CH₂Cl₂). After phase separation occurred, a 2.0 μ l aliquot of the CH₂Cl₂ was analyzed by GC-MS. Compounds identified on one of the fractions is illustrated in Table 2.

From the data obtained both qualitatively and quantitatively the following summary can be made (2).

- a. hydrophobic acid fraction -- phenolic compounds, e.g. phenol, cresol, xylenol.
- b. hydrophobic neutral fraction -- polynuclear aromatic hydrocarbons, e.g. naphthalene, anthracene, pyrene, benzo(a)anthracene, chrysene, fluoranthene, biphenyl.
- c. hydrophobic base fraction -- aza-aromatics and nitrogen base compounds, e.g. diphenylhydrazine, indole, nitrobenzene, pyridine, quinoline, benzamine.
- d. hydrophilic acid fraction -- phenolic compounds, aromatic acids, and volatile acids, e.g., phenol, cresol, xylenol, carboxylic acid,

- benzoic acids, fatty acids.
- e. hydrophilic neutral fraction -- cyclic polar compounds, e.g., ethylphthalate, benzylphthalate, cyclopentenone.
 - f. hydrophilic base fraction -- methoxybenzene (2).

DISCUSSION

The pre-separation of organics in coal wastewater via these resins is due to the following reasons:

1. It has a homogeneous surface, permitting the operation of only one adsorption mechanism at a time. Hence solutes can be quantitatively adsorbed or desorbed.
2. The large surface area produces high exchange capacity as well as good chemical and structural stability.
3. No high energy process (such as heat) is used which might alter the nature of the organic solutes or evaporate the volatile compounds which have relatively low boiling points.

The polymer resin used in this study is able to fractionate organic solute mixtures into more homogeneous fractions based on sorption mechanisms without serious alteration of the solutes or solute matrix. The general theory that hydrophobic (HO) or nonpolar molecules are attracted to hydrophobic surfaces, and hydrophilic (HI) or polar molecules to hydrophilic or polar surfaces, is adopted in this scheme. Thus adsorbents of intermediate polarity such as Amberlite XAD-7 and XAD-8 have an attraction for molecules of completely hydrophobic nature, or essentially hydrophobic compounds with some polar functionality. To adsorb hydrophilic compounds of polar or neutral functionalities, ion exchange resins were used.

The TOC data indicate the recovery efficiency is ca. 70-80%. The significant information is that the compounds found in the six fractions are largely different. This demonstrates that a sample method for characterizing the chemical nature of coal-derived wastewater effluents is available.

A drawback of the present method is that species do adsorb strongly at the resin surface sites and cannot recover completely with most powerful eluents such as acids and bases. Another inconvenience is that the inorganics contained in the wastewater will alter the sorbing nature of the macroreticular resin.

REFERENCES

- (1) Leeheer, J. A. and Huffman, E. W. D., Jr. Res. U.S. Geol. Survey 4, No. 6 737-751 (1976).
- (2) Tang, J. I. S., Kawahara, F. K. and Yen, T. F., Second Chemical Congress of North American Continent, Div. Geochemistry, paper 19, 1980.

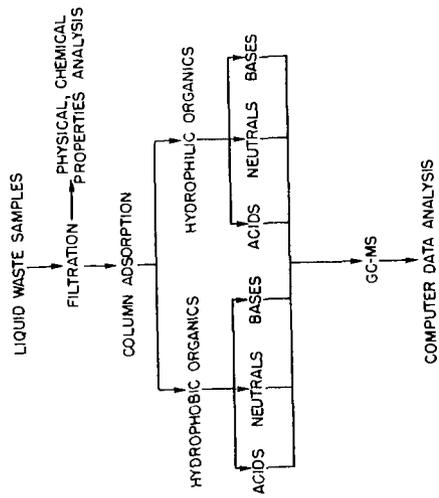


Figure 1. Schematic Diagram of Analytical Procedures for Coal Wastewater

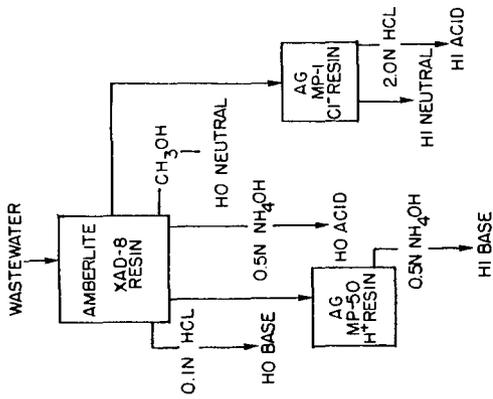


Figure 2. Flow Diagram of Column Adsorption to Separate Organics in Coal Wastewater

TABLE 1 PERCENTAGE OF TOTAL ORGANIC CARBON
DISTRIBUTION IN SEPARATED FRACTIONS

Separated Fraction	% of origin in-put TOC*	
	No.1	No.2
HI acid	2.7	3.4
HI base	2.4	6.8
HI neutral	10.7	15.2
HO acid	9.4	14.5
HO base	7.1	12.6
HO neutral	48**	40**

*The original in-put TOC for No.1 and No.2 are 2083 ppm,
1755 ppm, respectively.

**Values approximated from GC peaks of Solvent.

TABLE 2 COMPOUNDS IDENTIFIED FROM HYDROPHOBIC
FRACTION IN NO. 1 WATER SAMPLE

GC SCAN NO.	BASE M/E	MOLECULAR	
		WEIGHT	COMPOUND
77	91	92	Methylbenzene
131	43	88	Ethyl acetate
193	108	108	Methoxybenzene
244	94	94	Phenol
264	107	108	2-Methylphenol
286	107	108	3-Methylphenol
303	107	122	3,5-Dimethylphenol
315	107	122	2,5-Dimethylphenol
324	107	122	3,4-Dimethylphenol
331	121	136	4-(1-Methylethyl)-phenol
335	121	136	2-Ethyl-5-methylphenol
343	121	136	2-Ethyl-4-methylphenol
352	121	136	4-Ethyl-2-methylphenol
382	133	134	3,4-Dimethylbenzaldehyde
394	133	148	Pentamethylbenzene
451	144	144	3-Phenylfuran
506	170	170	(1-1-Biphenyl)-3-ol