

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

Honors Program

HONORS SENIOR PROJECT APPROVAL FORM

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Condensate from Steam Classified
Municipal Solid Waste

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Chemical Characterization of Condensate from Steam
Classified Municipal Solid Wastes

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Abstract

UAH has developed a process called steam classification to separate and recover cellulosic biomass from nonbiomass components of municipal solid waste. The process uses pulp and paper materials, food wastes, and soft yard wastes to obtain a product that could possibly be used as a feedstock for conversion to fuel, as well as fertilizer and sugars. The fuel derived by the UAH process has several advantages over conventional refuse derived fuels including more uniform and consistent size and moisture content, greater recovery of plastics/less chlorine, potentially higher percent of fuel firing, and the capability of indefinite storage. One of the byproducts of the UAH process is a condensate which is obtained from vented steam in a cold water tank/condenser. At this point, this condensate has yet to be chemically characterized with respect to toxic and hazardous constituents. The project provides a profile of the chemical components of the condensate following the Environmental Protection Agency (EPA) methods. The analysis includes qualitative and quantitative data to determine which of the 39 chemical compounds regulated by EPA are in fact present in hazardous amounts. The objective was accomplished using EPA's toxicity characteristic leaching procedure as outlined in Vol 49, No. 209 of the Federal Register/Rules and Regulations. Of the regulated chemicals, tetrachloroethene was found to be beyond regulatory limits with a concentration of 1.71mg/L. Five other contaminants were present, but below regulatory levels. Additionally, the project classifies unknown components of the condensate that are not regulated by EPA, utilizing results obtained from gas chromatographs, mass spectra, and atomic absorption to establish a match between the unknown and compounds characterized in chemical libraries.

Background

The disposal of municipal solid waste (MSW) continues to be a significant problem facing the United States. In fact, the problem is growing. The United States Environmental Protection Agency (EPA) estimates that in 1990 the United

States generated over 195 million tons of MSW (1), a rise of 44 million tons since 1980. MSW is defined by EPA as wastes from residences, commercial facilities, industries, and institutions. In 1990, the four largest components of MSW by weight were: yard trimmings (18%), corrugated boxes (12%), food wastes (7%), and newspapers (7%) - all of which are biomass material. Also, MSW typically contains recyclable ferrous metals, non-ferrous metals, glass, textiles, and plastics. Recycling or reusing these waste materials can significantly reduce the quantity of MSW reaching landfills and provide an additional means of obtaining natural resources.

Over the past several years, many small communities that are unable to finance incineration facilities have established recycling programs to separate and recover biomass materials. However, these programs have also proven to be somewhat expensive and limited in the scope of materials recovered from the waste stream. Often community recycling programs require separate collection and transport to waste facilities, substantially increasing costs in areas such as equipment, energy, and manpower.

Energy recovery is often the most cost-effective means of recovering resources from MSW. Waste can be converted to thermal energy and power which have a variety of applications, such as a boiler fuel to generate power for electric utilities. However, the Refuse Derived Fuel (RDF)

produced by conventional resource recovery facilities is often not suitable for use as a boiler fuel due to variation in content, high ash content, corrosion potential, and high moisture content (2).

The University of Alabama in Huntsville (UAH) has developed an alternative method for producing RDF which has several benefits over conventional processes such as mass burn in incinerators. The method involves steam processing of MSW in a pressurized apparatus and agitating for approximately 30 minutes. Conventional methods involve shredding to reduce particle size, as well as magnetic or aerodynamic separation techniques. By doing so, the product contains a high, and variable, ash and moisture content. Since the UAH method requires no shredding, the ash content is considerably lower. Moreover, the particle size and moisture content is more uniform (3). Thus, the UAH-RDF is more useful as a boiler fuel.

Introduction

MSW may contain potentially hazardous wastes such as pesticides, herbicides, and cleaning agents. One of the questions remaining in the production of UAH-RDF is whether or not the process generates by-products that contain these constituents in a quantity greater than EPA regulatory levels.

In the production of RDF, the UAH process requires the injection of steam into a large mixer drum containing MSW.

Steam is injected into the drum until the internal pressure reaches approximately 375 kPa. This pressure is maintained for about 30 minutes, creating an internal temperature of 150C. Once the steam injection is completed, the steam is vented from the mixer drum into a cold water tank/condenser in order to capture condensible vapors and heat. Since this by-product (liquid, less than 5% solid) should be a concentrate of volatile and semivolatile organics in addition to dissolved inorganics, researchers believe the condensate could possibly contain toxic or hazardous components as defined by the EPA. The research project thus involves laboratory analysis of the condenser material to profile all of its chemical components and establish which of the components are present in a quantity beyond the regulatory level that is considered hazardous under the Resource Conservation and Recovery Act. Additionally, the project identifies and quantifies nontoxic materials that may affect combustion characteristics with either detrimental or beneficial possibilities.

The scope of work includes chemical characterization of the condenser contents with respect to toxic and hazardous components by following EPA methods. This includes the use of EPA's toxicity characteristic leaching procedure (TCLP) to evaluate 39 distinct constituents in five categories of hazardous wastes:

- pesticides
- herbicides
- semi-volatiles
- volatiles
- metals

The presence of each constituent is determined by a series of procedures which include digestion, extraction, and concentration of the condenser contents. Components of the condensate are then characterized by examining data obtained from gas chromatographs, mass spectra, and atomic absorption spectra.

METHODOLOGY

I. Pesticides

Pesticides were determined by Organochlorine Pesticides and PCB's method (EPA Method 608). This is a gas chromatographic method applicable to pesticide and PCB compounds in municipal and industrial discharges.

A 1-L sample, was extracted with methylene chloride using a separatory funnel. The methylene chloride extract was dried and exchanged to hexane during concentration to a volume of 10-mL. The extract was separated by gas chromatography and the parameters were then measured with an electron capture detector. Analysis was performed on a Hewlett-Packard 5890 ECD-GC.

II Herbicides

Herbicides were determined by Phenoxy Acid Herbicides Rapid Extraction Procedure. This is a gas chromatographic

method applicable to herbicide compounds in municipal discharges.

A 100ml condensate sample was filtered and then acidified with HCL. The extraction column was conditioned with (2) column volumes of methanol followed by (2) column volumes of acidified distilled water. The condensate sample was then added to the column through a 75ml reservoir followed by a washing with acidified water. After drying, the sample was eluted from the column with hexane. Analysis was performed on a Hewlett-Packard 5890 ECD-GC.

III Semi-volatiles

Semivolatile organics were determined by Base/Neutrals and Acid Extractables Method (EPA Method 625). This covers a number of organic compounds that are partitioned into an organic solvent and can be characterized by gas chromatography (4). These constituents were examined by a Hewlett Packard 5890 gas chromatograph/mass spectrometer. This method required serial extraction of a 1 liter condensate sample with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatorv funnel. The methylene chloride extract was dried, concentrated to a volume of 1ml, and analyzed by GC/MS.

IV. Volatiles (Purgeable Organics)

Volatiles were determined by EPA Method 624 - Purgeables. This is a purge and trap gas chromatograph/mass

spectrometer method for the determination of purgeable organic compounds.

An inert gas (helium) was bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The purgeables were transferred from the aqueous phase to the vapor phase. The vapor was swept through a sorbent trap where the purgeables were trapped. After purging was completed, the trap was heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column (4). The gas chromatograph was temperature programmed to separate the purgeables which were detected with a mass spectrometer.

V. Metals

In the determination of metals, 50mL samples of the condenser contents were filtered through 125mm filter paper. To these samples, 5ml of nitric acid was added and the contents digested at 300C to ensure any metals present were in solution. The samples were digested to a final volume of 5ml. The samples were then diluted to 100ml with deionized water and analyzed for metals using a Varian Spectra AA-40 atomic absorption spectrophotometer.

RESULTS

Chemical characterization of pesticides, herbicides, and semi-volatiles was accomplished by comparing the chromatographs of various standards to the chromatographs

obtained from the condensate sample. Qualitative analysis was based on the characteristic retention times of the components of each standard. A match between the condensate sample and a component of a particular standard was determined by retention times which deviated by 0.05 minutes or less. Components of the condensate sample were quantified by the ratio of peak areas between a known standard and the condensate sample.

Table 1 lists the 39 contaminants and their regulatory levels as established by EPA, as well as their abundance in the condensate sample. Identifiable components of the condensate sample which are not regulated by the EPA are listed in Table 2.

Volatile components were characterized by mass-spectra comparison. Qualitative analysis was based on the characteristic masses of each parameter. Additionally, the retention times of the authentic compound (standard) and the retention time of the condensate sample were required to be within +/- 30 seconds (4). Components of the condensate sample were quantified by the ratio of peak areas as described above. (See Tables 1 & 2 for results).

For each metal analyzed, three standard solutions were made in order to obtain a standard curve to provide a measure for determining the quantity of each metal present. (See Tables 1 & 2 for results).

Chemical characterization of the condensate sample reveals (within instrument detection limits) the presence of

6 out of the 39 contaminants regulated by the EPA. Of these, only tetrachloroethene was found to be above regulatory levels. However, the pesticide, chlordane, was near regulatory levels at 0.025 mg/L.

Out of the components not regulated by the EPA, iron was present in the largest quantity. Other substituents to be noted were Toluene at 2.93 mg/L and 2-Nitrophenol at 0.88mg/L.

CONCLUSIONS

The most significant observations were the detection of chlordane and tetrachloroethene. Further testing of condensate samples from steam-classified MSW would be necessary to determine if these contaminants are regularly discarded into the MSW being treated by the steam classification facility. The main inorganic substituent was iron, which was most probably due to rust from the process equipment.

Several improvements could be made to enhance the accuracy of the data obtained. First, instrument conditions were unable to be maintained at specific settings over the span of the project. Accuracy in quantification could be improved by maintaining consistent gas flows, detector signals, and run times over the span of the project. This could not be accomplished due to the limited lab periods of the analyst.

Other improvements can be made in compound identifications by supporting the data by at least one additional qualitative technique. For instance, a second gas chromatographic column can be used to confirm measurements made with the primary column.

Condensate from steam classification of MSW was found to be free of most contaminants regulated by EPA. However, the presence of pesticides and volatiles such as chlordane and tetrachloroethene, respectively, suggests condensate materials should continue to be monitored for toxic or hazardous substances.

Table 1

EPA Regulated Contaminants

Contaminant	Regulatory Level (mg/L)	Condensate Sample (mg/L)
Arsenic	5.0	< 0.05*
Barium	100.0	< 0.01*
Benzene	0.5	0.020
Cadmium	1.0	< 0.01*
Carbon tetrachloride	1.0	< 0.005*
Chlordane	0.03	0.025
Chlorobenzene	100.0	< 0.005*
Chloroform	6.0	0.16
Chromium	5.0	< 0.01*
o-Cresol	200.0	< 0.1*
m-Cresol	200.0	< 0.1*
p-Cresol	200.0	< 0.1*
Cresol	200.0	< 0.1*
2,4-D	10.0	< 0.01*
1,4-Dichlorobenzene	7.5	< 0.005*
1,2-Dichloroethane	0.5	< 0.005*
1,1-Dichloroethylene	0.7	< 0.005*
2,4-Dinitrotoluene	0.13	< 0.1*
Endrin	0.02	< 0.01*
Heptachlor	0.008	< 0.01*
Hexachlorobenzene	0.13	< 0.1*
Hexachlorobutadiene	0.5	< 0.1*

Table 1 Cont.

Contaminant	Regulatory level (mg/L)	Condensate Sample (mg/L)
Hexachloroethane	3.0	< 0.1*
Lead	5.0	< 0.05*
Lindane	0.4	< 0.01*
Mercury	0.2	< 0.005*
Methoxychlor	10.0	< 0.01*
Methyl ethyl ketone	200.0	< 0.005*
Nitrobenzene	2.0	< 0.1*
Pentachlorophenol	100.0	< 0.1*
Pyridine	5.0	< 0.1*
Selenium	1.0	< 0.05*
Silver	5.0	< 0.05*
Tetrachlorethylene	0.7	1.71
Toxaphene	0.5	< 0.01*
Trichloroethylene	0.5	0.058
2,4,5-Trichlorophenol	400.0	< 0.1*
2,4,6-Trichlorophenol	2.0	0.18
2,4,5-TP (Silvex)	1.0	< 0.01*
Vinyl chloride	0.2	< 0.005*

* Quantity below instrument detection limits

Table 2

Components not Regulated by EPA

Component	Condensate Sample (mg/L)
Bis (2-Chloroethyl) ether	< 0.1*
Bis (2-Chloroethoxy) methane	0.20
4-chloro-3-methylphenol	< 0.1*
2-Chloronaphthalene	< 0.1*
2-Chlorophenol	< 0.1*
4-Chlorophenyl phenyl ether	< 0.1*
1,2-Dichlorobenzene	< 0.1*
1,3-Dichlorobenzene	< 0.1*
Dichloromethane	0.32
2,4-Dichlorophenol	< 0.1*
Diethylphthalate	< 0.1*
2,4-Dimethylphenol	< 0.1*
2,4-Dinitrophenol + 4 Nitrophenol	< 0.1*
Iron	410.0
Isophorone	< 0.1*
2-Methyl-4,6-Dinitrophenol	0.16
Naphthalene	< 0.1*
2-Nitrophenol	0.88
N-Nitroso-di-N-propylamine	0.28

Table 2 cont.

Component	Condensate Sample (mg/L)
Phenol	0.36
Surrogate	< 0.1*
1,2,4-Trichlorobenzene	< 0.1*
1,1,1-Trichloroethane	0.11
Toluene	2.93

* Quantity below instrument detection limits

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