Biomass Energy Production Effects on Environment

Ash Evaluation

**MINNESOTA AGRIPOWER PROJECT
TASK III RESEARCH REPORT**

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**Chemical Characterization of Ash Generated from Alfalfa Stem Gasification:
Agricultural and Environmental Implications**
(Progress Report, October 1997)

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This progress report provides results of Toxicity Characteristics Leaching Procedures (TCLP) and Synthetic Leachate Test Procedure (SLTP) for the alfalfa stem ash. The TCLP simulates solute leaching in landfill by using acetic acid as a solvent and SLTP simulates potential for leaching from synthetic acid rain. This report also provides information on detailed chemical characterization of organic and inorganic constituents of the ash. The analysis performed includes information on compounds that may represent a potential risk to human or animal health and those constituents that may have beneficial use as soil amendments and conditioners.

A sample of the fly (filter) ash from the test burn conducted in Finland was received in May 1997 and used for initial investigation. Three additional fly ash samples and one sample of bottom ash (reactor bed ash) were received in June 1997. The samples were either tested at the University of Minnesota or sent to a reputable laboratory and various tests were conducted according to the standard methods. The result of the comprehensive tests conducted in May 1997 (report submitted previously) were used as a screening procedure for conducting tests on June 1997 samples. To provide a more comprehensive representation of ash characteristics the results for fly ash received in May are presented along with results from fly ash samples received in July. The average, range and coefficient of variation (CV) are provided.

The TCLP and SLTP tests conducted in the laboratory indicated that the concentration of heavy metals were below or close to the detection limits for fly and bottom ash samples (Tables 1 and 2). The ash was also characterized for a number of classes of organic compounds that may pose potential environmental or health risks. These are polycyclic aromatic hydrocarbons (PAHs), total and individual dioxin and furan compounds.

In general, with the exception of Naphthalene, the range in concentration of PAHs were below or close to the detection limits (Table 3). Concentrations of total dioxin and furan compounds as well as selected important compounds in these classes were below the detection limit in fly and bottom ash samples (Table 4 and 5).

Chemical analysis indicated that organic carbon was the major constituent of the fly ash ranging 39-46% and it contained approximately 1% N and 0.4% S (Table 6). Concentration of Rb, Pb, Se, Co, As, Cd, and Be were below the detection limits in both fly and bottom ash samples (Table 6).

Analysis of saturated extracts of the ash indicated that both fly ash and bottom ash were high in K and Cl and the relative amount of both elements was at least two times higher in fly ash compared to the bottom ash (Table 7). Concentrations of heavy metals in fly ash were below or close to the detection limit.

To further explore the potential use of alfalfa stem ash as a soil amendment a number of agriculturally significant chemical parameters of the ash were determined. The average pH of the fly ash was 11.5 and that of the bottom ash was 13.1 (Table 8). Calcium carbonate equivalent of the fly ash was approximately 40%, suggesting its potential use as a liming agent. Fly ash contained an average of 2.2% available P_2O_5 and 12.8% available K_2O (Table 8).

Electron micrographs of the fly and bottom ash are presented in Figures 1 and 2. Elemental composition profile using X-ray micro analysis indicated that the relative abundance of elements in the fly ash is as follows: $C > K > Ca > Cl$ (Figure 3). The same technique indicated the following relative abundance in the bottom ash $K > Mg > Ca > Si > C$ (Figure 4) these results corroborate with the total elemental analysis data.

Greenhouse pot studies are currently in progress to evaluate the effect of fly ash amended soil on growth of field corn.

Table 1. Results of Toxicity Characteristics Leaching Procedure (TCLP) for heavy metals in alfalfa stem ash.

Element	Fly Ash Samples					Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Range	24/4/97	
	Concentration (mg/L) ^a						
Arsenic (As)	< 0.12	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
Barium (Ba)	< 0.5	< 0.1	< 0.1	0.13	< 0.1-0.13	0.11	A
Cadmium (Cd)	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	A
Chromium (Cr)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	A
Lead (Pb)	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	A
Selenium (Se)	< 0.13	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
Mercury (Hg)	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	B
Silver (Ag)	< 0.24	< 0.2	< 0.2	< 0.2	< 0.2-<0.24	< 0.2	C

^a All concentrations were below the analytical detection limits for the respective element.

A: EPA SW-846,6010A

B: EPA SW-846,7470A

C: EPA SW-846,7760A

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Table 2. Results of Synthetic Precipitation Leachates Test (SPLT) for heavy metals in alfalfa stem ash.

Element	Fly Ash Samples					Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	24/4/97	
	Concentration (mg/L) ^a						
Arsenic (As)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
Barium (Ba)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	A
Cadmium (Cd)	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	A
Chromium (Cr)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	A
Lead (Pb)	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	A
Selenium (Se)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
Mercury (Hg)	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	B
Silver (Ag)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	C

^a All concentrations were below the analytical detection limits for the respective element.

A: EPA SW-846,6010A

B: EPA SW-846,7470A

C: EPA SW-846,7760A

D: MOZAFFAR\reporet\SPLTREP.WPD

Table 3. Total solids and polyaromatic hydrocarbons (PAHs) in alfalfa stem ash.

Constituent	----- Fly Ash Samples -----							Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	Range	CV	24/4/97	
	----- Concentration (mg/kg) ^a -----								
Total Solids	94.5	99.2	98.8	99.8	98	94.5- 99.8	2.5	98	A
Naphthalene	20	74	6.2	48	37	6.2-74	81	< 0.31	B
Acenaphthylene	< 0.18 ^b	3.3	< 1.8 ^b	< 1.7		<1.7-3.3		< 0.18	B
Acenaphthene	2.3	4.9	< 2.0	4.4		<2.0-4.9		< 0.20	B
Fluorene	< 0.21	< 2.0	< 2.0	< 2.0		<0.21-< 2.1		< 0.20	B
Phenanthrene	3.4	6.4	< 1.8	< 1.8		< 1.8 -6.4		< 0.18	B
Anthracene	0.84	1.6	< 1.6	< 1.6		0.84-<1.6		< 0.17	B
Fluoranthene	2.5	< 2.4	< 2.4	< 2.4		<2.4-2.5		< 0.31	B
Pyrene	3.4	<3.0	< 3.0	< 3.0		< 3.0- 3.4		< 0.37	B
Benzo(a)anthracene	1.2	<3.6	< 3.6	< 3.6		1.2-< 3.6		< 0.18	B
Chrysene	2.6	< 1.8	< 1.8	< 1.8		<1.8-2.6		< 0.20	B
Benzo(b)fluoranthene	0.93	< 2.0	< 2.0	< 2.0		0.93-<2.0		< 0.35	B
Benzo(k)fluoranthene	0.67	< 3.4	< 3.5	< 3.4		0.67-<3.4		< 0.24	B
Benzo(a)pyrene	1.3	<2.4	< 2.4	< 2.4		1.3-<2.4		< 0.18	B
Indeno(1,2,3-cd) pyrene	0.32	< 1.8	< 1.8	< 1.8		0.32<1.8		< 0.18	B
Dibenzo(a,h) anthracene	<0.18	< 1.8	< 1.8	< 1.7		< 1.7- < 1.8		< 0.24	B
Bnzo(g,h,i)perylene	0.28	< 2.4	< 2.4	< 2.4		0.28-< 2.4		< 0.18	B
2- Methylnaphthalene	4.4	< 17	< 17	< 17		4.4-< 17		< 0.18	B

^a Concentrations preceded by < and a number were below the analytical detection limits for the respective chemical constituents.

^b The variation in detection limit is due to a 10 fold dilution needed for analysis of 25/4/97A, 25/4/97B, 23/4/97, and 24/4/97.

A: EPA 160.3

B: EPA SW-846,8270

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Table 4. Concentration of Dioxins and Furans in alfalfa stem ash.

Compound	Fly Ash					Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Mean ^a	24/4/97	
Dioxins	Concentration (ug/kg) ^a						
2,3,7,8-TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	A
1,2,3,7,8-PeCDD	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	A
1,2,3,4,7,8-HxCDD	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
1,2,3,6,7,8-HxCDD	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
1,2,3,7,8,9-HxCDD	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	A
1,2,3,4,6,7,8-HpCDD	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	A
1,2,3,4,6,7,8,9-OCDD	< 0.8	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	A
Furans							
2,3,7,8-TCDF	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	A
1,2,3,7,8-PeCDF	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
2,3,4,7,8-PeCDF	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
1,2,3,4,7,8-HxCDF	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	A
1,2,3,6,7,8-HxCDF	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	A
2,3,4,6,7,8-HxCDF	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
1,2,3,7,8,9-HxCDF	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
1,2,3,4,6,7,8-HpCDF	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
1,2,3,4,7,8,9-HpCDF	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	A
1,2,3,4,6,7,8,9-OCDF	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	A

^a All concentrations were below the analytical detection limits for the respective chemical constituent(s).

A: EPA SW-846,8280

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Table 5. Concentration of total Dioxins and Furans in alfalfa stem Ash.

Compound	Fly Ash Samples					Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Mean		
Total Dioxins	Concentration (ug/kg) ^a						
Total TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	A
Total PeCDD	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	A
Total HxCDD	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	A
Total HpCDD	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	A
Total Furans							
Total TCDF	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	A
Total PeCDF	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	A
Total HxCDF	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	A
Total HpCDF	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	A

^a All concentrations were below the analytical detection limits for the respective compound.

A:EPA SW-846,8280.

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Table 6. Elemental composition of alfalfa stem ash.

Constituent	Unit	----- Fly Ash Samples -----							Bottom Ash	Method
		9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	Range	CV		
Total Organic Carbon (TOC)	%	42.6	39.2	42	45.8	42.4	39.2-45.8	5.5	6.3	A
Total Nitrogen (TN)	%	1.07	1.10	0.96	1.04	1.04	0.96-1.07	5	0.13	B
TOC:TN		39.8	35.6	43.8	44	40.8	35.6-44	8.4	48.8	
Total S	%	0.40	0.38	0.38	0.36	0.38	0.38	0	0.13	C
SO ₄ -S	mg/kg	1,139	750	890	823	900.5	750-1139	19	787	D
K	g/kg	111	117	125.1	127.5	120.1	111-127.5	6.3	60.8	E
Ca		83	78.5	91.1	87.6	85	78.5-91.1	6.4	193	E
Cl		24.4	28.3	28.3	24.2	26.3	24.4-28.3	8.7	-	F
Mg		19.1	17.2	21.1	23.9	20.3	17.2-23.9	14.2	104.7	E
P		15.5	14.0	16.6	13.7	15	13.7-16.6	8.8	29.8	E
S		3.8	3.7	4.0	4.2	3.9	3.7-4.2	5.8	1.8	E
Na		2.8	2.7	2.5	2.7	2.7	2.5-2.8	4.9	1.9	E
Fe		2.3	2.5	2.0	2.8	2.4	2.3-2.8	12.7	5.9	E
Al		1.9	3.5	2.5	3.5	2.9	1.9-3.5	28.9	5.9	E
Si		-	9.5	6.6	6.4	7.5	6.4-9.5	23	5.2	E
Sr	mg/kg	250	221	254	223	237	221-250	7.4	98.9	E
Mn		240	244	248	270	250	240-270	5.35	597	E
Ba		177	205	219	197.4	199.7	177-219	8.8	133	E
B		166	157	200	155	169.5	155-200	12.3	70	E

Constituent	Unit	----- Fly Ash Samples -----							Bottom Ash	Method
		9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	Range	CV		
Ti	mg/kg	106	186	138	196	156.5	106-196	26.9	266.3	E
Zn		98.9	119	109	139	116.5	98.9-139	14.7	137	E
Cu		41.1	41.6	44.3	38.6	41.4	38.6-44.3	5.6	22.3	E
Mo		27.2	23.8	29.2	23.1	25.8	23.1-27.2	11	5.0	E
Ni		5.9	7.6	6.0	7.3	6.7	5.9-7.6	12.1	12.7	E
Li		5.9	7.6	6.1	7.3	6.7	5.9-7.6	12.9	8.8	E
V		5.7	6.6	5.5	6.7	6.1	5.5-6.7	10.2	11.2	E
Cr		5.5	9.1	6.3	10.0	7.7	5.5	28.2	20	E
Rb		<425	<425	<425	<425	<425			<425	E
Pb		<13.5	<13.5	<13.5	<13.5	<13.5			<13.5	E
Se		<2.4	<2.4	<2.4	<2.4	<2.4			<2.4	E
Co		<1.9	<1.9	<1.9	<1.9	<1.9			<1.9	E
As		<0.62	<0.62	<0.62	<0.62	<0.62			<0.62	E
Cd		<0.96	<0.96	<0.96	<0.96	<0.96			<0.96	E
Be		<0.32	<0.32	<0.32	<0.32	<0.32			<0.32	E

^a All concentrations preceded by < and a number were below the analytical detection limits for the respective chemical constituent(s).

A: Dry combustion and IR detection of CO₂.

B: Kjeldahl procedure with nitrate pre-reduction.

C: Dry combustion and Ir detection of SO₂.

D: Extracted with 0.008 M calcium phosphate and analyzed colorimetrically.

E: Inductively Coupled Plasma analysis (ICP) analysis of microwave digest with conc. HNO₃-H₂O₂.

F: 0.01 M CaSO₄ extraction and colorimetric analysis.

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Table 7. Elemental concentration of saturation extract of alfalfa stem ash.

Element	----- Fly Ash -----							Bottom Ash	Method
	----- Concentration ^a (mg/L) -----								
	9-5-97	23/4/97	25/4/97A	25/4/97B	Mean	Range	CV	24/4/97	
K	66,100	78,360	83,220	86,090	78,442	66,100-86,090	9.7	26,500	A
Cl	20,200	22,244	23,860	23,126	22,357	20,200-23,860	6.1	6,866	B
S	-	863	1,005	1,198	1,022	863-1,198	16.4	674	A
Na	762	1,092	965	999	954.5	762-1,092	12.6	573	A
Mg	651	<0.386	69.6	<0.386		<0.386-651		<0.198	A
Ca	90.3	42.5	22.4	39	48.5	22.4-90.3	52	6.9	A
Rb	48.3	55.7	68.7	63.4	59	48.3-68.7	13	10.4	A
Si	41.8	1,050	48	1,155	573.3	41.8-1,155	92.4	2,906	A
Mo	10.2	8.8	11.3	9.7	10	8.8-11.3	9	1.5	A
P	9.4	147	5.4	22	46	5.4-46	127.7	78.5	A
Fe	4.9	4.7	10.10	0.06	5.0	0.06-10.1	66.6	0.09	A
Al	0.81	0.36	1.16	0.66	0.66	0.36-1.16	63.9	0.44	A
V	0.28	0.44	0.31	0.45	0.37	0.28-0.45	19.7	0.52	A
Sr	0.17	0.13	0.13	0.21	0.16	0.13-0.21	19.7	0.05	A
B	0.13	11.28	1.17	5.27	4.46	0.13-11.28	98	2.6	A
Li	1.1	0.89	1.72	0.48	1.06	0.48-1.06	42.9	0.19	A
Ba	0.10	0.07	0.08	0.12	0.09	0.07-0.12	19.6	0.03	A
Ti	0.075	<0.03	0.035	<0.03		<0.03-0.075		0.02	A
Mn	0.058	0.008	0.012	0.022	0.02	0.008-0.22	98	0.004	A
Ag	<0.24	-	-	-	-	<0.24			C

Element	----- Fly Ash -----							Bottom Ash	Method
	9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	Range	CV	24/4/97	
	----- Concentration ^a (mg/L) -----								
As	<0.133	<0.079	0.122	<0.079		<0.079-0.122		0.055	A
Be	<0.007	0.004	0.004	0.004		<0.007-0.004		0.002	A
Cd	<0.020	<0.012	<0.012	<0.012		<0.012-<0.02		0.006	A
Co	<0.041	<0.024	0.039	0.024		0.024-<.039		0.013	A
Cr	<0.048	<0.028	0.037	<0.028		<0.028-<0.048		0.11	A
Cu	<0.089	<0.053	0.087	<0.053		0.053-<0.087		0.03	A
Pb	<0.287	<0.171	0.195	<0.171		<0.028-0.195		0.088	A
Zn	<0.024	0.02	0.03	0.02		<0.024-0.3		0.018	A
SO ₄ -S	1,230	872	958	766	956.5	766-1,230	20	1,022	B

^a Concentrations preceded by < and a number were below the analytical detection limit for that element.

A: Inductively Coupled Plasma.

B: Ion chromatography.

C: EPA 7760.

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Table 8. Selected agriculturally significant chemical characteristics of alfalfa stem ash.

Constituent	Unit	----- Fly Ash Samples -----							Bottom Ash	Method
		9-5-97	25/4/97A	25/4/97B	23/4/97	Mean	Range	CV		
pH		10.2	10.8	13.7	11.8	11.5	10.2-13.7	9.5	13.1	A
EC	mmhos/cm	91.7	142	146	130	127.4	91.7-146	17	78.5	B
Available P ₂ O ₅	%	2.389	2.52	2.039	1.789	2.18	1.789-2.389	13	0.558	C
Available K ₂ O	%	11.8	13.4	13.8	12.1	12.78	11.8-13.8	6.6	5.53	D
Total N	%	1.22	1.32	1.3	1.27	1.28	1.2-1.3	13	0.17	E
S	%	-	0.11	0.17	0.08	0.12	0.08-0.17	38	0.13	F
Organic matter	%	52	40.8	46.0	52.2	46.6	40.8-52.2	8.7	8.3	G
B	mg/kg	154.3	52.04	136.2	132.3	118.7	110.7-154.3	6.6	73.47	H
NO ₃ -N	mg/kg	<0.1	0.60	1.5	1.2		<0.1-1.5		5.3	I
NH ₄ -N	mg/kg	7.36	1.10	7.5	3.4	4.8	1.1-7.5	56	0.8	I
CaCO ₃ equivalent	%	32	42.8	45.2	39.8	39.9	32-45.2	12	93.6	J
Extractable SO ₄	mg/kg	-	750	890	823	821	750-890	8.5	787	K

^a All concentrations preceded by < and a number were below the analytical detection limits for the respective chemical constituent(s).

A: Measured in 1:1 ash:H₂O.

B: Measured in saturation extract.

C: AOAC 960.03.

D: AOAC 983.02.

E: AOAC 993.13.

F: ASTM D4239-85.

G: Dry ashed at 485° C for 10-12 hours.

H: EPA 6010.

I: extracted with 2 M KCl and analyzed by colorimetric methods.

J: Measured by acid titration.

K: Extracted with 0.008 M calcium phosphate and analyzed colorimetrically.

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Figure 1. Electron micrograph of alfalfa stem gasification fly ash (approx. 1250 X).

Figure 2. Electron micrograph of alfalfa stem gasification bottom ash (approx.180 X).

Figure 3. X-ray micro analysis of alfalfa stem gasification fly ash.

Figure 4. X-ray micro analysis of alfalfa stem gasification bottom ash.