Mass Spectrometry Characterization of

Evolved Gases from Catalytic Pyrolysis of

Cassava Starch Residues

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Abstract

By using the mass spectrometry technique, the catalytic effect of ferric sulfate on the evolved gases of the pyrolysis of residues from the cassava starch industry was studied. There were identified 31 m/e ratios in the evolved gases with enough signal to noise ratio. The presence (or absence) of m/e signals in the pyrolysis evolved gases with (or without) catalyst suggest a change in the product distribution

caused by the catalytic activity of the ferric sulfate. These signals were fitted with the DAEM using the kinetic parameters calculated from previous thermogravimetry data. As result, 90% of the *m/e* ratios presented a good fit. The poor description of the model for the rest of the signals could be attributed to secondary reactions in the gas phase.

Keywords: Biomass pyrolysis, Cassava industrial waste, Ferric sulfate, Mass spectrometry

1 Introduction

Since some decades ago, global concern has arisen about energy production and its role on sustainability, environmental impact, and possible future crisis which have boosted the development and implementation of renewable sources of energy [2]. Among renewables sources of energy, biomass for energy production has been targeted as an alternative in the race for slowing global warming: biomass has a carbon footprint close to zero, during growing it captures CO_2 and solar energy, then the CO_2 is released to the atmosphere and the energy is used for the intended application [8]. Several technologies are employed to transform the energy stored in biomass: fermentation, gasification, pyrolysis, anaerobic digestion, and mechanical extraction [10].

Pyrolysis is the main method to obtain liquid fuels from biomass (bio-oil); however, these fuels cannot be used directly because of issues related to its rheology, moisture, heating value, and stability. Therefore, the physicochemical properties of bio-oil must be improved by several technologies, among which, catalytic pyrolysis is a promising one [3]. Catalytic pyrolysis for bio-oil production potentially could eliminate condensation and re-evaporation processes in actual bio-oil production schemes. Other advantages are the operation pressure near atmospheric conditions, no need for hydrogen supply, and the possibility of increase bio-oil yield and quality [19].

The behavior of several kinds of biomass by thermogravimetric analysis has been described extensively in previous studies, nevertheless, the distribution of the specific products as a function of time or process temperature in the literature is scarce [4, 9, 12, 13, 18]. In order to obtain the identification and quantification of the products of the devolatization – thermal decomposition processes, thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) can be used [7, 12]. TG allows identify the kinetic parameters of the process, besides MS identifies the evolution of the products and its relation with time and temperature.

The effect of the addition of metallic salts in the pyrolysis process also has been of interest for several scientific researchers. Copper and iron salts as additives in wood pyrolysis [6], iron in fast pyrolysis of cellulose – wood mixtures [5] has been studied. Some others researchers had studied the effect of some catalyst on the thermal treatment of biomass [20]. Nevertheless, the effect of iron salts on the products of pyrolysis of CIW has not been made. In this work, the influence of ferric sulfate on the distribution of products in the evolved gases of the pyrolysis

of CIW using TG-MS at several heating rates was studied. Modeling of the mass/charge signals of the MS was made using the distribution of activation energy model DAEM, with kinetics parameters previously obtained using TGA.

2 Materials and methods

2.1 Materials

CIW was obtained from starch industries in San Juan de Betulia, Sucre department, Colombia. They were gently washed with tap water, rinsed with distilled water, and dried at 378 K before grinding. Samples between 200 and 400 μm were separated and stored in a desiccator for further use. Ferric sulfate was supplied by Sigma- Aldrich with a purity of 75%. Adequate amounts of ferric sulfate and biomass were added to water and stirred for two hours. The obtained slurry was dried at 80 °C for 2 hours and then at 105 °C for another 2 hours. The final iron concentration in the Fe-loaded sample was 1 %.

2.2 Evolved gas analysis (EGA)

EGA was performed using a Thermogravimetric Analyzer TA instruments TGA 2920 coupled to a mass spectrometer QMS Blazer Thermostar using a silicon tubing heated at 473 K linking both instruments to avoid gas condensation. Linear ramps of 10 and 100 K/min were employed. The purge of the gases was made with helium 5.0. Mass range of the MS analysis was selected based on preliminary studies.

2.3 Distributed Activation Energy Model

In this model, the product rate production is represented by several numbers of reactions that share the same frequency factor (A_j) with an activation energy distributed in Gaussian probability distribution. A media activation energy, E_{0j}, and the standard deviation of the activation energy, σ_j, are part of the model described by Equation 1 [16]:

$$Y^{calc}(t) = -\sum_{j=1}^{M} c_j \frac{dx_j}{dt} \tag{1}$$

where Y^{calc} represents the rate of production of the compound associated to the *m/e* signal intensity; *M* is the number of the set of reactions or pseudo components of the sample; c_j is a proportionality constant, and dx_j/dt is the rate of production *j* [14, 15, 17], which can be calculated as:

$$\frac{dx_j}{dt}(t) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[\mu_j{}^2] \exp[0{,}75\mu_j{}^2] \frac{dX_j(t,\mu_j)}{dt} d\mu_j \tag{2}$$

where $\mu_j = 2(E - E_{0j})/(\sqrt{2}\,\sigma_j)$ and $X_j(t,\mu_j)$ is the solution for dx_j/dt at the time, *t,* and the value of the energy of activation, *E*. Mass spectrometry signal intensities were standardized using the signal intensity of *m/e=3* and dry biomass

weight. Solution of equation (2) was made using Matlab® software as previously described [1].

3 Results

3.1 Fitting to DAEM model.

DAEM fitting results of thermogravimetric data are shown in Table 1. These results are employed to model MS data obtained in the same experiments. Kinetics data obtained from the thermogravimetric analysis are related to reactants decomposition and MS data are related to products production. Both data are related to stoichiometric relationships. If gas products are evolved directly from biomass, kinetic data from TA should reproduce MS behavior data. Results from Table 1 shows that the presence of iron sulfate affects mainly the second pseudo component, previously identified as lignin, reducing its activation energy and the standard deviation of this parameter. Previous studies have reported catalytic effects of the ferrous sulfate in the decomposition of lignin in wood pyrolysis [6].

Table 1. DAEM parameters 2 pseudo components for CIW and CIW + 1% Fe heated at 10 and 100 K/min.

Heating rate (K/min)	10		100	
Sample	Cassava	Cassava + 1 %Fe	Cassava	Cassava + 1 %Fe
c_1	1.61E+00	1.41E+00	1.75E+00	1.46E+00
A_1 (1/s)	5.10E+14	5.10E+14	5.10E+14	5.10E+14
E_{01} (kJ/mol)	1.89E+05	1.90E+05	1.87E+05	1.89E+05
σ_1 (kJ/mol)	1.15E+04	1.23E+04	1.23E+04	1.20E+04
c_2	3.96E-01	5.44E-01	2.22E-01	4.60E-01
A_2 (1/s)	4.24E+13	4.24E+13	4.24E+13	4.24E+13
E_{02} (kJ/mol)	1.92E+05	1.79E+05	1.90E+05	1.70E+05
σ_2 (kJ/mol)	3.56E+04	2.74E+04	4.48E+04	3.50E+04
SE*	8.34E-05	4.39E-05	5.17E-04	5.27E-04

* Standard error of the adjustment

3.2 Mass spectrometry

The *m/e* relations for the evolving gas of the pyrolysis are shown in Table 2. During the pyrolytic process of the CIW and CIW+1%Fe a significant amount of water is detected according to the signals *m/e* = 17 and 18. This water is due to the dehydration of cellulose and hemicellulose [9]. In the same way, the formation of carbon dioxide with m/e = 22, 24 is related to the decomposition of cellulose, hemicellulose, and lignin. Carbon dioxide can be produced also in decarboxylation reactions of lignin to high temperatures and secondary reactions in gas phase due to weak aliphatic bond breaking [11]. Is widely known, that syngas

besides carbon dioxide contains methane (m/e = 16), CO (m/e = 28) and hydrogen. Nevertheless, in the decomposition of CIW presence of hydrogen was not observed.

At the first stage of the pyrolysis at low temperatures, evolved gases are the result of the hemicellulose decomposition, while lignin decomposition is presented in the whole temperature range, increased in higher temperatures[18]. Relation m/e = 30 is associated with formaldehyde production, m/e = 58 corresponds mainly to isobutene, propanaldehyde, acetone, and propanol produced by cellulose decomposition [9]. Methoxy radical with m/e = 31 is related to oxygenated compounds as a result of cellulose and hemicellulose degradation [13].

Figures 1a and 1b show the DAEM model fitting for several m/e signals with and without a catalyst. For the m/e = 18 signal, a proper fitting is obtained with and without a catalyst for the heat rate of 10 K/min. m/e = 44 signal, represented in the figures 1c and 1d, had no good fitting to the DAEM model. There is a small shoulder in the curve below the maximum intensity that might be due to the CO_2 formation related to the decarboxylation of small molecules in the gas phase. Figures 4e and 4f show the data for m/e = 28 and heat rate of 100 K/min. The sample without catalyst shows a good fitting, nevertheless, for the catalyst process, experimental data exhibits a second peak after the main one that cannot be predicted with the DAEM model, which suggest that the ferric sulfate affects the production of CO during the pyrolysis of the CIW. Fitting of the signals presented in Table 2 is available upon request. About 90% of the m/e data shows a proper adjustment to the DAEM model. The poor fitting of the remaining signals might be attributed to secondary reactions in the gaseous phase.

Table 2. c_j values for the DAEM model with 2 pseudocomponents for detected m/e signals.

Heating rate (K/min)		10				100			
Sample		CIW		CIW + 1% Fe		CIW		CIW + 1% Fe	
m/e	Fragment/molecule	c_1	c_2	c_1	c_2	c_1	c_2	c_1	c_2
12	C	1.85	0.89	1.03	1.28	1.83	0.93	1.07	1.69
14	CH_2	2.12	2.23	2.36	3.21E-05	2.67	1.01	2.52	1.39
16	Methane, O_2	ND		3.35	0.31	ND		1.79	2.82
17	H_2O	33.54	6.33	ND		27.27	7.15	ND	
18	H_2O	138.8	26.6	109.9	22.12	120.4	28.1	45.5	104.6
20	HF	ND		0.25	1.33E-07	ND		0.28	0.20
22	CO_2	0.02	0.02	ND		0.03	0.017	ND	
26	Furfural; C_2H_2, CN	1.12	0.85	ND		1.08	0.24	ND	
28	CO	25.43	13.4	18.98	1.08	27.31	6.49	17.3	13.84
30	formaldehyde	3.07	1.56	ND		4.07	0.64	ND	
31	CH_3O^+	8.20	1.34	ND		7.79	1.51	ND	
32	Methanol	3.44	1.69	1.33	3.49	3.17	0.16	0.57	3.93

Table 2. (Continued): c_j values for the DAEM model with 2 pseudocomponents for detected *m/e* signals.

|								
34	H_2S	ND		0.01	0.03	ND		0.011	0.012
40	Furfural	0.24	0.24	0.38	0.29	0.23	0.11	0.44	0.31
44	CO_2	10.17	15.0	6.98	14.87	16.79	10.2	4.76	25.37
46	NO_2	1.40	0.08	ND		0.58	0.17	ND	
50	Furfural; benzene	0.036	0.12	0.048	0.095	0.043	0.04	0.05	0.067
51	Furfural; benzene	0.057	0.07	0.050	0.050	0.037	0.03	0.05	0.047
52	Benzene	ND		0.058	0.050	ND		0.04	0.062
53	2-Furanmethanol; 5-Methyl-2-furancarboxaldehyde	ND		0.12	0.074	ND		0.11	0.093
54	4,4-dimethylcyclohexene	ND		0.12	0.067	ND		0.10	0.10
55	Cyclohexanone; 2(5H)-Furanone; 1,4-Dimethylcyclohexane,$C_3H_3O^+$	0.22	0.49	0.17	0.088	0.23	0.11	0.15	0.15
56	4,4-dimethylcyclohexene	0.15	0.11	0.11	0.023	0.15	0.06	0.11	0.079
57	$C_4H_9^+$,C_xH_y, 2-Oxo-butanoic acid	ND		0.06	7.06E-08	ND		0.059	0.029
58	Isobutane, propanal, acetone, propanol	0.27	0.19	0.23	0.015	0.31	0.12	0.32	0.10
59	$C_2H_3O_2$, Acetate	ND		0.01	0.007	ND		0.014	0.010
60	Acetic acid; dodecanoic acid; hexadecanoicc acid; octadecanoic acid	0.38	0.56	0.17	0.18	0.50	0.27	0.20	0.17
69	2-Hydroxi-3-methyl-2-cyclopenten-1-one; 2,3-Anhydro-D-mannosan	0.09	0.092	ND		0.061	0.041	ND	
81	2-Furanmethanol acetate; 2-Methoxy-phenol	0.06	0.042	ND		0.027	0.024	ND	
84	2-Methyl-(E)-2-butenal; 2(5H)-Furanone	0.10	0.072	0.038	0.038	0.11	0.030	0.041	0.030
98	1,2-Cyclopentanedione; 4-Methyl-5H-furan-2-one; 3-Furanmethanol; ciclohexanone	0.050	0.073	2.38	3.54E-05	0.010	0.015	0.007	0.007
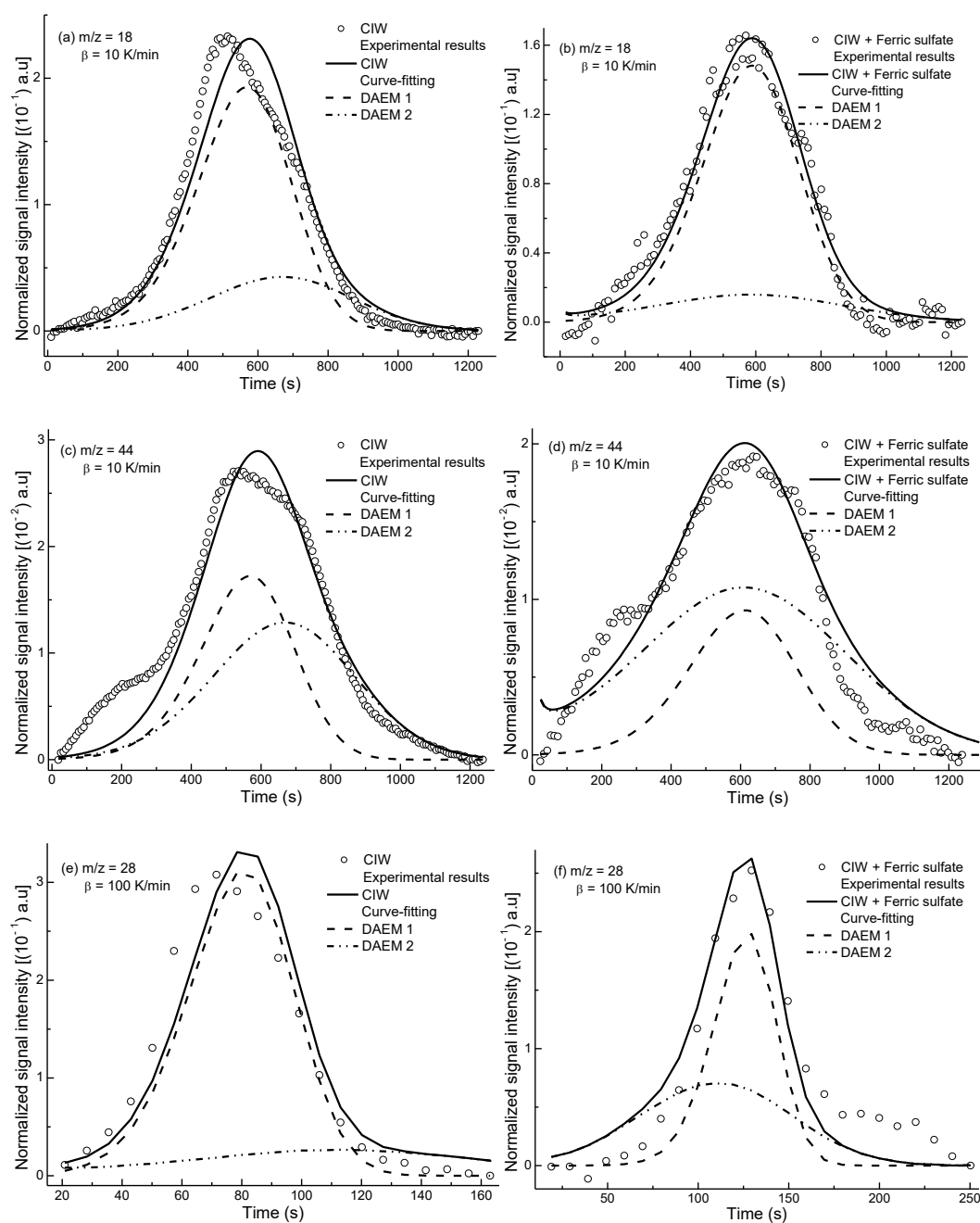
Figure 1. 2 pseudo components DAEM fitting of selected *m/e* signal intensities. a) *m/e* = 18: CIW heated at 10 K/min; b) *m/e* = 18: CIW + 1% Fe heated at 10 K/min; c) *m/e* = 44: CIW heated at 10 K/min; d) *m/e* = 44: CIW + 1% Fe heated at 10 K/min; d) *m/e* = 28: CIW heated at 100 K/min; b) *m/e* = 28: CIW + 1% Fe heated at 100 K/min.

4. Conclusions

The effect of ferric sulfate on the pyrolysis process of CIW using TG-MS was evaluated. Fitting parameters shows that the employed catalyst affects mainly the lignin pyrolysis of the CIW. 31 relations *m/e* of the evolved gases were identified for the pyrolysis process with and without ferric sulfate. There were differences between the signals obtained for both cases, indicating that there is an effect of the catalyst in the rate of production and the distribution of products of the reactions. Fitting of the MS signals to DAEM model shows that about 90% of the signals present a proper fitting of the experimental data, moreover, the remaining signals poor adjustment might be attributed to secondary gas phase reactions.

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