

# Thermogravimetric Analysis of Agricultural Residues: Oxygen Effect And Environmental Impact

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**ABSTRACT:** Agricultural by-products (wheat straw, WS; sugar beet, SB; corn cobs, CC; rape extracted meal, REM; soya bean hulls, SBH; bagasse, B; almond shells, AS; and olive stones; OS) were analyzed by dynamic and isothermal thermogravimetry (TG) in inert and oxidative environment. The goal was to evaluate the effect of oxygen presence on thermolysis and to compare the environmental impact of individual samples. In the inert environment at 250°C, the sequence according to decreasing residue amount under dynamic conditions is B (95%) > CC > WS > SBH = AS > OS > REM > SB (80%). This represents the decreasing role of hemicellulose and pectin components on thermal stability of individual samples. At 500°C the order changed to: REM (35%) > OS > AS > SB > SBH > B > CC > WS (24%). The TG/derivative thermogravimetry (DTG) values determined in air atmosphere could not be used for determination of individual macromolecular components due to overlapping of DTG maxima. For most of the studied samples, the measured residues under dynamic conditions were greater in the inert than in the oxidative environment. According to the thermooxidation maxima, the maximal difference of measured residues on dynamic TG curves run in nitrogen and oxygen environments in the order of decreasing thermooxidation resistance: B (32%; 325°C) > AS (29%; 450°C) > OS (23%; 450°C) > SBH (20%; 475°C) > WS (21%; 300°C) > SB (13%; 325°C) > REM (15%; 500°C). This is due to the largest protein content of REM (29%) as well as pectin,

hemicellulose, and lignin composition of samples. Under isothermal conditions the rate constants were determined by linear regression method and are considered as initial rate constants of material degradation. For inert conditions, the smallest rate constants and biggest activation energy ( $E^*$ ) were determined on CC. The values of the rate constants increase in the following order CC < WS < SBH < B < OS < AS < SB < REM. In general it can be concluded that the rate constant values measured in oxygen are greater than analogical values measured in nitrogen. The determined  $E^*$  values in oxygen were greater for AS, WS, B, SBH, and OS than the analogical values determined in nitrogen. They were decreasing in the following order: AS > WS > B > SBH > OS. On CC, SB and REM,  $E^*$  values were lower in comparison with the  $E^*$  calculated for inert conditions. We assume that when the  $E^*$  value decreased in the presence of oxygen and when simultaneously smaller residue was formed under dynamic conditions, then the material is more unsuitable as a fuel from environmental point of view. It is because more oxygen was consumed and more material was gasified than on samples with closer values in both environments. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1318–1322, 2006

**Key words:** thermogravimetry; kinetics; agricultural residues; oxygen; environmental impact

## INTRODUCTION

Agricultural crop residues are produced annually in enormous quantities, and thermochemical technologies for their utilization are predominant, although their negative environmental aspects are notoriously known. The formed gaseous products represent a complicated mixture of hazardous gases, while the residue is used as charcoal.<sup>1–6</sup> From the gaseous products, only hydrogen might be used as an environmentally safe fuel, but the low yield and presence of many other compounds does not predict this methodology

for success.<sup>7</sup> The production of charcoal also does not seem to be a solution, as it is also a fuel that produce the aforementioned gases during preparation and will have the same problem during the use. The best solution seems to be the transfer of the residues to landfill, where they could be used by microorganisms as a carbon source. This is not accompanied with environmental risks; even when lignin is not fermentable it is transformed to fossils. The consumption of oxygen during the combustion process must also be considered as a negative environmental impact because of its necessity for life.

Thermogravimetry (TG) is a good analytical method for the determination and comparison of environmental impacts of different plant residues under identical thermolysis and thermooxidation conditions. TG/DTG could also be used for determination of the major constituents of lignocellulosics.<sup>8</sup> The objective of this

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**TABLE I**  
**Elemental Composition, Lignin, and Protein Content of Samples**

Sample	Nitrogen content (%)	Carbon content (%)	Klason lignin (%)	Protein (%)
Corn cobs	0	44.96	17.2	0
Wheat straw	0	44.82	21.7	0
Bagasse	0.38	45.29	22.6	2
Soya-bean-hulls	1.77	41.56	2.7	11
Sugar beet	0.50	41.84	5.2	3
Rape-extracted-meal	4.67	43.20	9.0	29
Almond shells	0	46.32	27.7	0
Olive stones	0.89	44.24	30.0	6

work was to compare the course of thermolysis in different agricultural residues and to determine the effect of oxygen on their gasification. We also wanted to find out if the TG/DTG method could be used generally for determination of quantities of the macromolecular components in plant materials. The hypothesis in this work was that the positive evaluation of thermal degradation with TG from environmental point of view expects less gaseous products and more residues. On the other side, when the presence of oxygen is less influential on the process, then it can be considered as less environmentally harmful because of the lower consumption of oxygen. Wheat straw (WS), corn cobs (CC), bagasse (B), sugar beet (SB), rape extracted meal (REM), soybean hulls (SBH), olive stones (OS), and almond shells (AS) were chosen as suitable samples.

## EXPERIMENTAL

### Plant materials

Wheat straw,<sup>8</sup> corn cobs,<sup>9</sup> bagasse,<sup>10</sup> sugar beet meal (Gemercukor, Slovakia), rape extracted meal (Palma, Slovakia), soybean hulls (gift from W. E. Marshall, USDA), olive stones, and almond shells (gift from J. A. Conesa, University of Alicante, Spain) were homogenized to particles smaller than 0.2 mm. The nitrogen and carbon content as well as Klason lignin and calculated protein content of individual samples are listed in Table I. They were determined as described earlier.<sup>9</sup>

### Thermogravimetric analysis

A thermogravimetric analyzer Mettler-Toledo TGA/SDTA 851<sup>e</sup> was used for dynamic (10 K/min) and isothermal (10 K/min up to the desired temperature) experiments at 2 mg sample amounts in a dynamic (30 mL/min) nitrogen, air, or oxygen environment. The isothermal rate constants and activation energies were calculated using the linear regression method from

five point data measured within the initial 5 s after reaching the desired temperature.

## RESULTS AND DISCUSSION

### Dynamic conditions

The results of the dynamic TG measurements are listed in Table II. As it will be demonstrated, the differences in residues for individual samples at temperatures between 250 and 500°C are so close that we preferred to present the results in a table form instead of using a picture. All samples contained up to 6% of water as determined at 105°C in both environments. At 250°C bagasse (B) is the most stable under inert environment. Also corn cobs (CC) and wheat straw (WS) have residues over 90%, then almond shells (AS) and soybean hulls (SBH; 89%), olive stones (OS; 86%), rape extracted meal (REM; 82%), and sugar beet (SB; 80%) follow. It is known that hemicelluloses are degraded as first macromolecular component of lignocellulosics.<sup>11</sup> In annual plants a pectin component is also present, which degrades at the same temperature.<sup>12</sup> As B, CC, and WS contain xylan as hemicellulose component,<sup>8-10</sup> their thermolysis behavior is similar. The aforementioned sequence could be considered in relation to pectin and hemicellulose constituent's thermal stability for individual samples. At 350°C B gave 52% of residue, while only 37% was measured on CC. REM, a residue from rape after oil extraction, is the most stable sample from 375 to 500°C. It is due to high protein content (29%) calculated from nitrogen content (Table I).<sup>11</sup> OS with 40% residue at 375°C is the second most stable sample, while CC and WS gave 32% as the smallest value. After REM (with 41% residue at 400°C SBH), OS, SB, and AS (with 11, 6, and 3% of protein content) gave residues between 33 and 37%. The trend is the same up to 500°C (REM > OS > AS > SBH = SB > CC = B > WS). The relation between the sequence of decreasing thermal stability and the decreasing lignin content, as seen from Table I, could not be observed at temperatures up to 500°C. The residues are at this tem-

TABLE II  
Results of Dynamic TG Measurements (%) in Inert and Oxidative Environments

Sample	Environment	Temperature (°C)											
		105	250	275	300	325	350	375	400	425	450	475	500
Wheat straw	Nitrogen	96	92	88	78	63	41	32	30	28	27	24	24
	Oxygen	98	94	81	57	40	33	26	20	14	13	12	10
Sugar beet	Nitrogen	94	80	72	63	54	40	35	33	31	29	28	28
	Oxygen	95	79	67	54	41	34	29	24	21	16	8	4
Corn cobs	Nitrogen	96	93	86	73	56	37	32	31	29	28	27	25
	Oxygen	96	90	72	53	42	34	30	22	6	5	5	5
Rape-E-M	Nitrogen	95	82	76	68	58	48	45	41	40	38	36	35
	Oxygen	96	81	74	66	58	50	46	43	41	36	28	20
Soya-B-H	Nitrogen	94	89	84	76	67	52	36	33	31	29	28	27
	Oxygen	95	89	82	71	54	40	34	29	22	12	8	7
Bagasse	Nitrogen	98	95	89	79	66	52	33	30	29	28	27	26
	Oxygen	97	92	81	62	34	28	23	19	12	8	4	4
Almond shells	Nitrogen	94	89	82	72	58	43	38	36	34	33	33	31
	Oxygen	95	86	69	51	39	33	26	19	11	4	4	4
Olive stones	Nitrogen	96	86	88	69	57	44	40	37	36	35	34	32
	Oxygen	97	83	68	54	46	40	35	28	14	12	12	11

perature from 35 to 24%. As demonstrated on REM, the protein content seems to be of equal importance as lignin in relation to thermal stability. Because the lignin content of the sample is the third lowest (Table I), its thermal stability must be related to high protein content. The above sequence also shows the increasing negative effect on environment with decreasing amount of residue when the effect of oxygen is not considered.

To see how TG/DTG could be applied for constituent determination of different agricultural by-products we have run dynamic TG experiments in air. As seen from Table III, on none of the samples the correct content of individual macromolecular components could be determined. The DTG maximum of SB sample for hemicellulose degradation was at 244°C and only at this sample the DTG minimum for this component was observed at 262°C. Simultaneously pectin is also degraded in the same temperature range.<sup>12</sup> The DTG maximum for cellulose decomposition is at 324°C and the corresponding minimum at 378°C. It

was observed that there is an additional DTG maximum at 421°C, which we ascribe to protein presence with DTG minimum at 437°C. Lignin is decomposed at 517°C (DTG minimum), and it degrades at the highest rate at 488°C (DTG maximum). The difference remaining after lignin DTG minimum is listed as inorganics (Table III). The determined DTG temperatures of hemicelluloses, cellulose, and lignin are close to data obtained on *Populus tremuloides* wood with the suggested method.<sup>8</sup> On the rest of samples, the DTG maximum for hemicellulose and pectin degradation could be observed (289–337°C), but the corresponding minimum was overlapped because of cellulose degradation. In this way only the total value of hemicellulose, pectin, and cellulose could be assumed from cellulose DTG minimum (362–390°C). The protein determination by this method is impossible. The TG/DTG method could not be used for determination of the macromolecular components in annual plants.

Under oxygen atmosphere the decreasing residue order at 250°C is WS > B > CC > SBH > AS > OS

TABLE III  
Composition (%) of Agricultural Residues as Determined by TG/DTG

Sample	Hemicellulose/pectin	Cellulose	Protein	Lignin	Inorganics
Corn cobs	—	57 <sup>a</sup>	0	33	8
Almond shells	—	57 <sup>a</sup>	0	33	8
Sugar beet	17	42	9	21	5
Bagasse	—	74 <sup>a</sup>	0	20	5
Wheat straw	—	66 <sup>a</sup>	0	24	8
Olive stones	—	57 <sup>a</sup>	0	25	17
Soya-bean-hulls	—	55 <sup>a</sup>	0	29	12
Rape-extracted-meal	—	47 <sup>b</sup>	—	20 <sup>b</sup>	29 <sup>b</sup>

<sup>a</sup> Hemicellulose, pectin, and cellulose; cut-off point between hemicellulose, pectin, and cellulose was not recognized.

<sup>b</sup> Value affected by protein content.

TABLE IV  
Isothermal TG Data (the Rate Constant Values Are Multiplied by 1000)

Sample	Environment	Rate constants [ $\text{min}^{-1}$ ]					Activation energy (kJ/mol)
		220 (°C)	230 (°C)	240 (°C)	250 (°C)	260 (°C)	
Corn cobs	Nitrogen	2.6	4.3	8.9	16.0	24.5	127
	Oxygen	4.9	9.1	13.3	20.8	31.2	96
Wheat straw	Nitrogen	4.5	6.5	7.3	12.9	15.4	69
	Oxygen	6.6	8.5	14.9	26.6	48.1	111
Soy-B-H	Nitrogen	5.8	8.0	11.9	18.6	22.3	77
	Oxygen	5.4	9.3	14.2	17.9	29.7	89
Bagasse	Nitrogen	6.1	9.1	9.5	14.9	20.2	63
	Oxygen	8.7	11.1	16.2	23.3	35.7	78
Olive stones	Nitrogen	8.7	11.5	21.7	25.8	33.7	77
	Oxygen	14.8	19.5	27.5	41.3	62.8	79
Almond shells	Nitrogen	9.6	11.8	14.3	17.1	20.8	42
	Oxygen	8.5	11.5	19.6	36.2	60.0	110
Sugar beet	Nitrogen	10.7	31.5	47.9	51.5	104.5	111
	Oxygen	12.4	31.2	52.7	53.2	105.8	106
Rape-E-M	Nitrogen	12.6	17.8	24.5	28.6	46.2	67
	Oxygen	16.5	20.1	25.8	32.1	36.7	45

> REM > SB. On WS, SBH, and REM the residues are identical in nitrogen and oxygen environments at this temperature, while the rest of samples differ only in 3% lower values under oxidative conditions. The most resistant towards thermooxidation is REM, having equal residues content up to 450°C in both environments. At 500°C all the samples gave values close to their ash content except REM, OS and WS. The sequence (REM > OS > WS > SBH > CC > SB = B = AS) under these conditions shows the best resistance of REM against thermooxidation.

For most of the samples studied, the measured residues under dynamic conditions were greater in the inert than in the oxidative environment. The biggest difference was observed for B (32%) at 325°C. The only exception was REM, where the residue was bigger in oxygen environment at the interval between 350 and 425°C. The greater residue values for REM, OS, AS, and SB in inert atmosphere are also due to hemicellulose and pectin composition and protein content. We assume that (4-O-methyl-D-glucurono)-D-xylan is more degraded than arabinogalactan-protein fraction, because the latter could form a nitrogen containing heterocycles remaining longer in residue. According to the values of thermooxidation maxima,<sup>13</sup> calculated from maximal difference of measured residues on the dynamic TG curves run in nitrogen and oxygen environments the order of decreasing thermooxidation resistance is B (32%; 325°C) > AS (29%; 450°C) > OS (23%; 450°C) > SBH (20%; 475°C) > WS (21%; 300°C) > SB (13%; 325°C) > REM (15%; 500°C). This means B is more harmful for environment as a fuel, because more material could be gasified in presence of oxygen than from REM. It is also probable that more oxygen is consumed when more material is gasified at its presence.

#### Isothermal conditions

Under isothermal conditions, the rate constants were determined by linear regression method and are considered as initial rate constants of material degradation. They fitted the first order reaction kinetics with regression coefficients close to 1 ( $R > 0.95$ ). These conditions were fitting only at temperature interval from 220 to 260°C. At lower and higher temperatures, the  $R$  values were smaller than 0.95. For inert conditions the smallest rate constants and biggest activation energy ( $E^*$ ) were determined on CC. The values of rate constants at 220°C increase in order as it is listed in Table IV (CC < WS < SBH < B < OS < AS < SB < REM). The smallest  $E^*$  was determined on AS. The reason for the difference in  $E^*$  is in hemicellulose composition and pectin presence, as at 220 to 260°C they are degraded the most.<sup>12</sup>

The rate constants determined under isothermal oxidative conditions were not rising in the same order as those determined under inert conditions. REM, SB, and OS samples exhibited the highest values. In general, it could be concluded that the rate constant values observed in oxygen are greater than analogical values measured in nitrogen. The determined  $E^*$  values decreased in order: WS > AS > SB > CC > SBH > OS > B > REM. This indicates to the complexity of the thermooxidation process, which is affected by all the present constituents.

The measured activation energies are close to values determined by other authors on plant materials and their components.<sup>1-3,5,14,15</sup> All the the authors carried out their works under inert atmospheric conditions and used TG instruments from different manufacturers.<sup>13</sup> The presence of oxygen resulted in a decreases of  $E^*$  values for CC, SB, and REM in comparison to inert conditions. On



WS, SBH, B, OS and AS the opposite effect was observed. Those samples with decreased  $E^*$  values under oxidative conditions also gave smaller values of residue under dynamic TG conditions. This indicates that those materials that require less energy for thermooxidation are more dangerous for environment as fuel because of the greater amount of gaseous products formed. When the required  $E^*$  value reduces in presence of oxygen, then it indicates that oxygen was involved in their degradation mechanism, and it implies that more oxygen was consumed, and in most cases more material was gasified.

### CONCLUSIONS

TG study of eight agricultural by-products under dynamic and isothermal conditions in inert and oxidative environment demonstrated the effect of oxygen on the environmental impact of biomass combustion. Greater amount of material was gasified under oxidative dynamic conditions than in inert environment. The sequence of thermooxidation maxima reflexing the decreasing effect of oxygen is decreasing in order: B (32%; 325°C) > AS (29%; 450°C) > OS (23%; 450°C) > SBH (20%; 475°C) > WS (21%; 300°C) > SB (13%; 325°C) > REM (15%; 500°C). This means that, although all combusted materials have negative impact on the environment, those that form greater residues and their degradation course less affected by oxygen presence are less harmful.

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