

# New Aspects in Cationization of Lignocellulose Materials. X. Thermooxidation of TMAHP–Sawdust

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## Synopsis

With the help of dynamic and isothermic thermogravimetry in inert and oxidative atmosphere the thermooxidation of TMAHP–sawdust in individual anionic forms was studied. The values obtained indicate that the most resistant samples against thermooxidation are  $\text{H}_2\text{PO}_4^-$  and  $\text{Br}^-$  anionic forms. The most easily thermooxidized sample is the  $\text{OH}^-$  form. The thermooxidation seems to be a less energy-consuming reaction than thermolysis.

## INTRODUCTION

Thermooxidation (thermal degradation in the presence of oxygen) is the initial part of the burning process. At higher temperatures it could result in burning of wood and the heterogeneous process of glowing. Trimethylammoniumhydroxypropyl (TMAHP) modification of wood exhibited a flame retarding effect.<sup>1</sup> The process of thermooxidation was separately studied with different anionic forms of TMAHP–cellulose.<sup>2</sup> The purpose of the present paper is to study this process on wood sawdust to find out how the lignin component and hemicelluloses are influencing this process. From our previous study we can see that ESR spectroscopy is not suitable for the analysis of rapid free radical reactions of oxygen with cellulose or wood.<sup>1,2</sup> That is why we used only dynamic and isothermal thermogravimetry (TG) which has been proved to be sensitive to distinguish between different forms of TMAHP–cellulose during thermal degradation.<sup>3</sup>

## EXPERIMENTAL

**Materials.** Sawdust (0.2–2 mm) prepared from bark-free beech trunk (*Fagus silvatica* L.) extracted with a mixture of benzene/alcohol was used as starting material. The 50% vol. aqueous solution of 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) was used as alkylating agent.

**Preparation of Samples.** Sawdust (6 g) was activated with an excess of 85% phosphoric acid by stirring at 5°C for 30 min. The acid was eluted from the material with excess of acetone. To the dried sample 15 mL of CHMAC solution was added and the mixture was homogenized for 30 min. The 17.5% NaOH solution (9 mL) was then added and again homogenized for 30 min and tempered at 60°C for 120 min. The reaction was stopped by washing the

TABLE I  
 Elementary Composition of Analyzed Samples (%)

Sample	Form	Q (mmol/g)	C	H	N
Unmodified sawdust	—	—	44.7	5.8	0
TMAHP-sawdust	Cl <sup>-</sup>	0.35	44.6	6.1	0.3
		0.57	44.8	6.3	0.6
	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	0.35	44.2	6.5	0.6
		0.57	44.9	6.3	0.7
	Br <sup>-</sup>	0.35	44.6	6.4	0.6
		0.57	44.9	6.3	0.7
	NO <sub>3</sub> <sup>-</sup>	0.35	44.9	6.1	0.8
		0.57	44.9	6.5	1.1
	OH <sup>-</sup>	0.35	44.7	6.5	0.6
		0.57	44.7	6.2	0.6
	F <sup>-</sup>	0.35	44.3	6.5	0.5
		0.57	44.7	6.3	0.6
	I <sup>-</sup>	0.35	44.6	6.4	0.6
		0.57	44.6	6.3	0.6
	HCO <sub>3</sub> <sup>-</sup>	0.35	44.7	6.4	0.5
		0.57	44.7	6.3	0.7

mixture with ethanol until the eluate was neutral. The sample was dried at ambient temperature. The exchange capacity of the sample was 0.57 mmol/g. It was defined as  $Q = sf/10m$ , where  $s$  = amount of 0.1M HCl (mL) corresponding to the equivalent point,  $f$  = factor of the used 0.1M HCl, and  $m$  = weight of absolute dry TMAHP-sawdust (g).<sup>4</sup>

The second sample (different degree of substitution) was prepared by activation of 150 g of sawdust with 17.5% NaOH (225 mL) at 20°C for 30 min. Then the solution of CHMAC (225 mL) was added and the sample tempered at 60°C for 120 min. The reaction was stopped by washing the mixture with 1% ethanol solution of HCl and subsequently washed with ethanol and dried at ambient temperature ( $Q = 0.35$  mmol/g).

The samples were transformed into their individual anionic forms by washing with 1% water solution of NaCl, NaBr, NaI, NaH<sub>2</sub>PO<sub>4</sub>, NaNO<sub>3</sub>, NaOH, and NaHCO<sub>3</sub>. The elementary composition of individual samples is listed in Table 1. The nitrogen content was also determined by potentiometric titration of ammonium groups.<sup>4</sup>

**Methods.** The samples were analyzed using Perkin-Elmer TGS-1 thermobalance in nitrogen and oxygen atmosphere, respectively, as described previously.<sup>3</sup> Likewise, the calculations of rate constants and activation energies using a linear regression method and other methods were described previously.<sup>3,4</sup> For the calculation the programs in BASIC on an IBM PC Convertible were performed.

## RESULTS AND DISCUSSION

Although the elementary composition of individual samples is not much different (Table I) the results of dynamic TG measurements in Table II exhibit differences in stability during the course of degradation. The unmodified sawdust is more rapidly degraded in oxidative atmosphere in the temperature interval 250–400°C than in inert environment. The greatest difference between the residues obtained in inert and oxidative atmosphere was recorded

TABLE II  
Results of Dynamic TG Measurements (%) of Beech Sawdust and TMAHP-Beech Sawdust  
in Different Cycles in Inert and Oxidative Atmosphere

Substrate	Atmosphere	Q (mmol/g)	Temperature (°C)							
			105	250	275	300	325	350	375	400
Unmodified sawdust	Nitrogen	—	97.2	95.3	91.7	81.8	67.8	48.0	33.6	28.7
	Oxygen	—	98.2	95.0	86.9	71.4	43.0	31.3	25.3	19.1
TMAHP- sawdust	Nitrogen	0.35	96.3	92.3	84.6	66.7	54.9	51.9	48.3	45.4
	Oxygen	0.35	95.6	91.1	81.2	66.4	54.9	51.2	47.5	43.4
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Nitrogen	0.57	99.1	94.3	84.6	62.0	50.7	46.3	42.0	37.3
	Oxygen	0.57	97.2	93.2	82.6	60.3	49.2	44.0	39.6	34.7
TMAHP- sawdust	Nitrogen	0.35	96.0	89.3	83.5	75.5	64.8	52.0	41.0	36.8
	Oxygen	0.35	96.3	86.4	76.5	66.3	56.1	46.8	38.2	33.7
OH <sup>-</sup>	Nitrogen	0.57	97.0	93.4	88.0	78.1	60.9	42.1	36.8	32.4
	Oxygen	0.57	97.2	92.3	81.9	65.7	47.1	38.6	33.4	28.6
TMAHP- sawdust	Nitrogen	0.57	97.7	95.5	90.7	81.8	69.0	46.2	37.8	33.2
	Oxygen	0.57	98.0	95.3	89.9	80.7	67.3	47.4	39.2	34.2
F <sup>-</sup>										
TMAHP- sawdust	Nitrogen	0.35	96.5	94.6	91.1	81.2	68.2	55.2	42.3	37.6
	Oxygen	0.35	95.6	91.9	83.8	69.9	57.3	49.8	41.8	37.0
Cl <sup>-</sup>	Nitrogen	0.57	97.5	96.1	93.5	84.9	72.8	52.5	35.2	31.5
	Oxygen	0.57	95.8	93.1	87.3	73.9	53.4	40.2	34.2	29.9
TMAHP- sawdust	Nitrogen	0.57	97.8	95.9	91.9	80.7	63.8	42.5	34.2	29.1
	Oxygen	0.57	96.9	94.0	89.6	78.8	63.7	46.6	39.0	34.5
Br <sup>-</sup>										
TMAHP- sawdust	Nitrogen	0.57	97.8	96.0	92.0	82.7	67.4	47.9	38.7	33.5
	Oxygen	0.57	97.8	95.5	91.0	80.9	65.2	46.5	39.2	31.6
I <sup>-</sup>										
TMAHP- sawdust	Nitrogen	0.57	97.1	93.7	88.6	79.3	65.1	40.8	31.9	27.2
	Oxygen	0.57	96.6	92.9	86.7	76.0	60.7	42.2	35.1	30.2
HCO <sub>3</sub> <sup>-</sup>										
TMAHP- sawdust	Nitrogen	0.57	97.6	95.7	91.9	80.4	63.9	42.5	31.3	26.2
	Oxygen	0.57	97.4	96.0	91.8	79.4	61.2	42.7	35.1	29.7
NO <sub>3</sub> <sup>-</sup>										

at 325°C (24.8%). In none of the modified samples was this phenomenon so evident. It confirms the fact that the modified samples are more resistant to thermooxidation. With increasing exchange capacity (Q) the differences are greater. According to the decreasing difference in wt % between residues obtained in inert and oxidative atmosphere at 325°C, we can obtain a sequence: unmodified wood (24.8% > Cl<sup>-</sup> sample (19.4%) > OH<sup>-</sup> sample (13.8%) > HCO<sub>3</sub><sup>-</sup> sample (4.4%) > NO<sub>3</sub><sup>-</sup> sample (2.7%) > I<sup>-</sup> sample (2.2%) > F<sup>-</sup> sample (1.7%) > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> sample (1.5%) > Br<sup>-</sup> sample (0.1%). The residues obtained under inert and oxidative conditions at higher temperatures are greater than it is observed for unmodified samples. At 375°C the residue of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> form is greatest, the same as it was for TMAHP-cellulose in this anionic form.<sup>3</sup> While the Cl<sup>-</sup> form could be oxidized most easily out of all modified samples, I<sup>-</sup>, F<sup>-</sup>, and Br<sup>-</sup> forms are stable against thermooxidation. The results are similar to those obtained for TMAHP-cellulose.<sup>2</sup> In both cases the samples in OH<sup>-</sup> and Cl<sup>-</sup> form were the most easily oxidizing ones. The samples distinguished by a higher degree of substitution have lower

TABLE III  
 Values of Rate Constants ( $\text{min}^{-1}$ ) and Activation Energies (kJ/mol) of Thermal Degradation and Thermooxidation of TMAHP-Sawdust in Different Anionic Cycles

Substrate	Atmosphere	Q (mmol/g)	Rate constants ( $\text{min}^{-1}$ )					Activation energy
			250°C	260°C	270°C	280°C	290°C	
Unmodified sawdust	Nitrogen	—	0.0048	0.0086	0.0162	0.0230	0.0403	128.1
	Oxygen	—	0.0148	0.0237	0.0425	0.0780	0.1254	133.5
TMAHP- sawdust	Nitrogen	0.35	0.0078	0.0100	0.0166	0.0276	0.0387	103.2
	Oxygen	0.35	0.0150	0.0297	0.0433	0.0750	0.1216	126.5
Cl <sup>-</sup>	Nitrogen	0.57	0.0046	0.0088	0.0137	0.0215	0.0357	122.9
	Oxygen	0.57	0.0157	0.0269	0.0391	0.0439	0.0935	107.7
TMAHP- sawdust	Nitrogen	0.35	0.0086	0.0107	0.0133	0.0166	0.0199	52.2
	Oxygen	0.35	0.0131	0.0250	0.0277	0.0659	0.0914	119.0
OH <sup>-</sup>	Nitrogen	0.57	0.0058	0.0102	0.0124	0.0162	0.0231	79.2
	Oxygen	0.57	0.0298	0.0364	0.0453	0.0509	0.0618	44.1
TMAHP- sawdust	Nitrogen	0.35	0.0129	0.0232	0.0383	0.0858	0.1593	160.4
	Oxygen	0.35	0.0099	0.0186	0.0417	0.0518	0.0729	147.2
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Nitrogen	0.57	0.0153	0.0279	0.0508	0.0784	0.1306	126.6
	Oxygen	0.57	0.0185	0.0307	0.0459	0.0929	0.1708	136.0
TMAHP- sawdust	Nitrogen	0.57	0.0086	0.0135	0.0213	0.0250	0.0381	88.2
	Oxygen	0.57	0.0111	0.0149	0.0212	0.0242	0.0326	64.6
F <sup>-</sup>								
TMAHP- sawdust	Nitrogen	0.57	0.0068	0.0130	0.0215	0.0309	0.0527	121.8
	Oxygen	0.57	0.0085	0.0171	0.0203	0.0367	0.0544	109.6
NO <sub>3</sub> <sup>-</sup>								
TMAHP- sawdust	Nitrogen	0.57	0.0076	0.0128	0.0188	0.0247	0.0377	94.7
	Oxygen	0.57	0.0088	0.0153	0.0250	0.0279	0.0456	95.7
I <sup>-</sup>								
TMAHP- sawdust	Nitrogen	0.57	0.0093	0.0126	0.0150	0.0238	0.0294	71.9
	Oxygen	0.57	0.0071	0.0140	0.0218	0.0298	0.0503	114.5
Br <sup>-</sup>								
TMAHP- sawdust	Nitrogen	0.57	0.0087	0.0123	0.0158	0.0219	0.0287	72.6
	Oxygen	0.57	0.0101	0.0147	0.0180	0.0271	0.0353	76.0
HCO <sub>3</sub> <sup>-</sup>								

residues at temperatures higher than 300°C. This could be due to the greater catalytic effect of the anions during thermolysis (thermal degradation in inert environment) and thermooxidation.

The first-order rate constants of unmodified sawdust are higher in comparison to cellulose.<sup>3</sup> This is because the hemicellulose component is degraded much easier than the cellulose.<sup>5,6</sup> The activation energies of thermolysis of modified xylan, cellulose, and sawdust are similar.<sup>3,5,6</sup> The reason might be that the rate determining step of wood thermolysis is the cleavage of glycosidic bonds while the lignin does not dramatically contribute to the weight loss in this temperature region.<sup>7</sup>

The first-order rate constants for thermooxidation are always higher than those of thermolysis and the activation energy of thermal degradation in the oxygen environment of unmodified wood is close to the value of thermolysis of the same sample. The differences between the rate constants of thermolysis and thermooxidation of modified samples are not so evident as for unmodified

samples. This could be because all the salts enhance the thermal degradation. The exception is the  $\text{H}_2\text{PO}_4^-$  form, with  $Q = 0.35$  mmol/g, where the rate constants for thermooxidation are lower than those of thermolysis. This shows the resistance of  $\text{H}_2\text{PO}_4^-$  anions against thermooxidation. The highest rate constants of thermooxidation were obtained for  $\text{OH}^-$  form. At higher degree of substitution this effect is not so evident. This could be because the anion might act in some other catalytic pathway during degradation.

Because the activation energy of thermooxidation of the unmodified sample is very close to the value of thermolysis, we suppose that the thermooxidation is not the rate-determining step during thermal degradation of wood at temperatures lower than  $300^\circ\text{C}$ . It could be because the thermooxidation is less energy consuming a reaction than thermolysis. The lower activation energies obtained with modified samples indicate that thermolysis proceeds easier when salts are present. Again the exception is the  $\text{H}_2\text{PO}_4^-$  form. The higher activation energies of the thermooxidation of the sample in this form with  $Q = 0.35$  mmol/g in comparison with an unmodified sample could be explained by the idea that this bulky anion is hindering the access of oxygen to the reactive centers. At higher concentration of anions the glycosidic bonds may be cleaved more easily by the TMAHP group. This step could lower the activation energy not only in this case but also for some other forms. The lowest activation energy of thermooxidation was obtained for  $\text{OH}^-$  form ( $Q = 0.57$  mmol/g). This could be because this anion acts as the strongest hydrolytic agent of all the used forms. In this way the access of oxygen to the formed anomeric carbon could be facilitated.<sup>8</sup>

## CONCLUSIONS

The relative stability of individual anionic forms of TMAHP-sawdust against the thermooxidation could be interpreted by comparing the differences in residues at  $325^\circ\text{C}$  of samples measured in inert and oxidative environment. The first-order rate constants of thermolysis are higher than those of cellulose samples while the activation energies are practically the same. The values of rate constants and activation energies of thermooxidation on modified samples are probably affected by the hydrolytic effect of individual anions on polysaccharides.

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