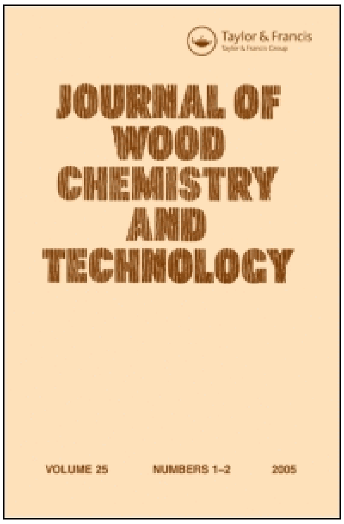


Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Thermal Analysis of Spent Pulping Liquor: Activation Energies

G. J. Kubes[a]; B. I. Fleming[a]; J. M. Macleod[a]; H. I. Bolker[a]
[a] Pulp and Paper Research Institute of Canada, Quebec, Canada

To cite this Article Kubes, G. J. , Fleming, B. I. , Macleod, J. M. and Bolker, H. I.(1982) 'Thermal Analysis of Spent Pulping Liquor: Activation Energies', Journal of Wood Chemistry and Technology, 2: 3, 279 — 295

To link to this Article: DOI: 10.1080/02773818208085136

URL: http://dx.doi.org/10.1080/02773818208085136

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(3), 279-295 (1982)

THERMAL ANALYSIS OF SPENT PULPING LIQUOR: ACTIVATION ENERGIES

G.J. Kubes, B.I. Fleming, J.M. MacLeod and H.I. Bolker
Pulp and Paper Research Institute of Canada
570 St. John's Boulevard
Pointe Claire, Quebec, Canada. H9R 3J9

ABSTRACT

Differential thermal analysis (DTA) and gravimetric thermal analysis (GTA) were evaluated as techniques for determining the activation energy (E_a) of the pyrolysis of kraft black liquor. Although more time consuming, DTA gave more meaningful values that were independent of the heating rate and of the (usually unknown) order of the reaction. The use of GTA required assumptions concerning order of reaction, but might be useful for rapid screening. The results may be significant for recovery furnace operation, because the higher E_a, the more difficult it is to maintain combustion. Some typical values of E_a, in cal/mol, (obtained under a nitrogen atmosphere) for the first exothermic reaction (temperature, °C, in brackets) are: kraft black liquor, 19,400 (290-350); glucose, 9,610 (320-450); kraft liquor plus 10% glucose, 11,100 (240-330); kraft lignin, 7,860 (345-420); spruce wood, 38,100 (290-310).

INTRODUCTION

The operating economics of the kraft process are significantly affected by the cost of pulping chemicals and the efficiency with which they are recycled. Moreover, the spent pulping liquor is a fuel which, on burning, can provide almost all the heat needed to operate the pulping plant[1]. Historically, the development of a high-efficiency recovery cycle was crucial to making kraft pulping an economic industrial process.

The kraft recovery furnace is, however, a source of operating problems; owing to its high capital cost, it is usually designed to operate always at full capacity, with no leeway for upsets. Therefore, any breakdown in the furnace can have an immediate detrimental effect on the operation of the entire mill, as well as on its energy balance. Maintain steady combustion in the recovery furnace is thus of particular importance to maintaining pulp production.

While some downtime in recovery furnaces is due to mechanical failures, certain pulp mills have experienced fluctuations in the combustion process, including "Blackouts", which appear to be linked to variations in the properties of the spent liquor itself. In these cases, the conventionally measured properties of spent liquor (heat value, solids content, specific gravity, viscosity) have not revealed the factor responsible for poor combustion [2]. It seems possible that a more fundamental understanding of the problem may be gained by investigating the thermodynamics of the combustion in order to predict the dynamic behaviour of any particular liquor in the furnace.

While calorimetry generally, though not always, gives adequate information on the combustion of fuels in a completely oxidizing furnace, the results are less useful, and may even be misleading, if applied to kraft furnace operation. The reason is that in a kraft furnace, many of the key reactions occur under reducing conditions [3]. Complete combustion to CO_2 and H_2O, at about 1200°C in an excess of air, occurs only in the upper, oxidizing zone of the furnace to which the gaseous intermediates have moved after reaction of the liquor in the lower, reducing zone. Pyrolysis of organic compounds occurs largely in a reducing atmosphere as do reactions in the smelt pile where endothermic reactions (at about 800°C) reduce sodium sulfate to sodium sulfide. The efficiency of such reduction depends upon the ratio of carbon to sodium sulphate in the pile [4], the amount of air present (optimally 65% of the theoretical amount needed for complete burning), and the continuous, steady flow of liquor through the nozzles into the furnace.

The energy changes that occur in the reducing zone are not completely described by ΔH, the heat of reaction, which is an expression of the difference between the heat content or enthalpy of the reactants and that of the products. To proceed from reactants to products also requires that energy be added so that the reaction may pass over the "energy hill" that prevents the reaction from occurring spontaneously [5]. This necessary, added energy, E_a, is the Arrhenius energy of activation. One reason that efficient pyrolysis is more difficult to achieve than combustion is that its activation energy is much higher.

The techniques for measuring the activation energies of ordinary laboratory reactions are well known. The high temperatures needed to pyrolyze and burn kraft pulping liquors require the application of special methods such as differential thermal analysis (DTA) and gravimetric thermal analysis (GTA)[6]. GTA records the changes in weight that a sample undergoes during heating; DTA indicates chemical or physical changes which occur during the temperature rise and are accompanied by the evolution or absorption of heat.

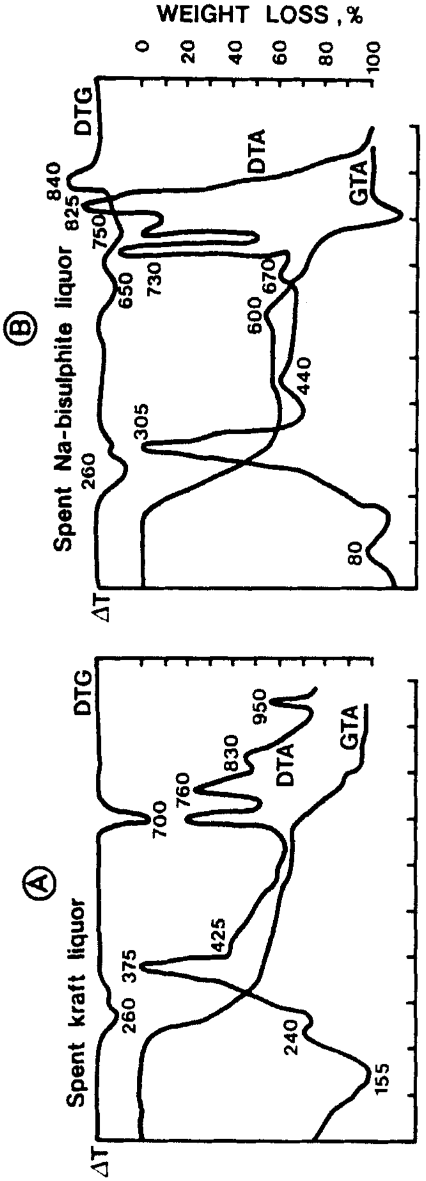
DTA is particularly well suited to fuel analysis, and has been applied extensively in the coal industry[7,8] for classifying different kinds of coal[9] and for predicting the behaviour of the coals during burning[10-12]. The pyrolysis of wood and its components has also been studied by means of DTA[13-19]. Although cellulose and lignin, both isolated from wood, behaved quite differently during pyrolysis, a mixture of the two yielded DTA curves similar to those of the original wood[20].

In the present work, thermal analysis curves have been obtained for samples of spent pulping liquors (Figures 1A-C) and for kraft lignin (Figure 1D).

The qualitative aspects of DTA and GTA curves are useful for identifying chemical changes in fuels or spent liquors[28,29], but more important from the viewpoint of recovery furnace operation is the potential of these techniques for giving activation energies of pyrolysis and combustion. The object of the investigations described in this report was to evaluate this potential.

DETERMINATION OF ACTIVATION ENERGIES BY DTA

In order to use DTA for determining the activation energies of pyrolytic or oxidative reactions, samples of the starting material must be heated at several different rates through the range of temperatures being investigated. The calculations are made from equation 1, whose derivation has been described elsewhere[6], and where ϕ is the heating rate of the thermal analysis furnace and T_m


Ⓐ
Spent kraft liquor
ΔT
DTG
DTA
GTA
260
375
425
240
155
700
760
830
950
Ⓑ
Spent Na-bisulphite liquor
WEIGHT LOSS , %
0
20
40
60
80
100
ΔT
DTG
DTA
GTA
840
825
750
650
730
670
600
440
305
260
80

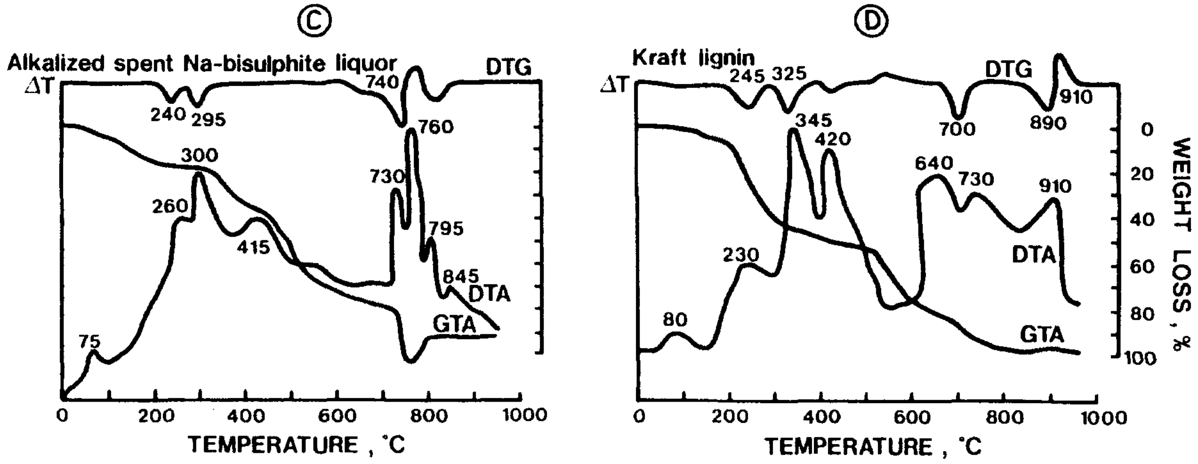
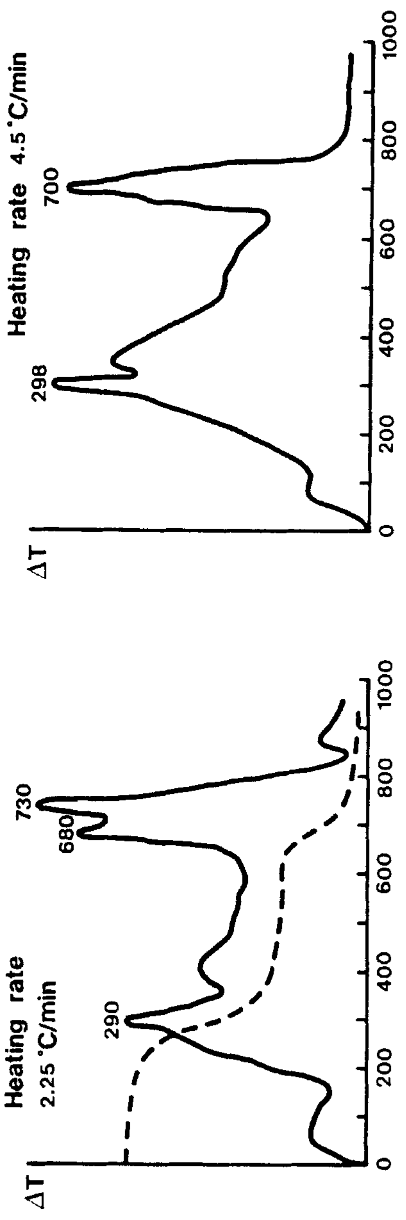


Fig. 1. Thermal analyses of different media tested as 200 mg oven dry samples at a heating rate of 4.60°/minute in a nitrogen atmosphere. Numbers represent temperatures in °C. DTA: differential thermal analysis, GTA: gravimetric thermal analysis. The DTG curve is the first derivative of the GTA curve, the peaks on the DTG curve therefore show either maximum increase or decrease of sample weight.


Heating rate 4.5 °C/min
ΔT
298
700
0
200
400
600
800
1000
Heating rate
2.25 °C/min
ΔT
290
680
730
0
200
400
600
800
1000

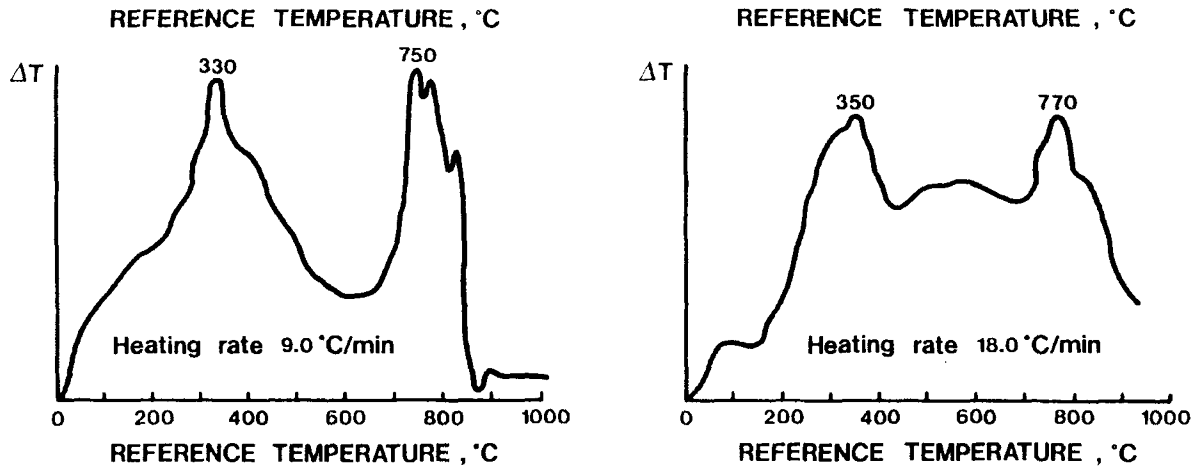


Fig. 2. DTA curves of kraft liquor solids tested at four different heating rates with 200 mg samples in N_2 atmosphere; numbers indicate temperatures in ^{o}C.

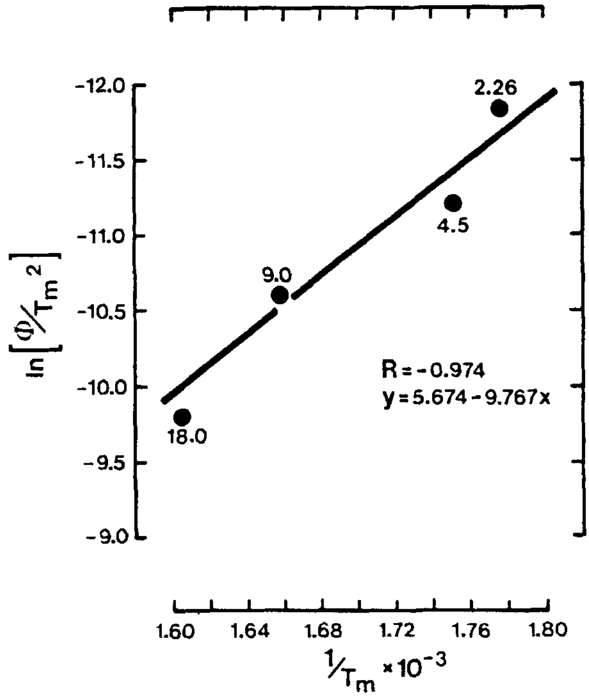


Fig. 3. An example of the calculation of activation energy by DTA. A sample of kraft liquor solids (oven-dried) was tested at four heating rates (numbers in the graph in °C/min). The slope of the correlation line corresponds to $-E_a/R$ from which the activation energy E_a can be calculated.

is the temperature of the peak of the DTA curve. This equation has the merit of being independent of the order of the pyrolysis reaction, an advantage which is not shared by GTA.

$$\frac{d[\ell n\phi/T_m^2]}{d[1/T_m]} = -\frac{E_a}{R} \qquad (1)$$

Sample Calculation

An example of the activation energy calculation is given below for a sample of kraft liquor which was analyzed at four different heating rates. All the thermograms are given in Figure 2.

The derivatograms were obtained by heating 100 or 200 mg of oven-dry samples in the differential thermal furnace in an atmosphere of

TABLE 1

Properties of Partially Evaporated Spent Pulping Liquors

Measured Parameters	Kraft Liquor	Na-Bisulphite Liquor	Alkalized Na-Bisulphite Liquor
pH	13.6	5.30	11.0
Density, g/cm^3 at 20^oC	1,235	1.094	1.095
Viscosity, mPa.sec. at 20^oC	6.00	6.15	1.84
Solids content, %	38.00	19.60	20.00
Ash content, %	30.7	28.8	33.5
Total alkali,			
g Na_2O/liter of liquor	121.65	19.55	35.0
% Na_2O on OD liquor solids	26.08	8.9	18.5
Total sulphur,			
g S/L of liquor	4.10	13.34	13.42
% S/OD solids of liquor	2.38	6.08	6.23
Oven-dried liquor solids			
heat value kcal/kg	3,970	3,760	3,500
heat value (organic part) kcal/kg	5,730	5,290	5,260
elemental analysis, % C	41.14	38.50	27.29
elemental analysis, % H	4.10	4.06	3.71

either oxygen or nitrogen. Temperature (T_m) was read at the peak of the first large exothermic maximum, which correlates with the large loss of weight on the GTA curve. Depending on the proportion of oxygen present, this is the region of combustion or pyrolysis of organic matter. The slope, b, of the plot of $\ell n\ \phi/T_m^2$ against $1/T_m$ (Figure 3) represents the value of activation energy divided by the gas constant, i.e. b = -(E/R), where R = 1.986 cal/mol.

For the kraft liquor (Figure 3), b = -9.769. Hence $-E_a = -9.769 \times 1.986$, and $E_a = 19,300$ cal/mol.

Table 1 shows the properties of spent liquors used in this study and Table 2 lists activation energies, calculated by this procedure, for either the pyrolysis or combustion of a wide range of materials.

TABLE 2

Activation Energies Determined from DTA

Material Analyzed	Atmosphere in the Instrument	Weight of Sample, mg	Location of Peak, °C	Activation Energy, cal/mol	Calorific Value, kcal/kg
Kraft liquor from spruce wood pulped to 48% yield	N_2	200	290-350	19,400	3,970
	N_2	100	290-360	18,700	
	Air	200	250-340	10,600	
	Air	100	260-360	10,700	
Sodium bisulphite liquor from spruce pulped to 55% yield	N_2	200	260-320	29,200	3,760
Alkalized sodium bisulphite liquor	N_2	200	250-320	21,800	3,500
Mixed kraft and alkalized sodium bisulphite liquor (3:1)	N_2	200	280-360	20,600	3,750
Glucose	N_2	100	320-450	9,610	
Kraft liquor	N_2	100	240-320	19,400	
Kraft liquor with the addition of 10% glucose	N_2	100	240-330	11,100	
Lignin isolated from Na-bisulphite liquor	N_2	100	335-415	7,620	
Kraft lignin	N_2	100	345-420	7,860	
Bituminous coal	N_2	100	280-245	19,000	7,380
Lignites - brown coal	N_2	100	315-400	10,200	3,750
Spruce wood	N_2	100	290-310	38,100	4,500
Calcium bisulphite liquor	N_2	100	220-345	9,970	4,400
Molasses-residue after distillation	N_2	100	375-420	39,600	4,170
Sulphite stillage - residue after distillation	N_2	100	300-350	25,400	4,350

DISCUSSION OF THE DTA RESULTS

There are usually several peaks on the DTA curve, especially when materials like coal, wood, or spent pulping liquors are analyzed. In this work, we have analyzed the peak which represents the largest exothermic maximum in the temperature range 250 to 450°C, and which results from combustion or pyrolysis of organic matter. Peaks at temperatures below 250°C usually correspond to the evaporation of chemically combined water, and peaks at temperatures above 450°C indicate oxidation, ashing or melting of inorganic compounds. Trial experiments showed that the E_a values for peaks in the range 650-900°C were 80,000-90,000 cal/mol and were independent of the type of starting material. The E_a values of the peaks in the region 250-450°C, on the other hand, are very sensitive to the nature of the liquor solids.

The activation energies of the reactions of kraft liquor (Table 2) suggested that DTA results were independent of sample size, but as expected, the atmosphere in the instrument had a considerable effect. For kraft liquor in an oxygen atmosphere, the value of the activation energy was half of that obtained in a nitrogen atmosphere.

Both glucose and kraft lignin have low activation energies for combustion or pyrolysis. When glucose was mixed with kraft liquor, the activation energy of the liquor decreased markedly (Table 2). The activation energy of sulphite stillage is much higher than that of the spent calcium bisulphite liquor, presumably because its sugar content has been diminished by conversion into alcohol.

Activation energies may also be decreased by adding inorganic compounds, as seen when caustic is added to bisulphite liquor (Table 2). During pyrolysis in the absence of alkali, sodium bisulphite must first be dehydrated to sodium pyrosulphite. This endothermic reaction is avoided when alkali is added.

The three materials at the bottom of Table 2 have similar calorific values, but their widely differing activation energies suggest that they would not behave similarly in a recovery furnace. An example of combustion problems caused by high activation energy was observed in a cyclone burner[21], designed and successfully operated for burning calcium bisulphite spent liquors. When it was used for burning molasses residues which had the same calorific value as the spent liquor, combustion could not be achieved in the absence of added fuel oil. This was predictable from the very high activation energy of the molasses residue (Table 2).

The dependence of ignition on activation energy rather than on calorific value is also demonstrated by comparing bituminous coal and lignite. It is well known from practice that the low activation energy lignites are much more reactive than the highly calorific bituminous coals; they have very low ignition temperatures which cause serious problems of spontaneous burning during storage.

The last piece of practical evidence showing the importance of activation energy comes from experience with a turbulent-flow coal burner normally fuelled by pulverized lignite. During experiments on the utilization of wood waste, sawdust was mixed with lignite and the mixture was burned for several hours[21]. The sawdust had a calorific value very much the same as that of the lignite (4000 kcal/kg), but its activation energy was nearly four times higher. At the end of the test, unburned wood was found in the fly ash collector, having passed through the entire furnace practically unchanged.

DETERMINATION OF ACTIVATION ENERGY BY GTA

Activation energies may also be determined by gravimetric thermal anlysis[22-25], but the method is more complicated than when using DTA. For a full discussion, the reader is referred to Horowitz and Metzger[26].

The calculations are made from equations 2 - 4, where W_o is the initial sample weight, W_f is the final sample weight, and W_t is the sample weight at time t. The equations employed are:

$$\ell n \ell n \frac{W_o - W_f}{W_t - W_f} = \frac{E_a \theta}{RT_s^2} \qquad (2)$$

$$W_s = C_s(W_o - W_f) + W_f \qquad (3)$$

$$\theta = T_t - T_s \qquad (4)$$

C_s is a constant which depends on the order of reaction, and is given in Table 3. In this work we have assumed the reactions to be first-order, and have used 0.368 as the value of C_s. The reference temperature T_s is graphically determined, and corresponds to

TABLE 3

Relationship between the Order of Reaction & C_s

Order of Reaction n	Concentration of Analyzed Sample in the Inflexion Point of GTA Curve-C_s
0	0.000
1/2	0.250
1	0.368
3/2	0.444
2	0.500
3	0.576
4	0.630
5	0.669
∞	1.000

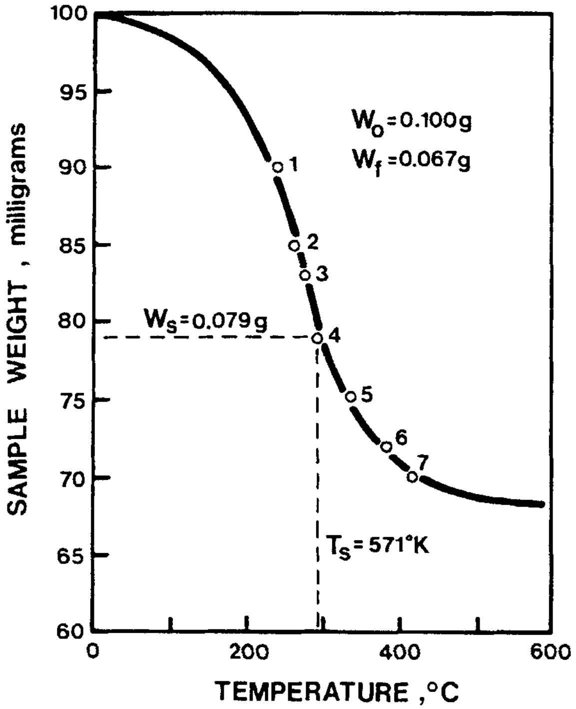


Fig. 4. GTA curve of kraft liquor tested at the heating rate of 2.25°C/minute in an atmosphere of air. A graphical calculation of W_s and T_s is shown.

TABLE 4

Calculation of Activation Energy from GTA

Number of Points	Weight of Sample W_t Grams	Temperature T_t °C	θ $(T_t - T_s)$	$\ln\ln \frac{W_o - W_f}{W_t - W_f}$
1	0.090	245	-53	-1.0188
2	0.085	263	-35	-0.5006
3	0.083	278	-20	-0.3231
4	0.079	298	0	0.01150
5	0.075	338	40	0.3486
6	0.072	385	87	0.6350
7	0.070	418	120	0.8746

W_o = 0.100 g W_s = 0.368(0.100 - 0.067) + 0.067 = 0.079 which corresponds to T_s = 571°K

W_f = 0.067

C_s = 0.368 (for the first order reaction)

W_s (calculated according to equation 3) as illustred in Figure 4. The temperature T_t is the temperature at time t corresponding to W_t.

First, the value of W_s was calculated according to equation 3 using the first-order value of C_s (Table 3). Next, T_s was determined graphically (Figure 4), and sample weights at a series of temperatures were determined. These temperatures differed from T_s by a value of θ°C.

When θ is plotted against $\ln\ln[(W_o - W_t)/(W_t - W_f)]$, the slope of the line equals $E_a/RT_s{}^2$. For liquor sample shown in Figure 4, the slope was 0.00996 and T_s was 571°K. Hence $E_a = 0.00996 \times 571^2 \times 1.986 =$ 6,449 cal/mol. Calculations for other heating rates and other liquors were done the same way, and the results are summarized in Table 5 where they may be compared with the results obtained from DTA. It is evident that GTA, though experimentally simple, gives activation energy values which depend greatly upon the heating rate, whereas values calculated from DTA do not suffer from this drawback.

TABLE 5

Comparison of Activation Energies Calculated from DTA & GTA

Sample	Atmosphere	Heating Rate °C/min	Activation Energy, cal/mol From DTA	From GTA
Kraft Liquor	N_2	2.25	19,400	12,000
		4.50		13,700
		9.00		19,000
		18.00		21,000
	Air	2.25	10,600	6,450
		4.50		8,600
		9.00		9,480
		18.00		11,200
Sodium Bisulphite Liquor	N_2	2.25	29,200	19,400
		4.50		21,400
		9.00		26,900
		18.00		28,600

CONCLUSIONS

The results presented in this paper suggest that determination of the activation energies of combustion and pyrolysis of spent kraft black liquor may shed considerable light on the failure of particular liquors to burn in the recovery furnace.

Both DTA and GTA may be used to determine activation energies. Although more time consuming, DTA gives more meaningful values that are independent of the heating rate and the order of the reaction, which is usually unknown. Nevertheless, the two techniques may be complementary: GTA may be useful for rapid screening, while DTA gives results of greater reliability.

EXPERIMENTAL

A "Derivatograph" type OD-102 MOM made by the Metrimpex Company was used for both differential thermal and thermogravimetric analysis. The equipment was built according to the patent by G. Paulik and

L. Erdey in Budapest, Hungary; a complete description of the apparatus is given in reference (27), which also contains a description of all other procedures used in this study.

REFERENCES

1. Tomlinson, C.L. and Richter, F.H., "The Pulping of Wood", Pulp & Paper Manufacture Vol. I, Ch.10, p. 586, McGraw-Hill Book Co. (1969).
2. Discussions with technical people at several Canadian pulp mills (1979).
3. Kubelka, V. and Votoupal, J., Sbornik Vyzk. Praci z Odboru Cel. a Pap. 1, 98 (1956).
4. Kubelka, V. and Hojnoš, J., Sbornik Vyzk. Praci z Odboru Cel. a Pap. 1, 113 (1956).
5. Gould, E.S., "Mechanisms and structure in organic chemistry", N.Y., Holt, p. 129 (1959).
6. Wendlant, W.W., "Thermal methods of analysis", 2nd Ed., J. Wiley & Sons Inc., p. 187 (1974).
7. Stott, J.B. and Baker, O.J., Fuel (London) 32, 415 (1953).
8. King, L.H. and Whitehead, W.L., Econ. Geol. 50, 22 (1955).
9. Glass, H.D., Econ. Geol. 49, 294 (1954).
10. King, L.H. and Kelley, D.G., Econ. Geol. 50, 832 (1955).
11. Gamel, C.M. and Smothers, W.J., Anal. Chim. Acta 6, 422 (1952).
12. Smothers, W.J. and Chiang, Y., Econ. Geol. 47, 384 (1952).
13. Sandermann, W. and Augustin, H., Holz als Roh u. Werkstoff 21, 256 (1963).
14. Sandermann, W. and Augustin, H., Holz als Roh u. Werkstoff 21, 305 (1963).
15. Sandermann, W. and Augustin, H., Holz als Roh u. Werkstoff 22, 377 (1964).
16. Tang, W.K. and Neill, W.K., J. Polymer Sci. Pt.C, 6, 65 (1963).
17. Stamm, A.J., Ind. Eng. Chem. 48, 413 (1956).
18. Breger, I.A., J. Fuel Science 30, 204 (1951) & 30, 247 (1951).
19. Browne, F.L. and Tang, W.K., Chem. Abstr. 60, 1928h (1963).

20. Domansky, R. and Rendoš, F., Holz als Roh u. Werkstoff 20, 473 (1962).

21. Votoupal, J. and Vyhňák, J., Private communication, 1st Brno Engineering Co., Research & Development Centre, Brno, Czechoslovakia.

22. Anderson, D.A. and Freeman, E.S., J. Polymer Sci. 54, 253 (1961).

23. Anderson, H.C., SPE Trans 2 No. 3,202 (1962).

24. Duval, C., "Inorganic Thermogravimetric Analysis", I, Elsevier, New York, (1953).

25. Smothers, W.J. and Chiang, Y., "Differential Thermal Analysis", Chem. Pub. Co., New York, (1958).

26. Horowitz, H.H. and Metzger, G., Analytical Chemistry 35 (10),1464 (Sept. 1963).

27. Kubes, G., "Mixing of kraft and sodium bisulphite spent liquors, technological aspects of cross recovery and an evaluation of thermal methods", Ph.D. thesis, Komensky University, Bratislava, Czechoslovakia (1967).

28. Oye, R. and Okayama, T., Japan Tappi 28 (10), 50 (1974).

29. Okayama, T. and Oye, R., Japan Tappi 31 (7), 50 (1977).