Thermochimica Acta, 84 (1985) 1-5
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

TG/DTG AS A RAPID METHOD FOR THE CHARACTERIZATION OF SOLID RESIDUES DERIVED FROM LIQUEFACTION OF LIGNOCELLULOSICS

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(Received 16 July 1984; in final form 30 July 1984)

ABSTRACT

Wood and wood residues derived from liquefaction of *Populus tremuloides* were studied by means of TG/DTG in order to establish a simple and rapid method to determine the major constituents.

It is shown that TG/DTG analysis in a dynamic air atmosphere is an appropriate method to distinguish between carbohydrate and lignin. The results agreed quantitatively with ASTM determinations.

INTRODUCTION

There is a need for a rapid and simple method to determine major constituents (i.e., hemicellulose, cellulose and lignin) present in pretreated wood. The need particularly arises in relation to the steam explosion method and the hydrolysis processes. Development of a simple and rapid methodology will facilitate better process control and thus uniform product distribution.

It is well established that the three constituent families mentioned above have distinct temperatures of decomposition [1]. The hemicelluloses are least resistant to thermal degradation, followed by cellulose and lignin [2,3]. Shimizo et al. showed that hemicelluloses decompose in the temperature range 280-330°C depending on the nature of the heteropolymers present [4].

Cellulose depolymerizes, via thermal degradation, at about 350°C mainly to form anhydro sugars. In a dynamic flow system using appropriate heating rates, the probability of char formation becomes small. Under these conditions a rather sharp peak can be observed in the DTG recording at 350°C [5,6]. The increase of crystallinity in cellulose results in a shift of the temperature of maximum degradation rate to about 380°C [7].

Concerning lignin, Arima studied the pyrolysis and combustion of lignin via DSC using N_2 and O_2 atmospheres. His results show that the nature of

0040-6031/85/$03.30

the lignin and its preparation and recovery have a strong influence on the temperature of decomposition. Major changes take place in the range 450–500°C [8]. With the former background a procedure and appropriate experimental conditions were established to evaluate the relative proportions of the two main polymer families present in the residue following wood pretreatment under explosive conditions. *Populus tremuloides* was focussed on as the species to test the approach.

The residues were also analyzed by the standard ASTM methods to quantify hemicelluloses, cellulose and lignin content.

EXPERIMENTAL

Wood substrate

All work reported herein was conducted with *Populus tremuloides* whose ASTM composition is as follows: hemicelluloses, 26.0%; cellulose, 48.1%; lignin, 19.8%; the remaining being moisture, extractives and ash.

Wood pretreatment

Pretreated wood residues were obtained via a thermo-mechanical method which consists of the preparation of a 7–8% ground wood suspension in water, introducing it into an autoclave, preheating the autoclave at temperatures of 150–240°C, and maintaining the slurry (or suspension) at the maximum temperature for a period of 10 min while pressurizing the reactors with N_2 at pressures of 5–20 MPa. The sudden discharge of the slurry through an appropriate orifice disrupts the polymeric structures and facilitates the solubilization of degraded polymer fractions. The discharged slurry was rapidly quenched and the product slurry recovered, vacuum filtered and washed with water to yield a solid residue for analysis.

Thermal analysis

A Perkin-Elmer TGS-2 system was used for TG/DTG analysis. A sample weight of 5–7 mg was placed in an open platinum crucible. A carrier gas was passed through the system at 50 cm^3 min^{-1} while the sample was heated at 20°C min^{-1}. TG and DTG profiles were monitored via a data station, DIGITAL MINC-11, which was interfaced to the PE TGS-2 system.

RESULTS AND DISCUSSION

In the search for optimum peak separation conditions, the effect of three different atmospheres on the thermal decomposition patterns was investigated.

With pure O_2, decomposition (essentially combustion) is easily achieved. No separation by families of constituents is possible and a single peak appears between 200 and 360°C as shown in Fig. 1A.

With dry N_2 no clear separation of the three families seemed to be possible as depicted by Fig. 1C.

When air is used (Fig. 1B) hemicellulose decomposition occurs between 200 and about 316°C with cellulose decomposing up to 360°C (maximum in the DTG at 347°C) and lignin showing a characteristic decomposition pattern between 360 and 480°C (maximum in the DTG at 457°C).

Quantitative estimates could be made following calibration with standard wet methods. The separation between hemicelluloses and cellulose in the thermogram proved to be more inconclusive than the separation between cellulose and lignin (Fig. 1B). Only through repeated tests did the temperature of 316°C represent a reasonable cut-off point between hemicelluloses and cellulose for this particular wood (*Populus tremuloides*). Generalization of this particular cut-off temperature to other samples should be considered with caution.

The application of the technique to pretreated wood is as follows.

(a) Wood material pretreated at 150°C for a few seconds followed by sudden decompression through an orifice with a pressure differential of 6.9 MPa yields a solid residue whose thermal curve is depicted in Fig. 2B. The solid contains 6.8% moisture, 26.3% hemicelluloses, 48.0% cellulose and 18.0% lignin. These values are not prorated and reflect the weight per-

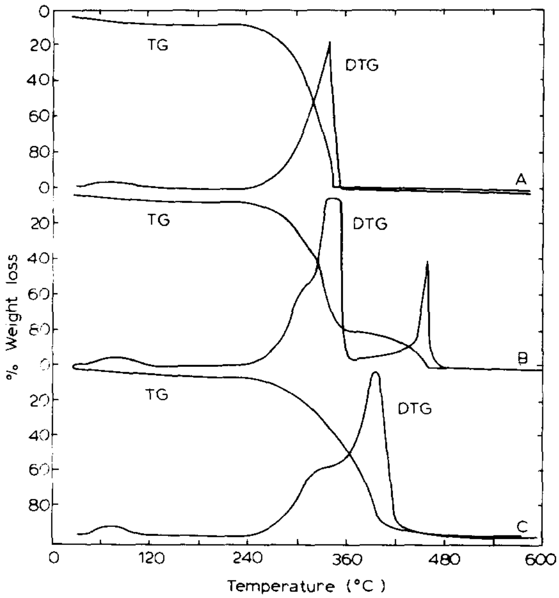

Fig. 1. TG/DTG curves of *Populus tremuloides* in: (A) oxygen; (B) air; (C) nitrogen.

centages obtained using the 316°C cut-off temperature.

(b) Wood material pretreated at 220°C for 10 min following sudden decompression as explained in (a) is shown in Fig. 2C. No hemicelluloses are present in the residue which contains 3.7% moisture, 75.6% cellulose and 18.4% lignin non-prorated values. The corresponding ASTM values are 76.1 and 19.2% for cellulose and lignin, respectively.

(c) Wood material pretreated at 240°C under the conditions given in (b) is shown in Fig. 2D. Again, only cellulose and lignin are present in proportions of 73.8 and 24%, respectively.

In discussing the results we can consider the thermal separation observed between carbohydrates and lignin to be satisfactory. The shift in the DTG maxima observed in certain cases for the lignin should, however, be an indication of the inherent limitations of the method in so far as the definition of a "particular lignin" is concerned. The observed shifts should be interpreted as being caused by structural changes in the lignin itself during the thermo-mechanical treatment.

The separation between hemicelluloses and cellulose is indeed a difficult problem and the procedure outlined in this work will require tedious repetitions for other wood species (treated or untreated) before precise cut-off points can be defined.

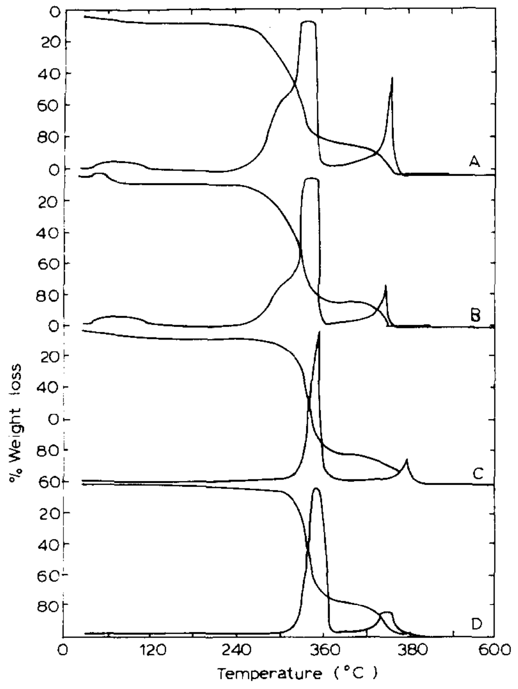

Fig. 2. TG/DTG curves of *Populus tremuloides* in a dynamic air atmosphere: (A) no treatment; (B) pretreated at 150°C; (C) pretreated at 220°C; (D) pretreated at 240°C.

The above considerations lead to the conclusion that the method proposed is adequate to quantify carbohydrate content versus lignin content but it must be considered with caution when quantifying cellulose versus hemicelluloses particularly when low percentages of hemicelluloses are present.

CONCLUSIONS

It has been shown that TG/DTG analysis in an air atmosphere is an appropriate method to distinguish between carbohydrate and lignin in untreated and pretreated wood (in particular, exploded wood). The method can also be extended, with caution, to distinguish between hemicellulose and cellulose contents.

This method has been applied to quantify residual materials resulting from the thermo-mechanical treatment of *Populus tremuloides*. The agreement between the thermal analysis and ASTM methods is satisfactory.

It must therefore be concluded that TG/DTG in a dynamic air atmosphere could become a rapid (about 60 min) and simple method for the determination of major constituents in pretreated wood.

ACKNOWLEDGMENTS

The thermal analysis facilities of the Laboratoire de Caractérisation de l'Amiante were used for this work.

Financial support of the National Research Council, Natural Sciences and Engineering Research Council (Canada) and Programme de Formation de Chercheurs et Action Concertée (M.E.Q.) is also acknowledged.

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