Thermochimica Acta, 41 (1980) 129—131
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THE UTILITY OF SIMULTANEOUS PARAMETER MEASUREMENTS IN THERMAL ANALYSIS

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(Received 17 March 1980)

In recent years, it has become increasingly apparent that the information gleaned from conventional thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TG) can be considerably magnified in scope by combining them with mechanistic probes which are responsive to changes taking place in the sample on a molecular level. This is particularly true in the case of naturally occurring complex materials such as coals, oil shales and tar sands. The utility of simultaneous parameter measurements was illustrated for such materials by combining dielectric measurements with differential thermal analysis (DTA) [1—3]. On the basis of this approach, it was proposed that an ideal combination would be that coupling "primary" thermal analysis techniques such as DSC (or DTA) and TG with mechanistic probes such as thermoelectrometry and thermoacoustimetry [4]. In this communication, we present yet another piece of experimental evidence in favor of the above concept. It is shown that a combined use of the two techniques of DSC and thermoacoustimetry results in a powerful analytical tool which is responsive to changes both in the thermal as well as in the mechanical properties of the test sample as a function of temperature. More significantly, the extreme sensitivity of the thermoacoustimetric probe and the loss of valuable mechanistic information that would have resulted from a DSC examination alone are highlighted by the present results. The proof-of-concept measurements are illustrated on a sample of Utah tar sand bitumen, although, in principle, the conclusions apply equally well to all materials.

Thermoacoustimetry was carried out according to the technique and procedures outlined in a previous paper [5]. Differential scanning calorimetry was performed on a DuPont 990 Thermal Analysis System ** equipped with the DSC accessory module. Both sets of measurements were carried out under identical conditions of heating rate, sample preparation, ambient atmosphere, etc. to eliminate artifacts in the correlation of thermoacoustimetric and DSC data. The sample of Utah tar sand bitumen (P.R. Springs, Main Canyon) was obtained from the Laramie Energy Technology Center.

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** Reference to a brand name or product does not imply endorsement by the authors or by the U.S. Department of Energy.

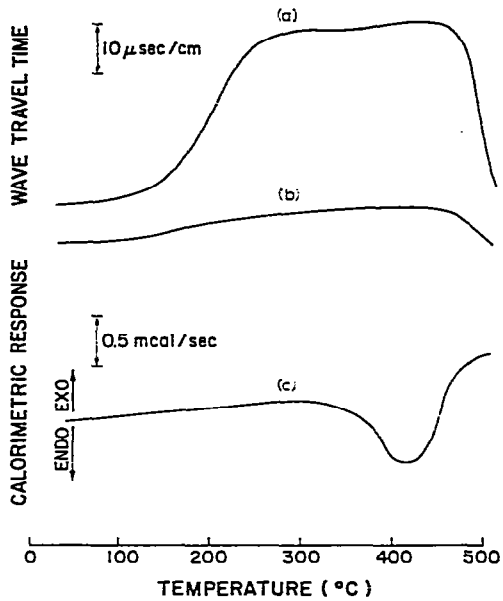

Fig. 1. Comparison of thermoacoustimetry and DSC data for Utah tar sand bitumen. (a) S-Wave travel time; (b) P-wave travel time; (c) DSC trace. Heating rate: 5°C min^{-1}; atmosphere: flowing N_2.

Details of the source of this sample are found elsewhere [6].

Figure 1 is a comparison of the thermoacoustimetric response [Fig. 1(a) and (b)] and a DSC trace for the tar sand sample. Immediately obvious is the abrupt range in the shear (S) wave travel time (i.e. velocity^{-1}) at a temperature around 150°C and the lack of any corresponding activity in the DSC response. The compressional or P-wave transmission characteristics, on the other hand, are relatively insensitive to temperature. A second point worthy of note in the data in Fig. 1 is the dual nature of the S-wave peak; the DSC trace, on the other hand, shows a single endothermic peak in the 350—500°C range. The significance of these results rests on the knowledge that thermal decomposition of tar sand bitumen is a two-step process, the first step corresponding to the distillation of maltenes and the second to the decomposition of asphaltenes [7]. Thermoacoustimetry is able to resolve both stages of the process; the enthalpy changes associated with the first step are, however, too small to be reflected in the DSC trace. Examination of the DSC data alone would have led to erroneous conclusions regarding the mechanistic aspects and regions of temperature stability of the test sample.

A detailed discussion of the thermo-mechanical behavior of the tar sand sample is the subject of another paper [8]. The observed changes in the S-wave velocities with temperature are, however, consistent with the sample undergoing expansive deformation with simultaneous development of microfissures brought about by thermal decomposition. Also significant is the mechanical recovery at temperatures around 500°C, which is reflected in a pronounced increase in the S-wave velocities after pyrolysis of the indigenous bitumen. Although similar trends are also seen for the P-waves (Fig. 1), the magnitude of P-wave travel times, which is characteristically observed, is

insufficiently large for such temperature-induced changes to be amplified with the present instrumentation.

In summary, the utility of simultaneous measurements in thermal analysis has been illustrated by a combined use of the techniques of thermoacoustimetry and differential scanning colorimetry on a Utah tar sand sample. The complementary nature of the two techniques and the loss of valuable information that would have resulted from an application of either technique alone are clearly demonstrated by the present data.

ACKNOWLEDGEMENTS

The authors thank the U.S. Department of Energy and the Laramie Energy Technology Center for financial support of this research.

REFERENCES

1 K. Rajeshwar, R. Nottenburg and J. DuBow, Thermochim. Acta, 26 (1978) 1.
2 R. Nottenburg, K. Rajeshwar, M. Freeman and J. DuBow, J. Solid State Chem., 28 (1979) 195.
3 R. Nottenburg, M. Freeman, K. Rajeshwar and J. DuBow, Anal. Chem., 51 (1979) 1149.
4 K. Rajeshwar, R. Nottenburg, M. Freeman and J. DuBow, Thermohim. Acta, 33 (1979) 157.
5 T. Mraz, K. Rajeshwar and J. DuBow, Thermochim. Acta, 38 (1980) 211.
6 J.W. Bunger, Chem. Ser., 151 (1976) 121.
7 R.G.S. Ritchie, R.S. Roche and W. Steedman, Fuel, 58 (1979) 523.
8 T. Mraz, K. Rajeshwar and J. DuBow, Ind. Eng. Chem. Prod. Res. Dev., submitted for publication.