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NEW PRESSURE DSC MODULE FOR APPLICATIONS TO 7MPa

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Abstract

The temperature is normally the main parameter for all applications in thermal analysis. In most DSC applications pressure is ambient (0.1 MPa) and therefore not specifically mentioned. Pressure becomes important when measurements are performed under elevated or reduced pressure. It is common knowledge, that properties such as melting and boiling point, as well as crystallizations or chemical reactions also depend on pressure. At elevated pressure it is possible to accelerate, magnify or even make visible certain thermal effects.

A new measuring module for pressure DSC (METTLER DSC27HP) has been developed, which features different modes of operation, an intrinsically safe design and ease of use. The METTLER TA4000 system with a DSC27HP module measures thermal effects from room temperature up to 600 °C from ambient pressure up to 7 MPa.

Introduction

DSC measurements under elevated pressure open a new field of applications including:

- Determination of vapor pressure and heat of vaporization.
- Separation of overlapping melting and vaporization peaks.
- Studies of heterogeneous chemical reactions:
  Hydrogenation of organic compounds,
  Reduction of metal oxides under elevated pressure,
  Research and development of catalysts.
- Determination of adsorption and desorption equilibria.
- Investigation of crystallization behavior.
- Oxidation stability of fuels and motor oils under elevated pressure and with use of a purge gas.

In the presentation the design of the pressure DSC, especially concerning safety aspects, and the various modes of operation will be shown. The influence of pressure will be discussed by means of selected measurements.

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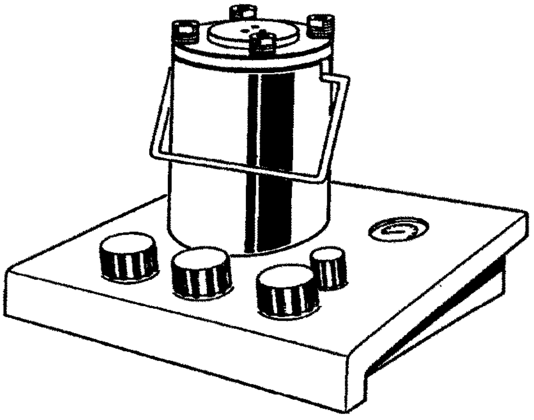
Instrumentation

The module for pressure DSC (METTLER DSC27HP) is shown in Fig. 1. The module combined with the TC11 processor (METTLER TA 4000 System) can measure thermal effects between room temperature and 600 °C from ambient pressure up to 7 MPa in different gas atmospheres. Gases like oxygen, nitrogen, carbon dioxide can be used as well as flammable gases, e.g. hydrogen, carbon monoxide etc. The standard METTLER DSC ceramic sensor is surrounded by the furnace and is positioned in the center of the pressure cylinder (see Fig. 2, schematic cross-section).

The gas and electrical power supply are implemented in the bottom plate of the pressure cylinder. Besides the gas inlet and outlet system there is a separate inlet for purge gas with a control valve. The actual pressure can be observed by a built-in manometer. For safety reasons a rupture disk is incorporated into the system. For substituting or removing samples the cover plate must be taken off. After removing the four screws and using the built-in bracket this is easy to do. A water cooling system thermostats the pressure cylinder during high temperature investigations.
Crucibles of different shape and material e.g. aluminum, gold, may be used.

Investigated materials

Ethanol, benzoic acid, caffeine, kerosene (aircraft fuel), motor oil, rapeseed oil, Raney nickel (FLUKA), charcoal of beech wood, graphite (Sri Lanka), gold oxide (Au_2O_3) FLUKA, iron oxides (wuestite, hematite and magnetite).



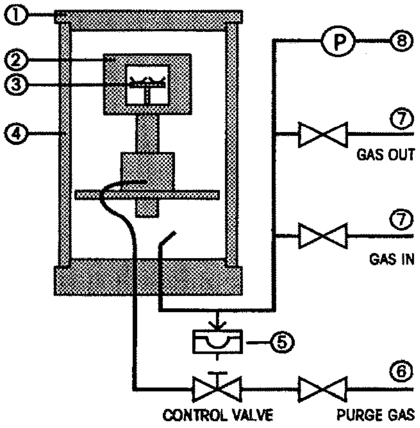


Fig. 1 Module for pressure DSC, METTLER DSC27HP (left).

Fig. 2 Cross-section of the module for pressure DSC (right):

1 Pressure cylinder cover	5 Burst disk
2 Measuring cell	6 Gas inlet
3 Sensor	7 Gas inlet and outlet
4 Pressure cylinder	8 Manometer

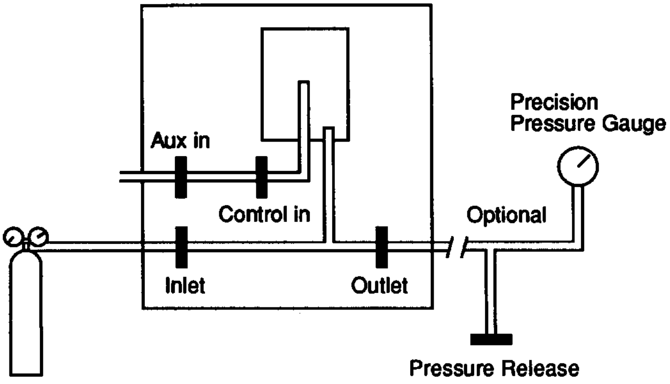


Fig. 3 Basic set-up for investigations under constant and isothermal temperature conditions.

Modes of operation

Investigations under isothermal conditions were done with a basic set-up, shown in Fig. 3. Heating programs with constant pressure require an automatic pressure control system (Fig. 4). The gas outlet is connected to a programmable valve which maintains a selected pressure.

During an experiment the purge gas flow can be programmed by a mass flow controller (Fig. 4). Other arrangements and special requirements are dealt with in the operating manual. The gas distributing box (Fig. 4) is a helpful tool to connect the system to other accessories (gas chromatograph, mass spectrometer or a pressure controller, e.g.).

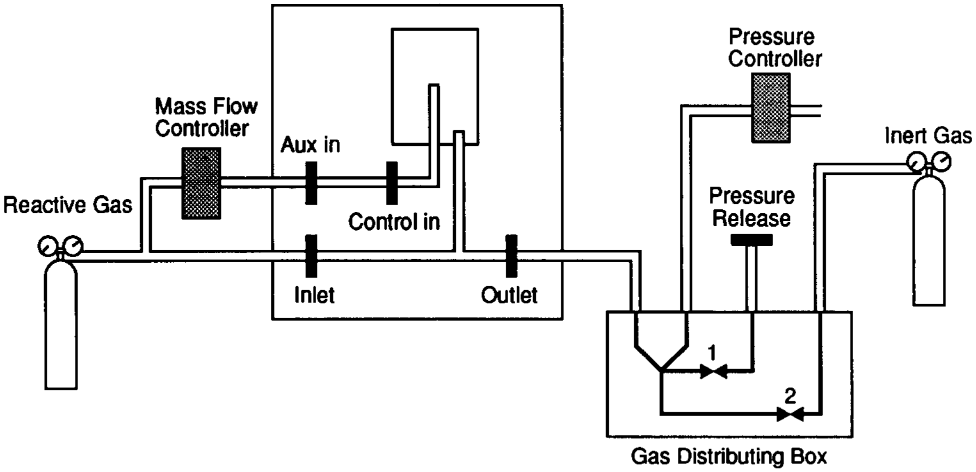


Fig. 4 Instrumental set-up for measurements under constant pressure, dynamic temperature program and flammable purge gases.

Heat of Vaporization of Ethanol and Benzoic Acid

The melting and the boiling point are important physical properties of chemical compounds. The Clausius Clapeyron equation (1) can be used to determine the vapor pressure by knowledge of the maximum speed of vaporization at the applied pressure (boiling point) and the corresponding peak temperature (T-peak):

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta v} \qquad \Delta v = v_g - v_l \cong v_g \approx \frac{R\,T}{p} \qquad \frac{dP}{dT} = \frac{\Delta H_v\, p}{R\,T^2} \qquad \ln(p) = \frac{\Delta H_v}{R\,T} + C \quad (1)$$

The liquid-vapor transition shows a great dependence on pressure due to the volume work. A liquid begins to boil when a temperature increase causes its vapor pressure to be equal to the actual pressure. Thus the DSC peak temperature depends on pressure. Fig. 5 shows some curves for these measurements. Table I contains all measured values from which the vapor pressure curve of ethanol was calculated (Fig.7 a). The experiments were carried out with an aluminum crucible with a pierced lid (hole diameter 0.1 mm).

The DSC curve at 3 MPa pressure in Fig. 6 shows some exothermic effects between 150 °C and 230 °C which could be correlated to an oxidation of the aluminum crucible. The value of vaporization of ethanol is not influenced by the oxidation of Al. Measurements with gold crucibles show only the vaporization. Experiments under elevated pressures require sample sizes of 5 to 10 mg.

Fig. 7 b, compares vapor pressures of benzoic acid from different kinds of measurements. Some of the data have been obtained by measuring the vaporization

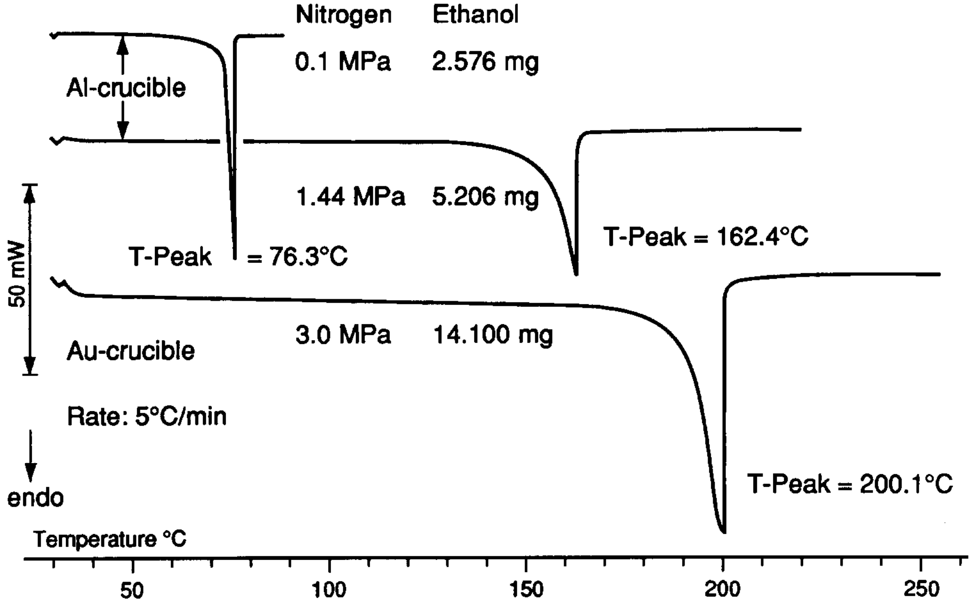


Fig. 5 DSC curves of the vaporization of ethanol under different pressures.

TABLE I

Sample weight (mg)	T-Peak (°C)	pressure (MPa)
2.576	76.3	0.1
10.273	125.7	0.51
12.11	149.4	0.98
5.206	162.4	1.44
14.593	178.7	1.99
14.410	196.3	3.00

Lid orifice 0.1 mm, crucible material Al

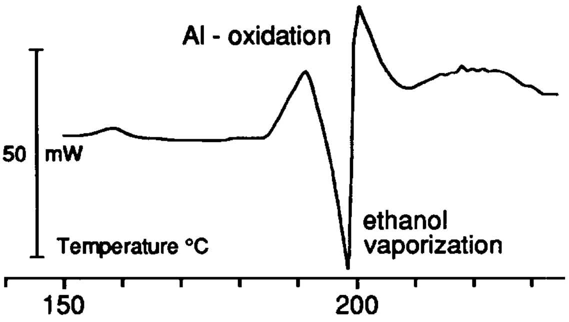


Fig. 6 DSC curve of the vaporization of ethanol in an aluminum crucible .

using a thermobalance with Knudsen cell [2-3], whereas the other data have been obtained by measurements with the pressure DSC.

The data differ not due to the applied method but possibly due to the different association or dimerization of the benzoic acid molecules under different pressures. In this case, mass spectrometer measurements of the proportion of associated and monomolecular benzoic molecules could give an answer of the difference in the heat of vaporization. Not taking into account that the molar heat of vaporization and entropy are temperature dependent, the vapor pressure curves in Fig. 7 are linear (the representation ln(p/po) versus 1/T).

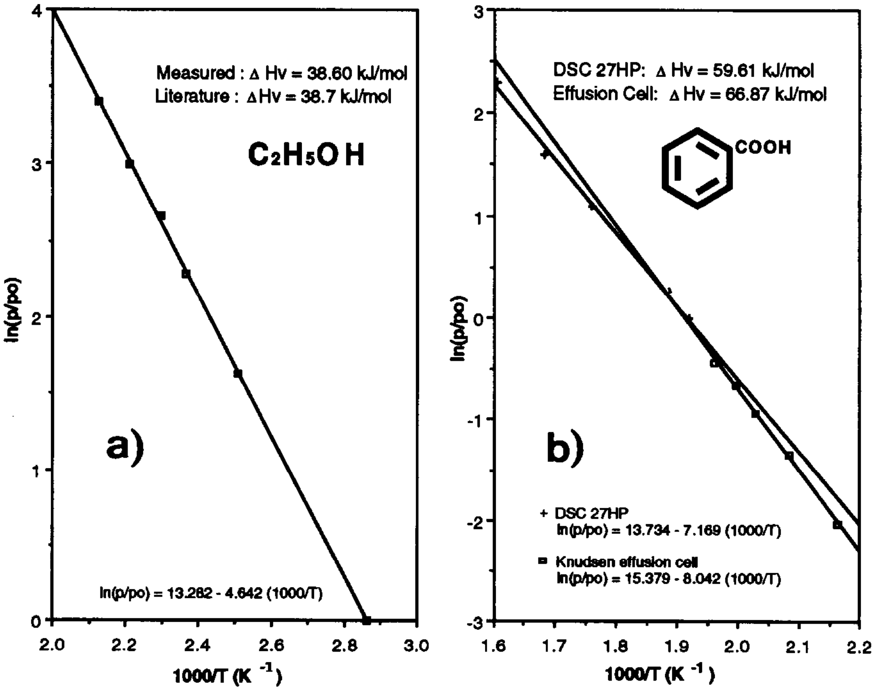


Fig. 7 Vapor pressure curves of ethanol (a) and benzoic acid (b).

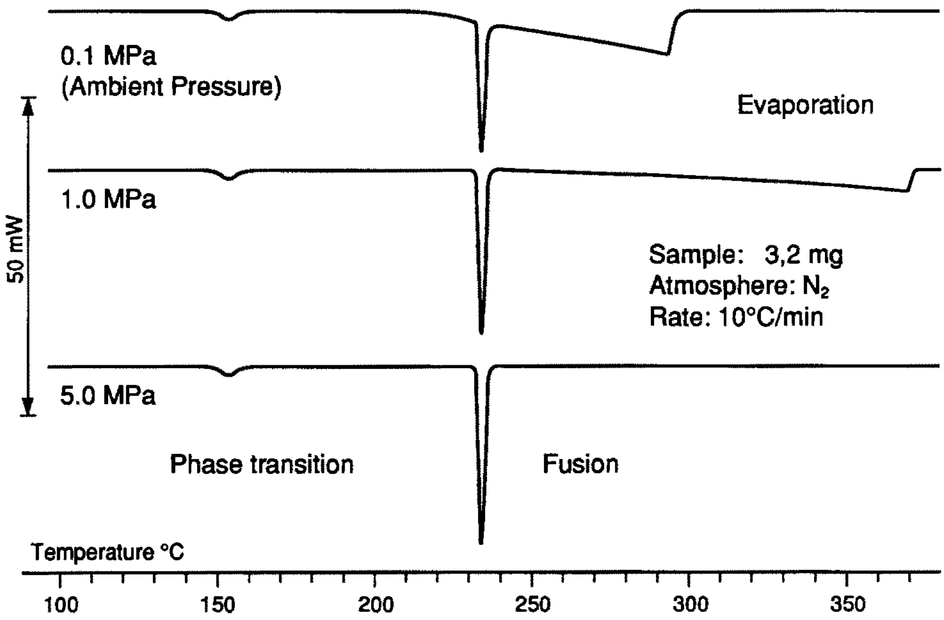


Fig. 8 DSC curves of caffeine under different pressures.

Melting and Vaporization of an Organic Compound

Most organic compounds sublimate over a widerange of temperatures below the melting point, although the tendency for sublimation varies widely from compound to compound. In Fig. 8 the top curve, measured at ambient pressure, shows a melting peak due to sublimation followed by evaporation of the caffeine above 240 °C. In the bottom curve, measured under 5 MPa, these effects are suppressed, and only the melting peak is visible. The middle curve measured at 1MPa shows separated mel-ting and vaporization peaks.

In all experiments the phase transition and fusion occurs at the same temperature. The experiments are performed with an aluminum crucible with a pierced lid (orifice diameter 0.1 mm). Similar investigations at ambient pressure have been done by thermomicroscopy [4].

Vaporization and Oxidation Stability of Kerosene

Kerosene (Shell Jet A1 / aircraft fuel) is a hydrocarbon obtained from fractional distillation (C_{13} - C_{16}) of crude oil. With a DSC experiment at ambient pressure, it is impossible to observe the oxidation of such a product because of the complete evaporation of the sample (bottom curve, Fig.9). This evaporation takes place between 85 °C and 235 °C. The top curve is measured under nitrogen at a pressure of 5 MPa with oxygen as purge gas (80 Nml/min). The oxidation starts at ~200 °C. The experiments are performed with an aluminum crucible with a pierced lid (orifice diameter 1 mm).

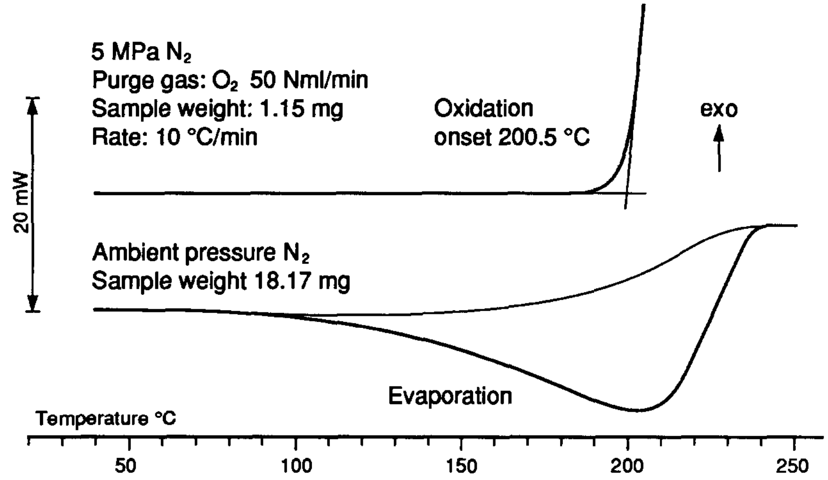


Fig. 9 DSC curves of the vaporization of kerosene under ambient pressure and the oxidation stability of kerosene with nitrogen an oxygen purge gas flow.

Oxidation Stability of New and Used Motor Oils

The oxidation stability of natural or synthetic motor oils is higher after addition of antioxidants. DSC experiments at elevated pressure confirm this behaviour. High quality motor oils show a small change in oxidation stability after using them for

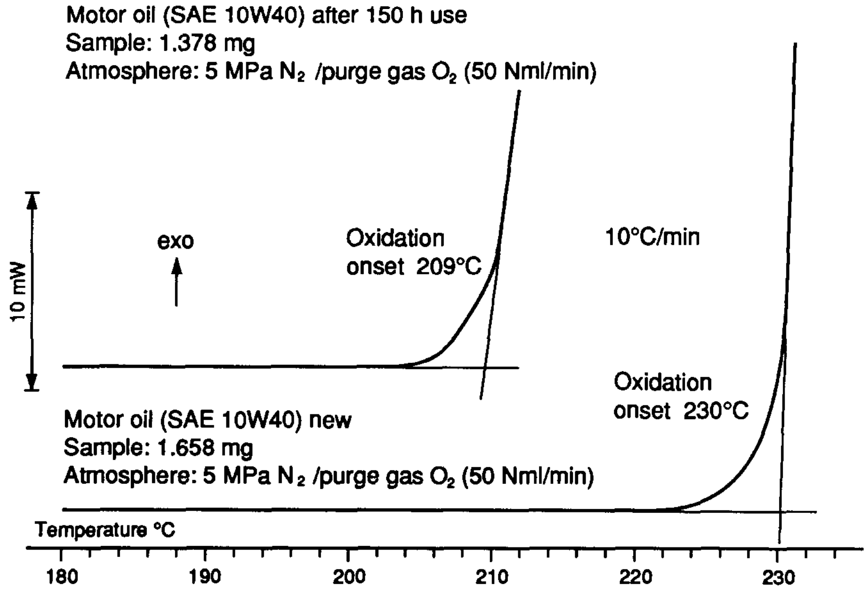


Fig.10 Onset of DSC curves of the oxidation of new and used motor oils.

about 150 hours. The onset of the oxidation peak with 5 MPa nitrogen and a purge gas (oxygen 50 Nml/min) is lowered by about 20 °C.

Fig. 10 shows the results for the unused motor oil in comparison to the used one. The experimental data are given in the figure. The effectiveness was also studied with other high quality motor oils. These results should be the subject of another publication.

Hydrogenation of Triglycerides in Unsaturated Fatty Acids

Margarine production is based on the hydrogenation of edible oils, e.g. rapeseed, palm and nut oils. Edible oils are triglycerides of different unsaturated fatty acids. With increasing saturation by hydrogenation, the temperature range of fusion increases. The oils are transformed in fats. The melting of rapeseed oil before and after hydrogenation was studied with DSC measurements under ambient pressure (N_2). Pressure DSC allows to follow the reaction of hydrogenation itself (1 MPa hydrogen). Fig. 11 shows all curves of the investigated rapeseed oil. With this investigation an Al crucible with pierced lid (orifice diameter 0.8 um) was used, the rapeseed oil was mixed with 0.4 mg of Raney nickel [5-7] as a catalyst of hydrogenation. The temperature of the melting peak of the rapeseed oil increases from less than -20 °C up to almost 70 °C after hydrogenation.

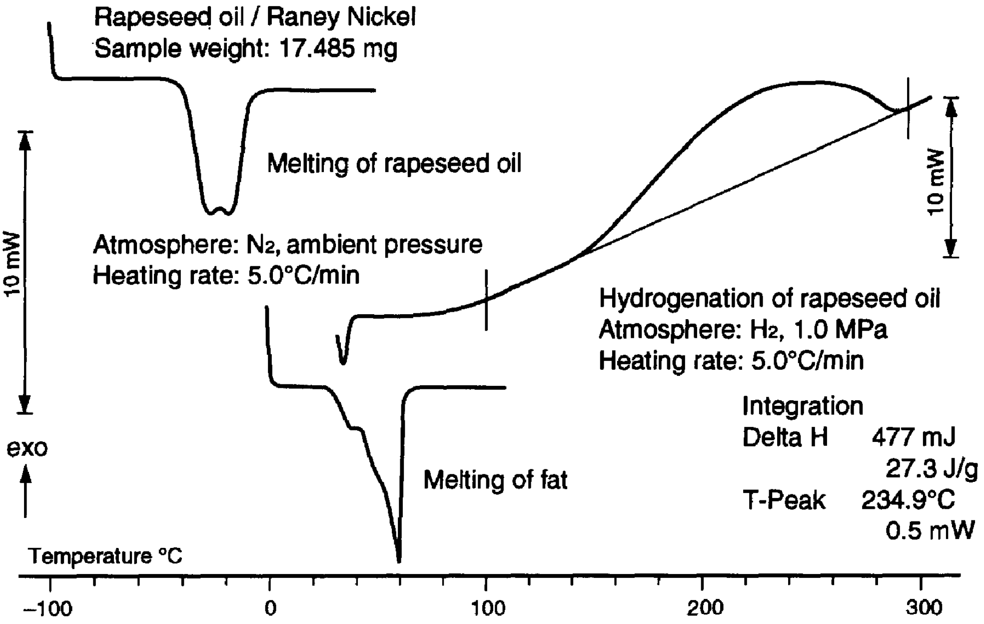


Fig.11 DSC curves of the melting and hydrogenation of rapeseed oil, continued by the melting of the produced fat. Pressures: Hydrogenation of rapeseed oil with Raney nickel at 1MPa hydrogen, the melting of the oil and fat at ambient pressure (0,1 MPa N_2).

Carbonization Process of Charcoal

The carbonization process of wood to the product charcoal has been characterized by thermoanalytical methods [8]. Lignite, bituminous coal, anthracite or poorly ordered graphite are obtained as essential degradation products of the natural carbonization. Comparative studies of pure cellulose and lignin reveal that time aging effects the lignin degradation, whereas thermal aging (i.e. the charring process) leads to the decomposition of the cellulose and turns lignin into charcoal. The continuation of carbonization of the formed charcoal was carried out at high temperatures in oxygen free atmosphere and at ambient or elevated pressure.

Fig. 12 shows four TG curves of different beech wood charcoal samples and graphite. The sample size was in the order of 2.5 mg, the ambient atmosphere was air and the used heating rate 1 °C/min. Curve a) shows the thermal stability of untreated charcoal, curve b) charcoal which was heated for 144 h at 600 °C in N_2 at 6 MPa. The next sample was heated for 168 h at 1525 °C in N_2 at 0.1 MPa, i.e. at ambient pressure (curve c). The TG curve of a graphite sample from Sri Lanka shows the thermal stability of a pure graphite (for comparison). High resolution electron microscope images confirm that poorly ordered graphite was formed (sample b and c).

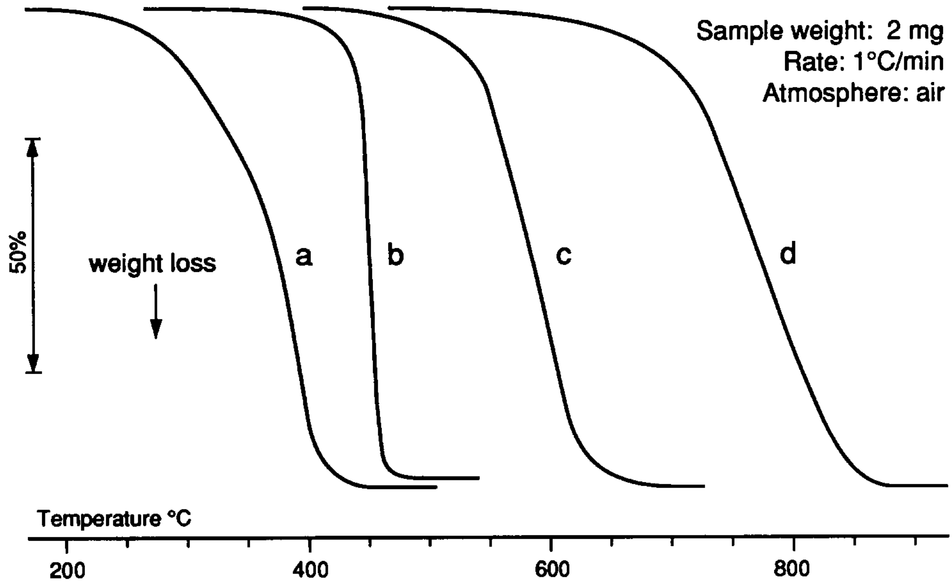


Fig.12 TG curves of different treated charcoal samples and graphite:
a) charcoal sample of beech wood,
b) charcoal sample of beech wood 144h at 600°C in N_2, 6MPa
c) charcoal sample of beechwood 168h at 1525°C in N_2 0.1MPa
d) graphite sample (Sri Lanka).

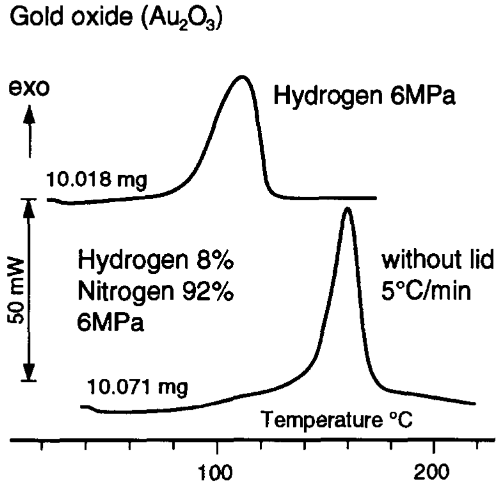
Reduction of metal oxides under hydrogen

The oxides of noble metals are reduced at moderate temperatures, e.g. gold oxide [9] between 80°C and 180°C:

$$Au_20_3 + 3H_2 = 2Au + 3H_20$$

For completion of the reaction and a correct determination of temperature of reaction the metal oxide has to be reduced in an open crucible. Fig. 13 shows two similar runs with gold oxide in crucibles without lids. To determine the completion of the the reaction during DSC experiments, the metal oxide was weighed before and after the investigation. The stoichiometric weight loss indicates the reduction to the metal. Gas mixtures, e.g. H_2/N_2 (8 : 92%) cause a slower reduction and as a result a small account of impurities is visible (see Fig.13, bottom curve),while by using pure hydrogen, this effect is missing. X-ray photographs indicate that metals produced in such a way metals show high specific surfaces (> 100 m^2/g) which decrease after recrystallization by heating the sample to higher temperatures. Similar investigations with natural iron oxides [10], like wuestite (FeO), haematite (Fe_2O_3) and magnetite (Fe_3O_4) show that the temperature of reduction is much lower than at ambient pressure of hydrogen (Fig. 14).

The determined heat of reduction by peak integration of the investigated iron oxides lead to values which were comparable to the heat of formation reduced by the heat of formation of the developed, water and with respect to the specific heat. Especially the values of haematite and magnetite are in good agreement with the calculated values (in the order of 97%). Wuestite and gold oxide (Au_2O_3) show a larger distinction (up to 27%). The DSC curve of haematite shows under these experimental conditions, a separation of the soluted FeO in Fe_2O_3.



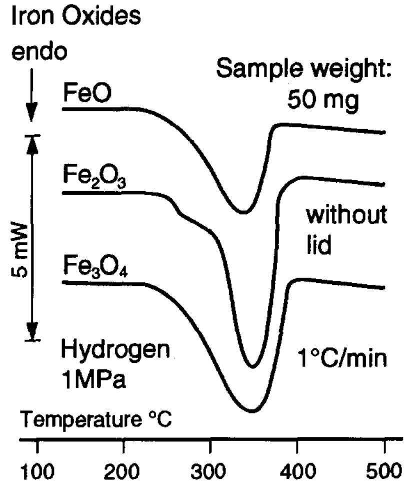


Fig.13 DSC curves of the reduction of gold oxide (Au_2O_3) by pure hydrogen and a mixture of 8% H_2 and 92% N_2 (left).

Fig.14 DSC curves of the reduction of different iron oxides by hydrogen (right).

CONCLUSION

Results of these investigations demonstrate the usefulness of this new pressure DSC module. The METTLER DSC27HP can be applied for high pressure measurements in the range 0.1 to 7MPa, from room temperature up to 600°C. The instrumentation is able to produce useful results in a comparable short time. The time required to change samples and conditions is also very efficient, and is complete as easy as with standard DSC. By use of mass flow and pressure controllers the unit becomes more comfortable and gives an additional safety and an insurance for reproducible measurements.

Experiences and results especially of adsorption and desorption studies in different pressure and temperature ranges will be reported in future publications.

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