High Pressure Gravimetric Measurements with the MSB: Natural Gas Storage Capacity of Rock Samples and Gasification Studies on Coal and Biomass

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JCAT 48
29 mai – 1er juin 2017
IFPEN, Rueil Malmaison
Outline

- Rubotherm / TA Instruments: background & company history
- Magnetic Suspension Balance: technology and benefits
- MSB instruments for sorption analysis
- Natural gas storage capacity of rock samples
- MSB instruments for TGA applications
- Gasification studies on coal and biomass
- Summary
Rubotherm: Background and Company History

- Founded 1990 as spin-off of the chair of Thermodynamics, Ruhr-University Bochum
- Key technology: MSB
- Magnetic Suspension Balance for gravimetric measurements under extreme conditions (temperature, pressure, vapor, corrosive atmospheres).
- Office and manufacturing facilities in Bochum, Germany
- 900 instruments installed worldwide
- Main markets: Germany, Europe, Japan, China, USA, Gulf region
- Continuous collaboration with Universities and Research Organizations in the framework of research projects
- Acquisition of Rubotherm by TA Instruments September 1st 2016
Magnetic Suspension Balance: Technology

Objective: Measuring mass changes in a challenging environment (under pressure or in the presence of vapor or corrosive atmospheres).

Conventional setup:
- Inert purge gas to protect balance

MSB setup:
- Sample hanging on magnet
- Magnetic coupling through wall of measuring chamber
- Complete separation of sample and balance
- No purge gas required

Operating conditions*:
- -196°C – 1550°C
- Vacuum – 700 bar
- High vapor concentrations
- Corrosive atmospheres

*depending on instrument configuration

Magnetic Suspension Balance: Gravimetric measurement under extreme conditions
MSB Technology – Zero Point Function

Zero point function:
Automatic decoupling of sample during measurement

→ Base line drift correction, Long term stability
→ Calibration of balance (scale) during experiment
Volumetry is the primary method of choice for sorption analysis:
- Standardized method for the characterization of porous solids (BET, specific surface area, pore size distribution)
- Sorption data by pressure measurement
- Adsorbed gas volumes calculated based on appropriate equations of state (EOS)
- Application range from vacuum to ambient pressure
- Limitations: error accumulation, uncertainty at higher pressures

Gravimetric sorption analysis with MSB:
- Direct gravimetric method
- No error accumulation
- Buoyancy correction possible by measuring fluid density, EOS not required for data analysis
- Method of choice for sorption analysis at higher pressures
Simultaneous Weight Measurement:

- Measures density of reaction atmosphere for automatic buoyancy correction (baseline) by weighing an inert 2\textsuperscript{nd} sample (sinker). Extremely valuable information for high pressure measurement, particularly with dense fluids like CO\textsubscript{2}

- Improves sample throughput by measuring two samples simultaneously under same P and T conditions

In a compressed gas atmosphere at elevated pressures, the density of the atmosphere causes a buoyancy effect: data correction required.
MSB Instruments for Sorption Analysis: Sample Temperature Control

How to control temperature:
- The measuring chamber is thermostated with a liquid circulator (20-150°C)
- Electrical heating (50-400°C) is also available and usually used for sample pretreatment (removal of preadsorbed gases prior to analysis)
- Cryo options available (e.g. 77K, liq. N₂)
- Magnetic Suspension Coupling can be heated to max. 200°C

Reaction atmosphere: very accurate control of pressure and flowrate required.

Measurement of adsorption isotherms:
- Constant sample temperature
- Increasing pressure stepwise and measuring uptake until equilibrium
MSB Instruments for Sorption Analysis

Typical application example: measurement of H₂ adsorption on chemically modified Carbon Nano Tubes (CNT)
- Comparison of sorption capacity of various porous materials
- Adsorption, Desorption, Kinetics

Natural Gas Storage Capacity of Rock Samples

Measuring reservoir capacity under natural conditions
- CH$_4$ and CO$_2$ capacity of coal or shale material
- ECBM: Enhanced Coal Bed Methane
  - CO$_2$ Storage
  - Replacement of fracking fluids to improve CH$_4$ recovery

S. Ottiger, R. Pini, G. Storti, M. Mazzotti, R. Bencini, F. Quattrocchi, G. Sardu and G. Deriu: Adsorption of Pure Carbon Dioxide and Methane on Dry Coal from the Sulcis Coal Province (SW Sardinia, Italy); Environmental Progress; 25 (2006) 355-364
MSB Instruments for TGA Applications

Two types of high pressure Gravimetric Analyzer with MSB:

- Sorption Analysis: isothermal operation, static gas control
- Thermogravimetric Analysis: temperature gradient, flowing gas atmosphere, max. T often above 1000°C

MSB advantage: separation of sample and balance, no purge gas required
- TGA reactor design should allow pressure and corrosive atmospheres at high temperatures.
- Preference for ceramic materials for long term use
- Required p and T range defines reactor design

Isothermal operation
-196 °C…400 °C
Vac…700 bar Gas, Vapor, SCF

Dynamic T-operation
RT…1550 °C
Vac…80 bar Gas, Gas & Vapor
MSB Instruments for TGA Applications – Reactor design

**Hot wall** versions:
- Heater located outside the reactor tube. Heats sample through the wall of the reactor.

Models:
- LP (1100-1), LP (1550-1): reactor tube made of ceramics (Al₂O₃)
- MP (750-50): reactor tube made of high temperature resistant metal alloy

**Cold wall** versions:
- Heater located inside the pressure vessel. Separated by a Al₂O₃ reactor tube from the reaction atmosphere.

Models:
- MP (1100-40), MP (1200-30), MP (1300-20), HP (900-80)
Catalyst optimization for DRM reactions (Dry Reforming of Methane): Ni/MgAlOx catalyst - calcination and activation in 5% H₂ atmosphere
Catalyst optimization for Dry Reforming of Methane:
Ni/MgAlOx Catalyst - coking behaviour depending on reaction conditions (temperature, gas flow rates)

Data provided by A. Tarasov, M. Behrens, Fritz Haber Institute Berlin, 2013

Gasification Studies on Coal and Biomass

Effect of pressure on kinetics: elevated pressure reduces required reaction temperature

Sample: anthracite - reaction gas: 2% O\textsubscript{2} in N\textsubscript{2}
Gasification of rice husk: biomass as resource for chemicals or polymer production.

- Material conversion is slow in nitrogen but increased with 10% water vapor.
- Conversion rate depending on pressure 7 bar / 10 bar.
Gasification Studies on Coal and Biomass

Variation of effect of temperature and reaction gas composition

- Sample: 50 mg char produced from Rhenish lignite, 63-200 µm particles
- Reaction gas: 10, 20, 50 and 70% CO₂ in Ar, total flow of 380 ml/min
- Reaction rate increases with T and CO₂ volume fraction

Summary

Magnetic Suspension Balance provides technology for gravimetric experiments under extreme conditions:

High Pressure TGA compatible with vapors and corrosive reaction atmospheres.

Main benefits:
- Complete separation of sample and balance by magnetic coupling of sample to balance through the wall of the measuring chamber
- Multiple measuring positions allow automated zero point correction and buoyancy correction during measurement

Main applications:

Gravimetric Sorption Analysis:
- Method of choice at elevated pressures
- Optimization of porous solids and process conditions for HP gas storage applications with H₂, CH₄, CO₂ etc.

Thermogravimetric measurements with vapors and reaction atmospheres, e.g.
- Catalyst optimization studies under realistic reaction conditions
- Gasification studies with coal or biomass with vapor, O₂ or CO₂ at 30 bar
Thank You

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