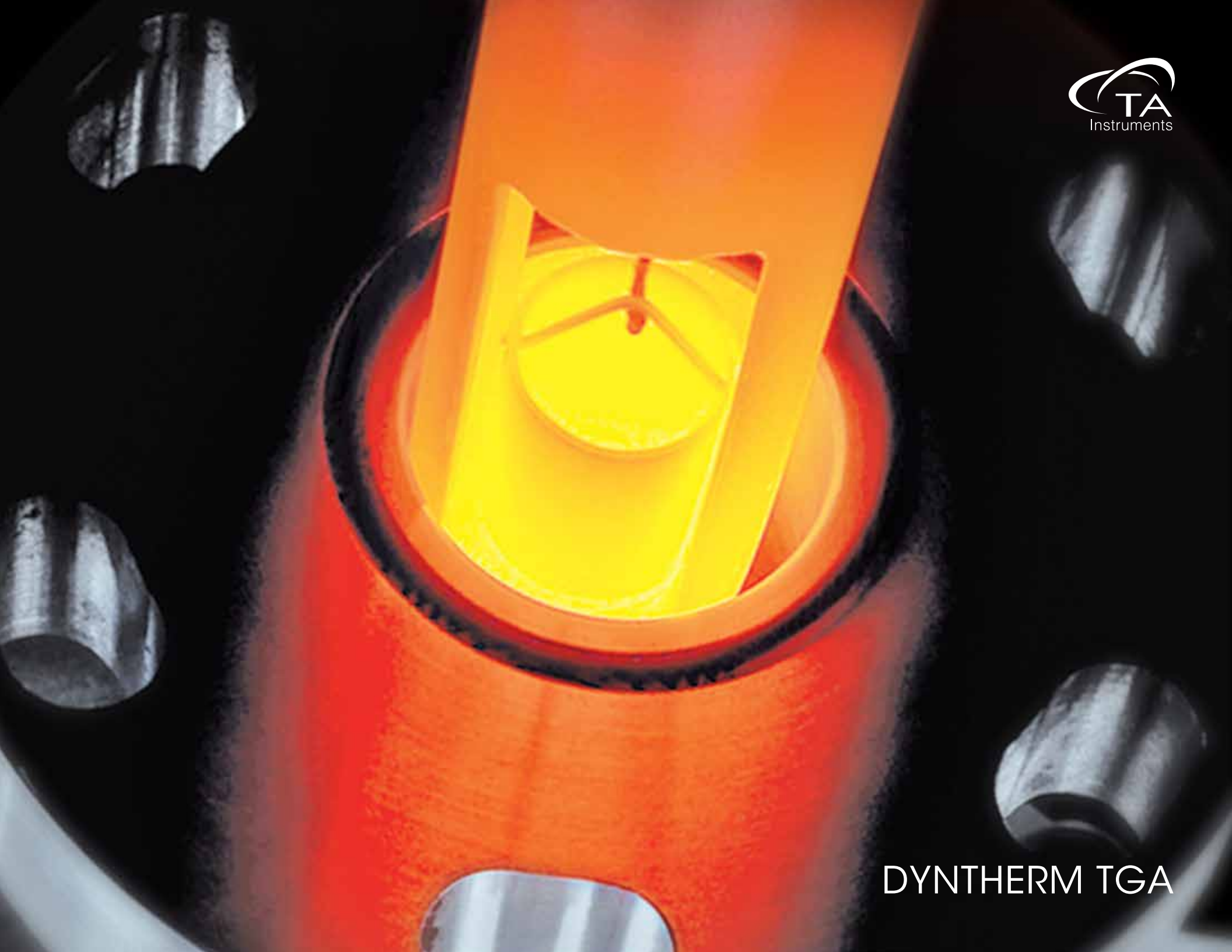

TA
Instruments
DYNTHERM TGA

TGA
INSTRUMENTS **with** MAGNETIC **Suspension** BALANCE

High Pressure

High Temperature

Corrosion Resistant

DYNTHERM | TGA

The DynTHERM TGA is an advanced gravimetric instrument for high temperature and high pressure thermogravimetric analysis. At the heart of every Rubotherm instrument is the patented* Magnetic Suspension Balance, MSB.

The incorporated flexible gas & vapor dosing and blending devices with pressure controller provide accurate control of the composition and the pressure of the reaction atmosphere in the DynTHERM.

Designed and build with more than 20 years of experience and proven by hundreds of customers applying Rubotherm Series instruments the DynTHERM provide reliability, robustness and most accurate results in the widest application range for TGA.

DynTHERM instruments are available in 14 different configuration to meet all experimental needs.

* German Patent no. 10 2009 009 204.8

Features and Benefits:

- Coal and Biomass Gasification by TGA measurements at high temperatures and high pressures with different gases and vapors
- Catalyst Testing by temperature programmed processes (TPx), sulphidation and coking
- High Temperature Corrosion Testing by contactless weighing in corrosive atmospheres and dri-Free
- Pyrolysis Processes at different temperatures and pressures
- Decomposition and Degrading Reactions of toxic substances and waste material
- CVD Coating Processes even with aggressive chemicals
- O2 and H2 Getter Material Testing for chemical looping application

FPO

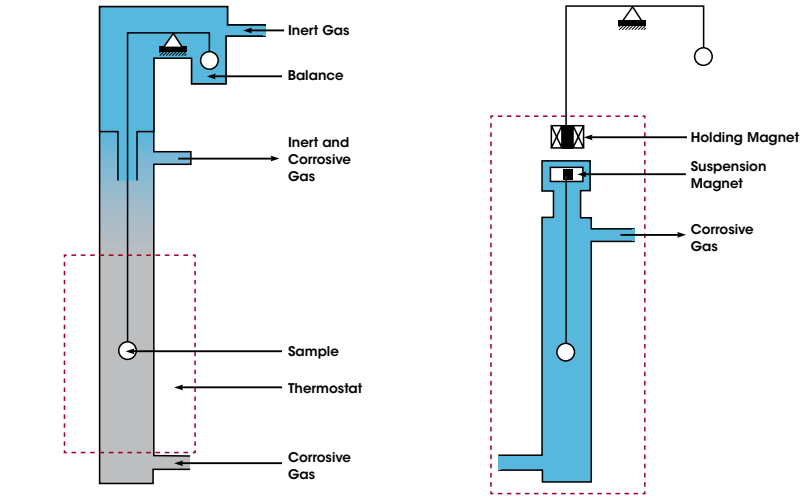
DynTHERM TGA

Advantages of Magnetic Suspension Balance

Every Rubotherm Series instrument is equipped with the patented Magnetic Suspension Balance, MSB.The unique MSB offers features which are beneficial for accurate gravimetric measurements under application relevant conditions: high pressure, high temperature, and using corrosive or condensable reaction atmospheres.

Feature	MSB	Conv. TGA	Benefit
Separation of balance form reaction atmosphere	Yes	No	BCorrosive, toxic and explosive reaction gases can be used in MSB
Balance heated to 200°C	Yes	No	Vapor / Steam can be introduced without condensation
Internal volume	Small	Larger	Evacuation to low vacuum and application of high pressure
Decoupling sample from balance during measurement	Yes	No	Correction of the base line drift of the balance, excellent long term stability
Automatic calibration of balance (during measurement)	Yes	No	Highest weighing accuracy throughout the whole measurement
Sample mass and volume	High	Samll	Big samples can be used without cutting / grinding
Weighing range	High	Samll	Large weight changes can be measured

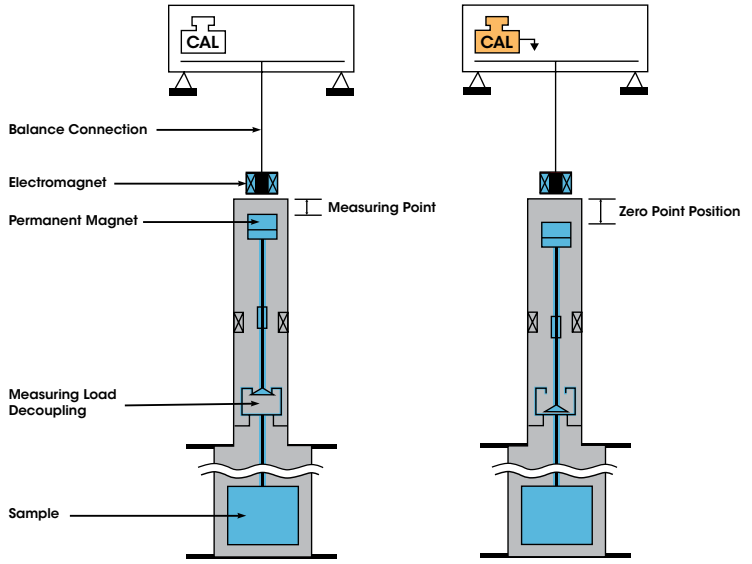
Gravimetric Measurements in Controlled Atmospheres



Conventional Measuring Instrument

Magnetic Suspension Balance

Automatic Decoupling of the Measuring Load by the Suspension Coupling for Taring and Calibration of the Balance



Measuring

Taring and Calibration

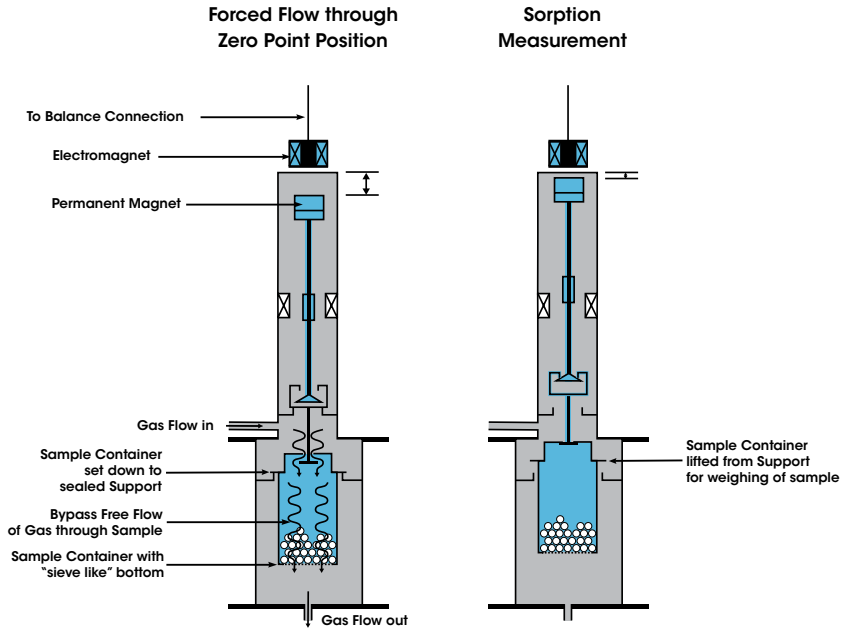
Weight changes of bulk materials in forced gas flow through

For applications which require enforced flow of reaction gas through sample material bed.

The sample container is set down on a by-pass free support in the zero point position of the MSB. The reaction gas flow must pass through the sample and leaves container through "sieve like" bottom. The sample is weighed in certain time intervals by lifting up the sample container with the MSB.

With this feature real process conditions of a sample material in a bulk reactor can be mimicked in a TGA.

Available for the DynTHERM TGA (750-50, F-G and F-G+V) models.



DynTHERM | TITLE?

Advanced Reactor Design for optimal Sample Temperature Control

The DynTHERM TGA instruments are equipped with low or high pressure sample cells with electrical heaters for accurate temperature control under all pressure and gas flow conditions.

Cold wall reactor design

Installation of the electrical heater into a pressure vessel – the cold wall reactor setup – allows to use only corrosion resistant ceramics materials in the high temperature zone. The cold wall heaters can be applied using very corrosive reaction atmospheres in temperature range up to 1300°C* and at pressures up to 80 bar*.

Hot wall reactor design

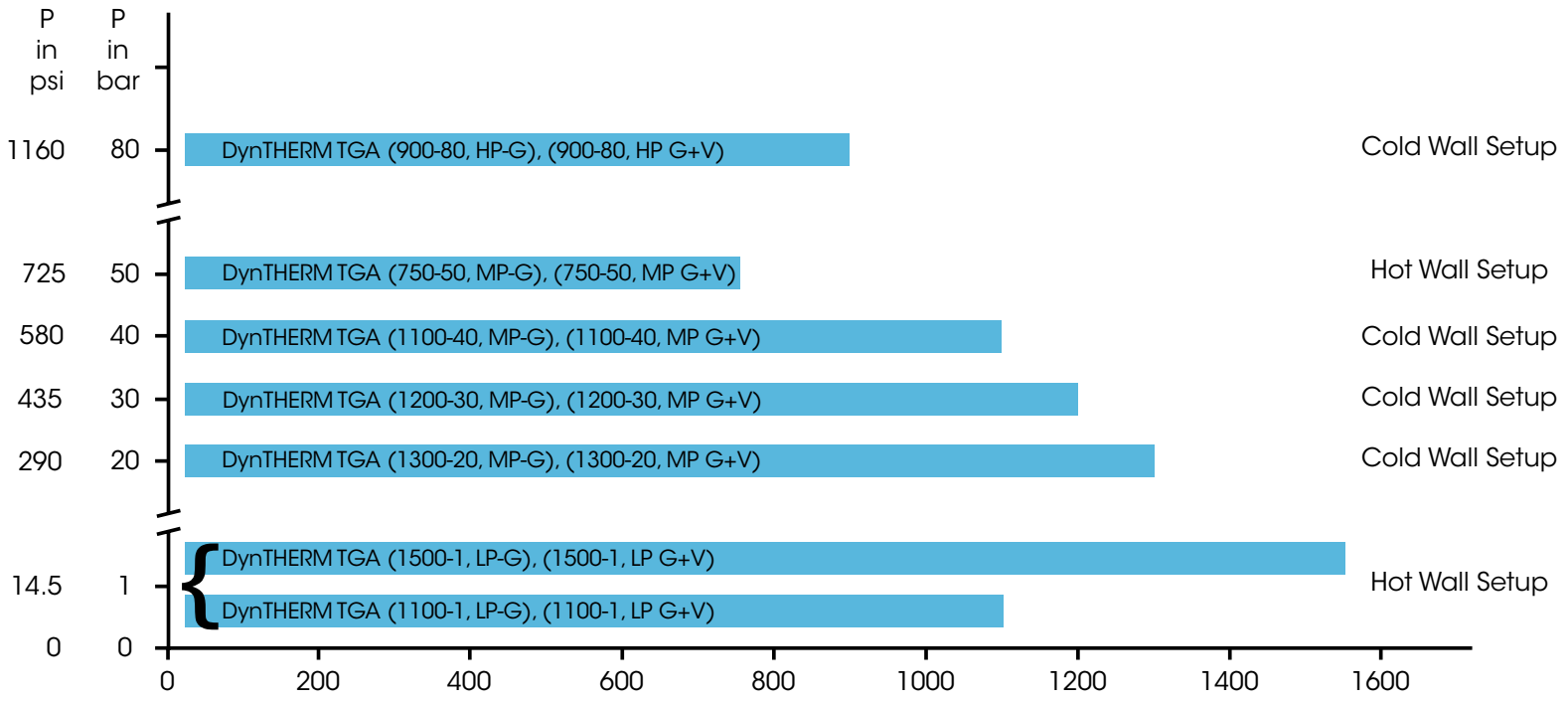
Hot wall reactors are sample cells made of temperature and corrosion resistant ceramics or special metal alloys. The temperature of the sample in the reactor is controlled by an outside electrical heater heating the sample through the wall. The hot wall reactors provide especially large temperature constant zones for measurements in the temperature range up to 1550°C* and at pressures up to 50 bar*.

Temperature control

Sample temperature is measured by a thermocouple directly adjacent to the sample. Furnace temperature and temperatures in other parts of the reactor are measured with additional thermocouples. A fast PID temperature controller realizes precise temperature control of the sample under all operating conditions.

* Specifications are model dependent

Different DynTHERM TGA versions are available. DynTHERM models for seven different temperature & pressure ranges can be configured either with a gas dosing or with gas and vapor (steam?) dosing system. The available P & T configurations are shown in the below diagram.



Gas Blending, Steam Dosing and Pressure Controlling Systems

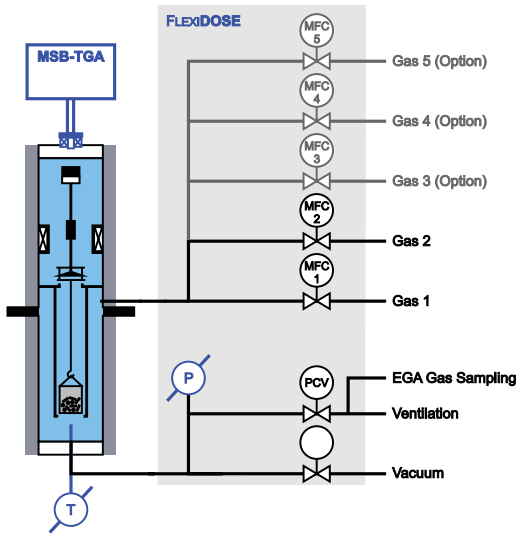
For achieving reliable results in thermogravimetry accurate control of the composition and the pressure of the reaction atmosphere in the TGA is essential. Sophisticated flexible gas and vapor dosing & blending systems with dynamic pressure controllers are applied for this purpose.

A flow of pure reaction gas, gas mixture or gas and vapor mixture with controlled composition is generated. It flows continuously through the reactor (sample cell?) of the connected TGA. The pressure of the flowing atmosphere is exactly controlled by means of a dynamic backpressure controller in the outlet flow.

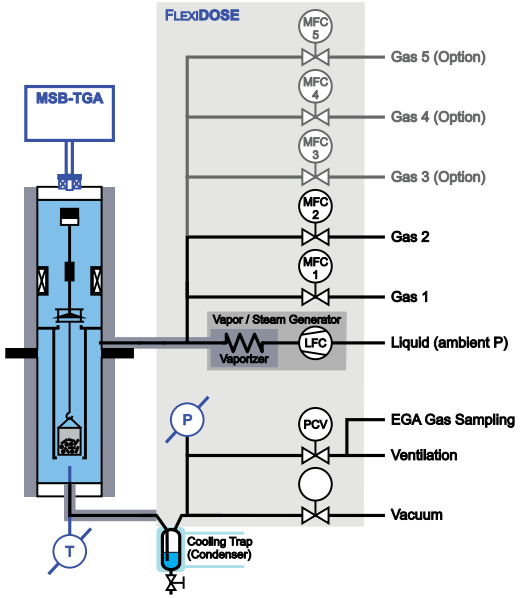
Dosing devices for different pressures and/or measuring fluids consist of the following main functional units:

- two mass flow controllers (MFC 1, MFC 2) for dosing pure gas or blending gas mixtures and dosing into the TGA reactor (more gas lines with MFCs can be added optionally)
- if equipped with vapor / steam generator: a liquid compressing and metering pump (LFC) for dosing a controlled flow of liquid into a vaporizer in which the steam is generated. The steam is then mixed with the gas flow(s) and flowing into the TGA reactor through heated transfer lines
- an accurate pressure sensor (P), a PID controller and pressure controlling valve (PCV) in the gas flow coming out of the TGA reactor for pressure control
- a gas sampling connection for evolved gas analysis

FlexiDOSE Gas Dosing System with Pressure Controller



FlexiDOSE Gas & Vapor Dosing System with Pressure Controller



Baseline Stability

In high pressure TGA baseline correction by subtraction of a blank run is a standard. This leads to very accurate results, if the measurement is sufficiently reproducible. The next diagram shows baseline stability and reproducibility for XYZ repeated heating cycles corrected by the same blank run. Drift of the corrected baseline during heating is minimal and an excellent reproducibility of ±0.XX mg is achieved.

Diagram 1: baseline stability during heating (will be generated)

Reference Material Testing – TGA Calibration

Calcium Oxalate is a known reference material for TGA. It decomposes with heating in three pronounced steps at known temperatures. Decomposition temperatures are only minimally affected by changing pressure of the gas phase.

If a high pressure TGA is working properly the decomposition of Ca-Oxalate will be detected under high pressure at the same temperature as at ambient pressure.

In the next diagram Ca-Oxalate decomposition at three different pressures are compared and demonstrate the excellent accuracy and reproducibility of the Rubotherm Series HP-TGA.

Diagram 2: Ca-Oxalate Decomposition at different pressures (will be generated)

Maybe third diagram 3: Reproducibility of Ca-Oxalate using different sample masses?

Application Example: Pyrolysis and Gasification

Coal, biomass, waste and other organic materials are gasified for energetic utilization or as alternative feedstock. Such processes can be measured under application relevant conditions in the DynTHERM high pressure TGA instruments with gas and steam dosing.

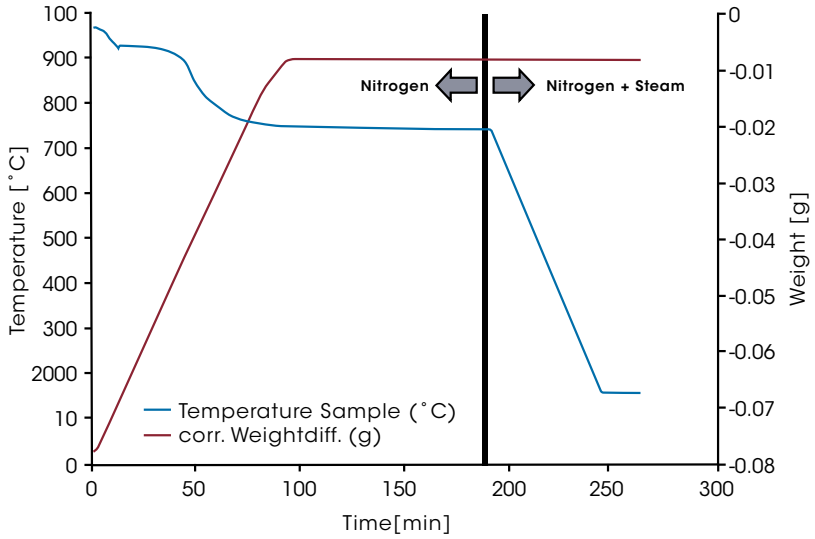
First step in gasification processes is pyrolysis of the raw material. When heating the organic material in a inert atmosphere (N2, Ar) volatile components are evaporated (water, hydrocarbons, tar) and char is generated from the raw material.

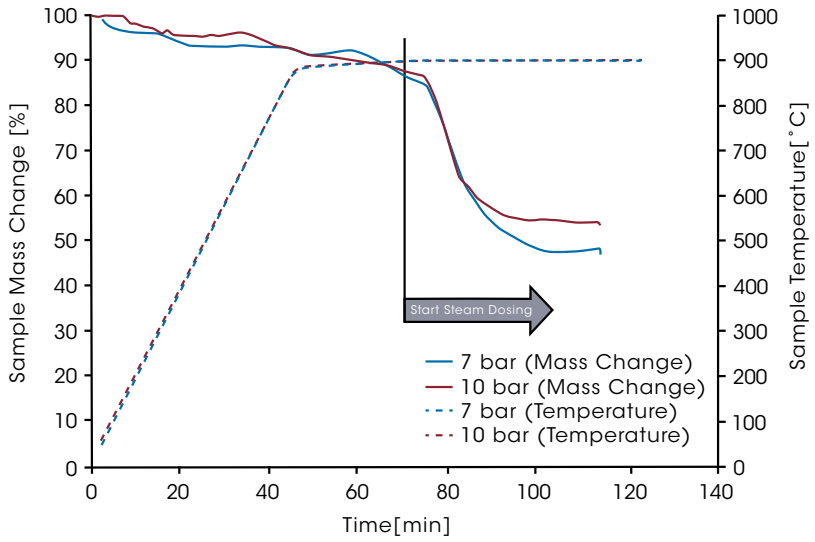
For gasifying this carbon-rich char a gasifying agent is required. Normally steam is used. The superheated steam and the carbon generate gases according to the below schematic main reaction:
H2O + C -> CO + H2

In parallel conversions and side reactions further product gases are generated:
mC + nH -> C_mH_n | CO + H_2O -> H_2 + CO_2 | CO + $3H_2$ -> CH_4 + H_2O

Depending on the reaction conditions and the raw material the kinetics of the process and the composition and the pressure of the generated gases vary.

DynTHERM instruments allow studying the optimal operating conditions for a given raw material – ideally equipped with a mass spectrometer for evolved gas analysis.
In the next diagram the kinetics of a pyrolysis and gasification process of charcoal at 900°C and 10 bar is displayed. In the right diagram the pyrolysis and gasification of a biomass (rice husk) is compared for 7 bar and 10 bar.





Application Example: Catalyst Coking

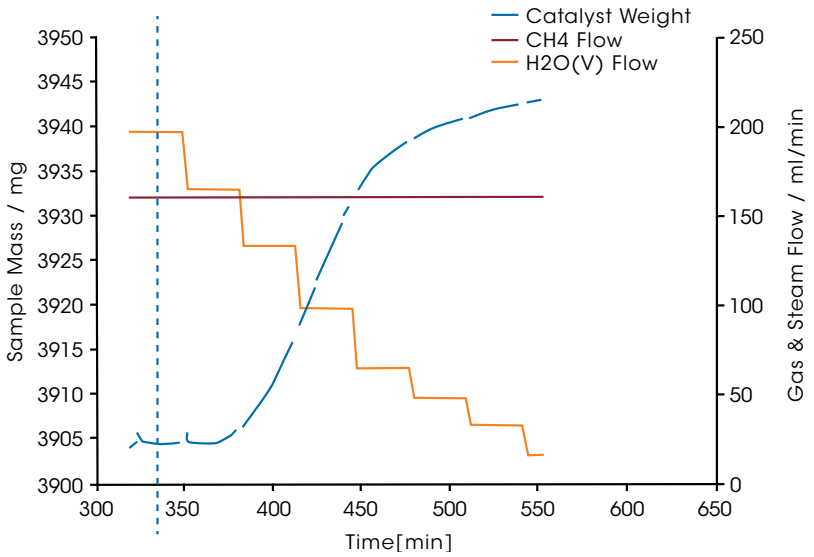
Catalyst deactivation due to coking is an unavoidable important technological and economic problem in petroleum refining and in the petrochemical industry. Coking occurs when hydro-carbon rich feed gases react with the catalyst and solid carbon deposits are build up on the surface of the catalyst. These carbon containing deposits can reach easily and quickly a level where they are disturbing the process by creating, for example, pressure drop problems or blocking off catalytic sites.

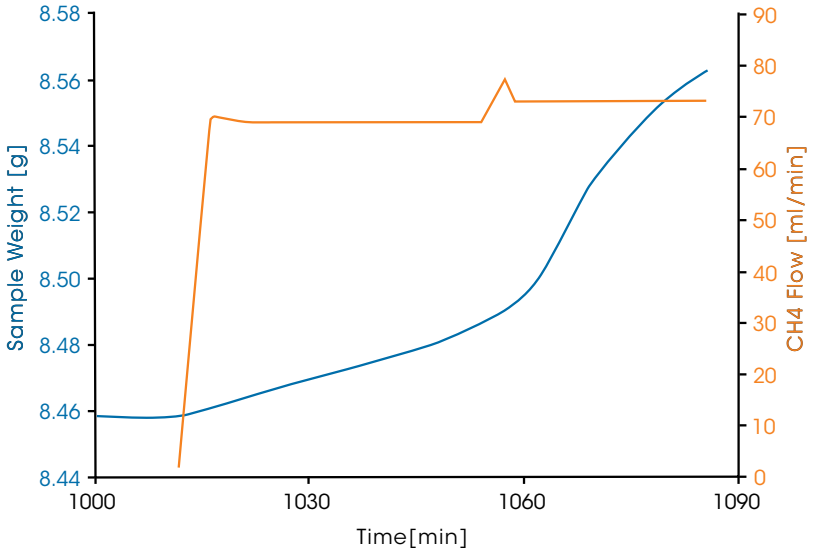
Methods to prevent or delay the catalyst deactivation are for instance the modification of catalyst surface composition and/or changing of the reaction environment (P, T, and feed gas composition). After deactivation a regeneration by burning off carbon residues may be an alternative.

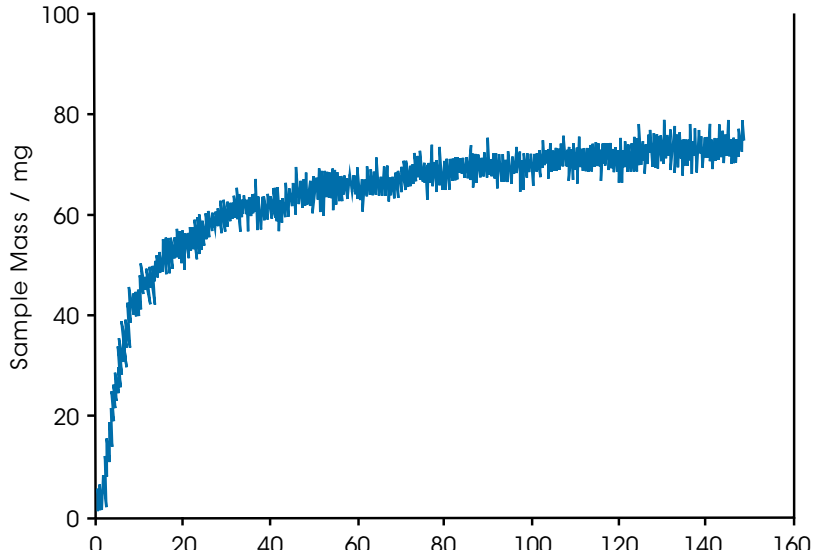
Process optimization of catalyst decay and/or regeneration is an engineering problem that requires a knowledge of the catalyst deactivation kinetic. DynTHERM instruments allow studying the weight of catalyst and the development of coking under realistic refinery operating conditions.

The left diagram shows the build up of coke on a catalyst material at 20 bar and 650°C in a mixture of CH4 and steam as reaction atmosphere. The stream partial pressure is reduced stepwise which leads to the mass increase of the catalyst material due to coke formation. The maximum specific coke deposition rate in mg per g of catalyst and second in this example is 0.32 mg g-1 s-1.

In the right diagram the starting of coking on a commercial catalyst at 700°C and 20 bar is measured in a steam / CH4 mixture at a CH4 flow of 70 ml/min. Following to the change of the CH4 feed gas flow to 73 ml/min the increased coking rate can be observed.







Application Example: Corrosion and Oxidation

Key to improvement for many technical processes and achieving increased efficiency is the corrosion resistance of the used materials. As an example the efficiency of gas or steam turbines and jet engines is directly related to their maximum operation temperature. The maximum temperature is limited by the high temperature corrosion of the used construction materials.

The DynTHERM TGA are corrosion resistant instruments able to measure with corrosive reaction atmospheres at high temperature. Depending on the tested material the sample size and mass are relatively big while the mass change caused by the corrosion very small. Additionally, high temperature corrosion is usually a slow process. Due to the patented MSB principle to tare and calibrate the balance during measurement long term corrosion studies can be carried out.

The next diagram shows the mass increase of a diamond coated titanium sample. The weight gain is caused by oxidation of the sample in pure O2 at 600 °C. The total mass change here is ca. 140 µg over 6 days.

Add'tl Diagram: corrosion of Inconel in air, TBP

Application Example: Chemical Looping

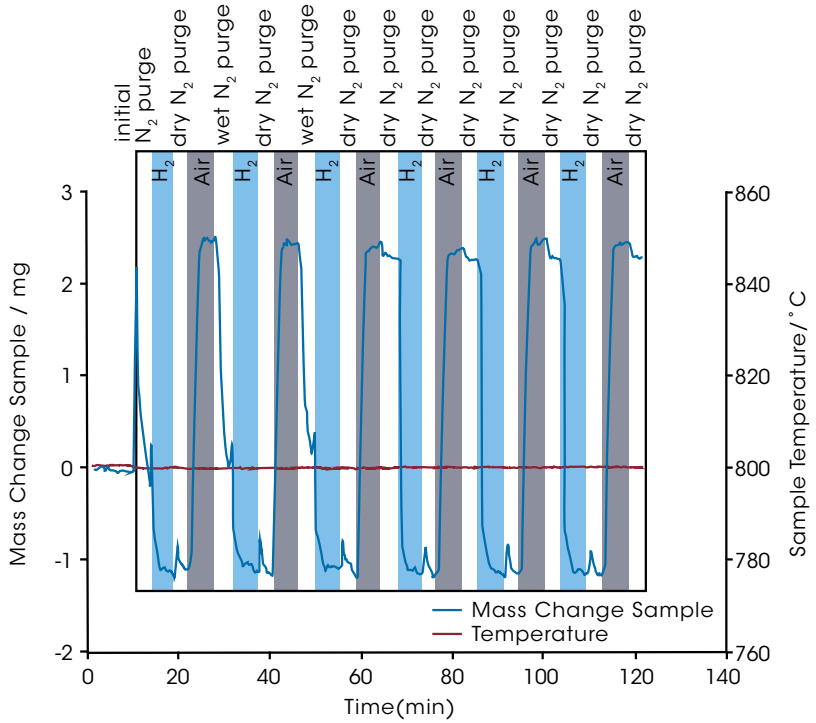
The combustion of fossil fuels in nearly pure oxygen, rather than air, presents an opportunity to simplify carbon dioxide capture in power plant applications. Chemical looping systems supply oxygen internal to the process, eliminating large capital and operating costs associated with pre-combustion oxygen generation. Chemical looping combustion (CLC) is considered a transformational technology with the potential to meet program cost and performance goals for CO2 reduced electricity generation from fossil fuels.

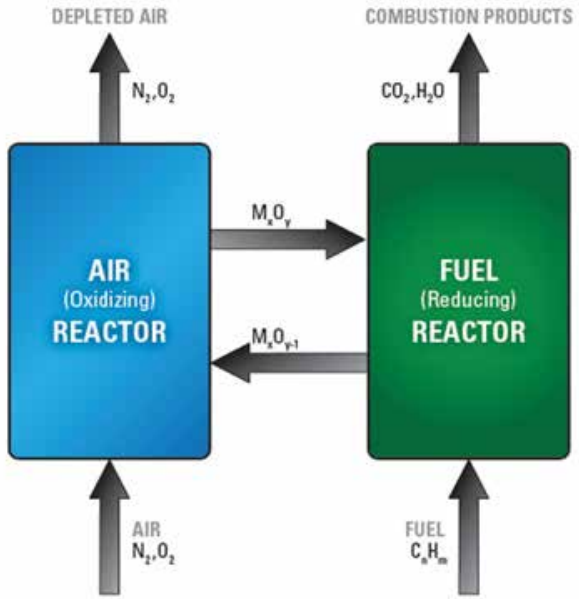
In CLC systems, oxygen is introduced to the system via oxidation-reduction cycling of an oxygen carrier material. The oxygen carrier is usually a solid, metal-based compound. For a typical CLC process, combustion is split into separate reduction and oxidation reactions in multiple reactors (please see below schematics). The metal oxide supplies oxygen for combustion and is reduced by the fuel in the fuel reactor, which is operated at elevated temperature.

This reaction can be exothermic or endothermic, depending on the fuel and the oxygen carrier. The combustion product from the fuel reactor is a highly concentrated CO2 and H2O stream that can be purified, compressed, and sent to storage or for beneficial use. The reduced oxygen carrier is then sent to the air reactor, also operated at elevated temperature, where it is regenerated to its oxidized state. The air reactor produces a hot spent air stream, which is used to produce steam to drive a turbine, generating power. Then the oxygen carrier is returned to the fuel reactor, re-starting the reduction-oxidation cycle.

Current CLC R&D efforts are focused on developing oxygen carrier materials with sufficient oxygen capacity and durability to withstand harsh CLC environments. DynTHERM instruments allow studying the weight of oxygen carrier materials under realistic operating conditions, including cycling the materials many times through oxidation and reduction cycles at high temperatures, high pressure, using oxygen rich and flammable (reducing) gas blends and steam.

The next diagram shows the result of cycling an oxygen carrier material at 10 bar and 800°C. The material is reduced in humidified H2 and oxidized in dry air. The weight changes recorded in the redox cycles are fairly constant and amount to ca. 9% of the sample weight.





Specifications

In the below table the key specification for 14 different Magnetic Suspension Balance equipped Rubotherm Series DynTHERM TGA models are summarized.

For all models operation under vacuum is possible. Gas dosing systems are equipped with two gas lines – each one with a separate MFC – as standard. Optionally more gas lines can be added to the dosing system.

Special optional feature of the models DynTHERM TGA (750-50, MP-G) and (750-50, MP-G+V) is the possibility of having a forced flow of the reaction atmosphere through the sample fixed bed. This is proven to be a extremely useful option for catalyst research since the real operating conditions of the catalyst sample can be realized in the DynTHERM.

DynTHEMRM TGA Model	Max. Sample Temperature	Max. Pressure	MSB Resolution / Weighing Range	Reaction Atmosphere	Sample Volume	FFT
1100-1, LP-G **1100-1, LP-G+V**	1100°C	atm		Gas Gas + Vapor	< 4 ml	
DynTHERM TGA (1550-1, LP-G) **DynTHERM TGA (1550-1, LP-G+V)**	1550°C	atm		Gas Gas + Vapor	< 4 ml	
DynTHERM TGA (750-50, MP-G)* **DynTHERM TGA (750-50, MP-G+V)***	750°C	50 bar		Gas Gas + Steam	< 0.5 ml	Yes
DynTHERM TGA (1100-40, MP-G) **DynTHERM TGA (1100-40, MP-G+V)**	1100°C	40 bar	10 mg / 25 g	Gas Gas + Steam	< 4 ml	
DynTHERM TGA (1200-30, LP-G) **DynTHERM TGA (1200-30, LP-G+V)**	1200°C	30 bar		Gas Gas + Steam	< 4 ml	
DynTHERM TGA (1300-20, LP-G) **DynTHERM TGA (1300-20, LP-G+V)**	1300°C	20 bar		Gas Gas + Steam	< 4 ml	
DynTHERM TGA (900-80, HP-G) **DynTHERM TGA (900-80, HP-G+V)**	900°C	80 bar		Gas Gas + Steam	< 0.5 ml	

Please consult you local TA technical sales representative to get further information about the Rubotherm SeriesDynTHERM TGA instruments.

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