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The CPA122 Reaction Calorimeter

ChemiSens
Reaction Calorimeter Systems

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OBJECTIVE

ChemiSens has been working in the field of reaction calorimetry for many years and is specialized in the field of reaction calorimetry where analytical precision is essential.
Based on our experience in precision calorimetric measurements our objective has been to offer reaction calorimeters based on the best measuring principles.
Our reaction calorimeters shows all the facilities that can be expected for process development combined with the versatility of handy laboratory reactors.

APPROACH

Reaction calorimetry is a well established technique within chemical engineering since many years. Traditionally, reaction calorimeters have been build as standard laboratory reactors with an add on of a few extra sensors and an electrical calibration heater.
ChemiSens reaction calorimeters are designed with all considerations to be a precision tool for analysing chemical processes.
The major output from experiments in a reaction calorimeter is the heat production rate, associated with the processes inside the reactor. The heat production curve is then the base for the calculations of a number of important parameters.
The technique to measure and the way to calculate the heat production rate is of utmost importance for the reliability of all related calculations and considerations.
ChemiSens CPA122 reaction calorimeter is designed and build in a way that makes it possible to precalibrate the instrument. The relation between the measured signals and the presented heat production rate is defined by parameters not influenced by properties of the reacting system.

RESULT

The engineering efforts have led to the construction of the CPA122 system. This system is designed for a wide use within the field of chemical engineering including small scale production under well defined conditions.

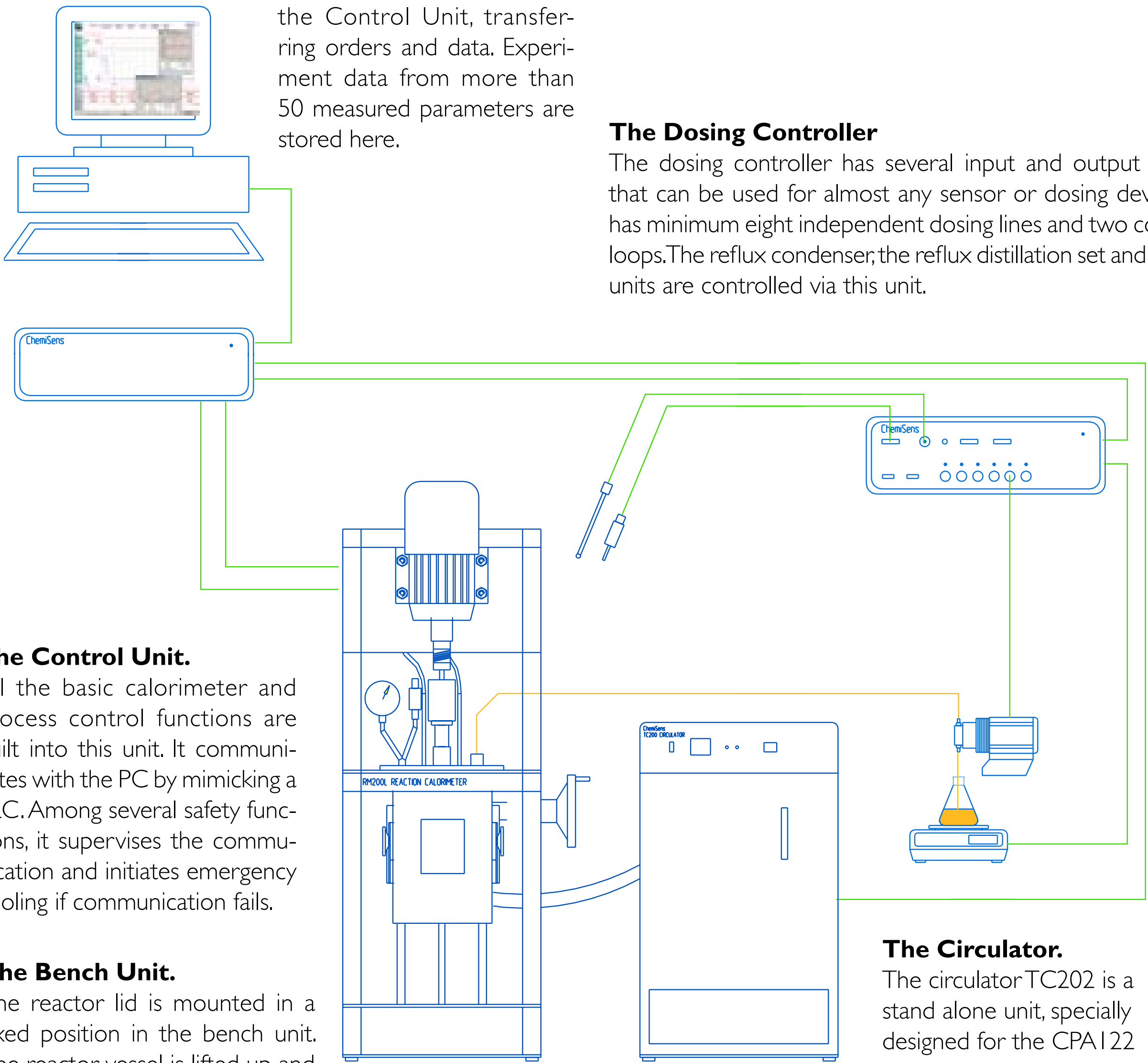
The CPA122 System

A Two Litres Work Horse.

The CPA122 is a complete laboratory reactor system; designed for engineering reaction calorimetry. The system philosophy is up to date process control.

The Operator Interface.

Control of the CPA122 system is via a dedicated application of the user-friendly Human Machine Interface "InTouch" (Wonderware, USA). The advanced, PC driven, software allows for manual as well as automatic experiments to be performed.



The PC

The PC communicates with the Control Unit, transferring orders and data. Experiment data from more than 50 measured parameters are stored here.

The Dosing Controller

The dosing controller has several input and output ports that can be used for almost any sensor or dosing device. It has minimum eight independent dosing lines and two control loops. The reflux condenser, the reflux distillation set and other units are controlled via this unit.

The Control Unit.

All the basic calorimeter and process control functions are built into this unit. It communicates with the PC by mimicking a PLC. Among several safety functions, it supervises the communication and initiates emergency cooling if communication fails.

The Bench Unit.

The reactor lid is mounted in a fixed position in the bench unit. The reactor vessel is lifted up and down with a built-in lifting device. The stirring motor is mounted on the bench unit in vertical position above the reactor. The bench unit is also prepared for the installation of a reflux condenser (optional equipment).

The Circulator.

The circulator TC202 is a stand alone unit, specially designed for the CPA122 system.

The Reactors.

Reactors for different pressure ranges are available. The reactor vessel has an outer insulation jacket that covers the heat balance measuring sensors and the jacket with its armature. The jacket has a helical baffle to improve the heat transfer. To support the calorimetric measurements the reactor lid is separately thermostated by the use of an electrical heating plate on top of the lid. All the reactors can be used with either a magnetic drive or a pressurised mechanical seal.

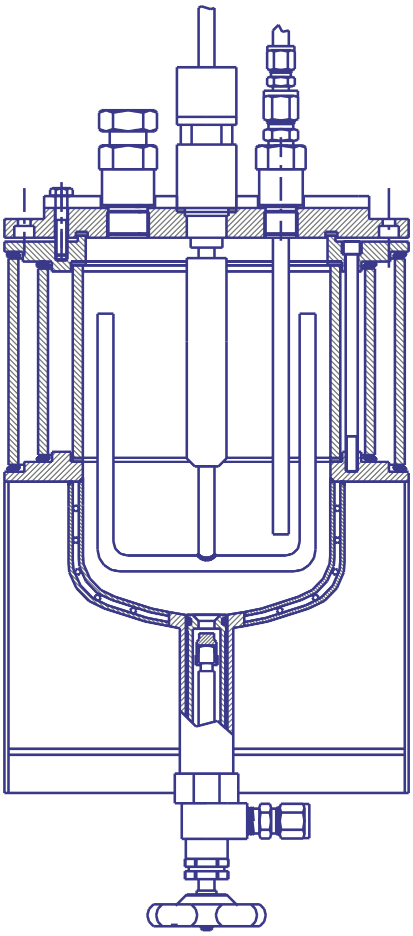
The CPA122 reactors

The CPA122 system includes a range of different reactors to cover pressures from vacuum to 100 bar and for temperatures up to 300 °C. The standard material for the reactors is 316 SS. A special reactor version has an interchangeable inner vessel combined with a separate thermostating jacket. The inner vessel can then be made of corrosion resistant material to meet special needs.

The reactor for ambient pressure operations has the midsection composed of coaxial glass cylinders to allow visual inspection of the reacting system. Only the lower part of this reactor is jacketed and used for the thermostating.
All reactors have an outer insulation jacket that covers the heat balance measuring sensors and armature. A drain port in all vessels allows for the installation of a special valve with no dead volume.

To support calorimetric measurements and prevent from internal reflux the reactor lid is separately thermostated to the same temperature as the reactor content. An electrical heating plate on top of the lid is used for this purpose.

Tantalum plated lid - 25 bars reactor - with the lid heating plate installed.



Ambient pressure reactor with base port drain valve.

All reactors can be used with either a magnetic drive or a pressurised mechanical seal. The mechanical seal supports a higher torque than can be used with the magnetic drive.

The reactor lid has five ports for armature and dosing. The temperature sensor and the safety armature as relief valve/bursting disk, pressure gauge and pressure transducer always occupy two of these ports. The remaining three ports are free for dosing, internal cooling coil for cooling boost and eventually the calibration heater. The heat balance principle supports that the system calibration can be carried out at any time and with any system in the reactor. The calibration heater does not then have to be installed during the real experiment. The size for the dosing/armature ports for all pressure reactors is NPT "3/8" female. The free inner diameter is 10.5 mm. The glass-jacketed reactor for ambient pressure has one of the ports with larger diameter NPT "1/2". This port can be used for a reflux condenser or for dosing of solid materials.

All types of reactors are easily installed to the CPA122 bench unit. The reactors are mounted to the bench unit via the lid. Lowering down the vessel from the fixed lid opens them. A build in lifting device supports this operation.

All reactors fulfil the adequate EU regulatory standards.

Reactor lid installed in the bench unit. Pressurised shaft seal with armature shown.

The reactor stirring

Three types of stirrers are used as standard equipment, anchor, turbine and propeller. The stirring speed is controlled in a closed loop and ranges from 50 to 2000 rpm. It can be constant or follow any profile. The stirring power can be measured by direct torque measurements with the optional torque transducer.

For more intensive mixing the reactor accepts the installation of a an baffle.

Auxiliaries

The versatile CPA122 reactor accepts the installation of a number of different auxiliary devices.
Fixed catalyst basket.
Base port drain valve with no dead volume.
Multi-dosing head for lid ports. Used for non-mixed dosing of three components through the same port.
Multi-dosing head for base port. Used for sampling or dosing of three non-mixed components.
Baffle for more intensive stirring.

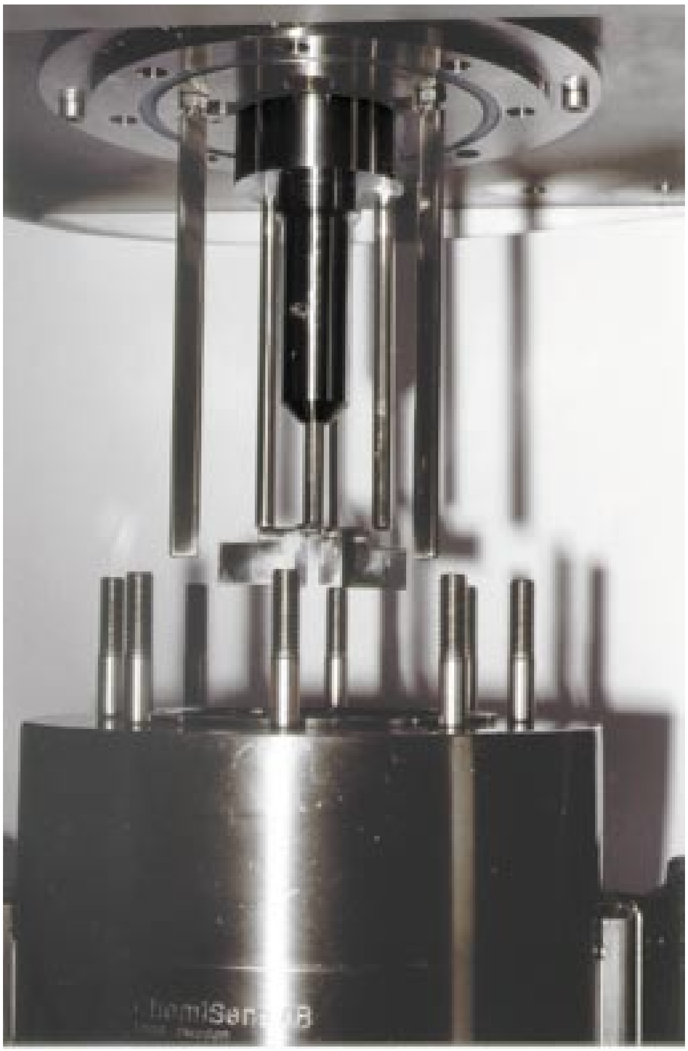
The torque transducer.

Reactors with magnetic drive can be used with a torque transducer placed outside the reactor vessel. The friction losses in the magnetic drive are small and can be corrected for.

Reactors with a mechanical shaft seal require a torque transducer that is placed inside the reactor vessel and below the shaft seal.

The correct torque will then be measured, since no friction losses in the shaft seal will be included.

A change in the stirring power might reflect a change in the viscosity or it indicates an unstable system, the beginning of reactor wall fouling or particle agglomeration etc.



Internal torque transducer with turbine stirrer mounted. Three baffles are also installed in the reactor lid.

Standard stirrer set made from 316 SS.

Base port drain valve with no dead volume.

The torque transducer.
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The calorimetric measurement.
The CPA122 reactor is designed to measure according to the heat balance. During operation adjusting the temperature of the media that passes the reactor jacket controls the temperature of the reactor. The temperature difference that arises between the reactor content and the media in the jacket is the driving potential for the heat flow from or into the reactor. This heat flow power can be expressed:

HF power = U∗A∗(Tr-Tj)

where UxA is the product of the total heat transfer coefficient U and the wetted area A inside the reactor. The value for U is an experimental parameter, it changes during the reaction and at different stirring intensity. This fact is the major drawback of the heat flow technique. In the CPA122 system this temperature difference (Tr-Tj) is available as a measured parameter but is used for power calculations only as an option.

All the heat transported out from the reactor will leave via the thermostating media passing the reactor jacket. A heat balance equation between the outlet and inlet of the thermostating jacket gives:

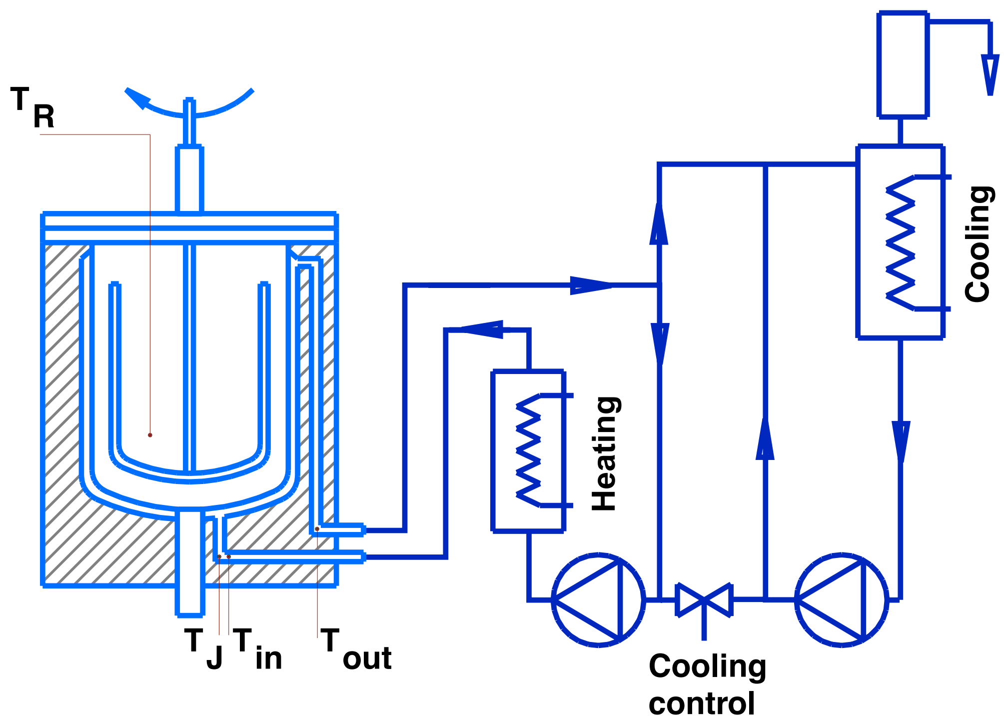
HB power = dM/dt∗Cp∗(Tout – Tin)

In this equation (Tout – Tin) is the measured temperature difference between the outlet and inlet of the thermostating media to the reactor jacket. The flow rate - dM/dt - and the heat capacity - Cp - are system properties of the CPA122. They just refer to the flow rate and the heat capacity of the used thermostating media. By knowing their values at each operating temperature the thermal power from the process can be directly calculated from the measured temperature difference.

Both the flow rate and the heat capacity are best determined through calibration experiments where known electrical power is generated inside the reactor. From the response in the temperature difference (Tout – Tin) a value for the product is calculated. These calibration experiments can be made at any time and with any media in the reactor.

During the ongoing process in the reactor the CPA122 system uses the calibration data from file to calculate the power. This power is continuously presented.

The possibility to calibrate in advance will significantly reduce the time consumption of most experiments and the measuring principle - heat balance - will eliminate most of the work and errors in the data evaluation.



The thermal modes

The CPA122 can be run in different "thermal modes", i.e. isothermal, isoperibolic, temperature scanning and set new temperature.

In the isothermal mode the reactor operates at the temperature set point. The cascade PID/PID temperature control gives no proportional offset at steady state.

Isoperibolic mode means that the temperature set point refers to the reactor jacket temperature.

The temperature scanning means that the reactor temperature is increased or decreased linearly. The maximum scan rate is +/- 6 deg/min.

Set new temperature means the highest heating or cooling to reach the temperature set point of the instrument.

During any thermal mode all safety measures are active. If the "Maximum temperature" set value is reached the system starts cooling down to the set minimum (safety) temperature for the system.

Dosing of chemicals

Dosing of chemicals to the reaction calorimeter during the course of a reaction is very essential. Dosing normally means a thermal disturbance. Depending of the reactor temperature the disturbance might be endothermic or exothermic. Special dosing armature is available where the inlet temperature of the dosing stream is measured. This temperature is then multiplied with the heat capacity and the dosing flow-rate to give a correction term. This correction is used in the post data treatment.

The CPA122 reactor accepts a number of simultaneous dosing, solid material, liquid as well as gas. The dosing can reach the reacting system either via the gas phase or directly into the liquid phase. All kind of dosing controlled by the CPA122 system is handled by the dosing controller VRC202.

Reactor CPA122 for 60 bar pressure. Two open lid ports for dosing armature. Third open port for safety armature

Dosing head for lid ports. Three non-mixed dosing lines enter through the same port.

Dosing head for reactor base port. Used for non-mixed dosing into the liquid phase and /or sampling from the liquid phase.

Other parameters to be measured.

The reaction data from the calorimetric measurements very often need to be complemented with auxiliary parameters as pH, pressure, spectrophotometric measurements etc.
Optionally one lid port can be ordered with angular entrance to support the installation of special probes.

Optional reactor materials

The standard material for the CPA122 pressure reactors is stainless steel 316. Many reacting systems require more corrosive resistant reactor material than 316 SS.
The CPA122 reactor for 25 bars is therefore also available in a special version with an interchangeable inner vessel. This type of vessel can be made from tantalum plated stainless steel or from a corrosive resistant material or alloy. Tantalum has a corrosion resistance close to that of glass.

Ph measurement

Pressure resistant glass- and reference electrodes for pH measurements. Special installation armature support the use of the same lid port for both an electrode and as an dosing port.

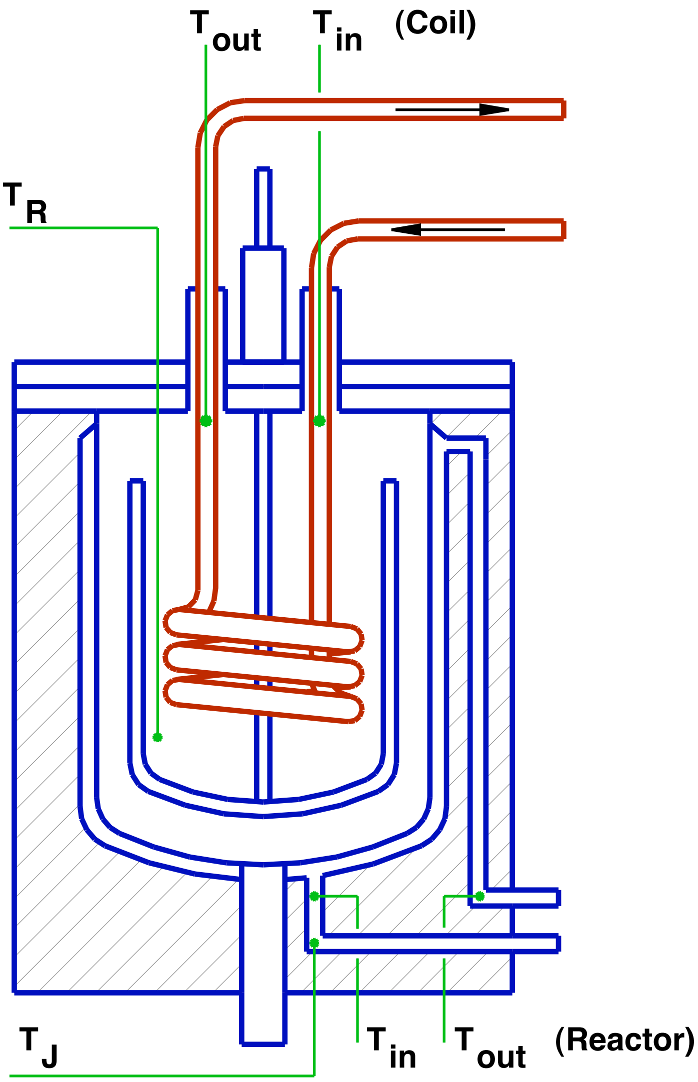
Reactor inner vessel - Tantalum plated - for pressures up to 25 bars.

Stirrer set made from Tantalum for use in corrosive media

Cooling power boost.

For special applications, where the cooling capacity of the standard reactor is insufficient,
there is the possibility to add on an internal cooling coil for increased cooling power.
The power measurement on the additional cooling coil is based on the heat balance principle. The flow rate of the media through the cooling coil is controlled by the CPA122 system to achieve the required add-on cooling power boost.
The total reactor power is then composed of two independent power measurements, i.e. from the build in heat balance measurement of the reactor and the contribution from the heat balance measurements on the cooling coil.

Power = dm/dt*Cp*(T(out)-T(in))



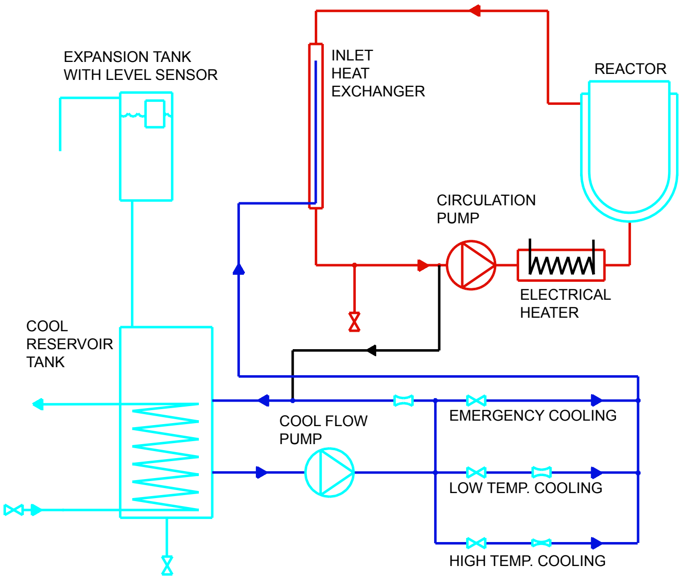
Schematic figure showing the internal cooling coil

The internal cooling coil.

The circulator TC202

This is a specially designed circulator for use with the CPA122 system. The primary circuit of the circulator only holds a small amount of liquid to achieve fast heating and cooling response. An electrical heater is operating directly in the circuit while cooling is based on a controlled inlet of cold liquid from a separate cooling reservoir. The circulator must be located very close the CPA122 bench unit.

The TC202 needs an external cooling source. For reactor temperatures above around 50 °C it might be process water. At lower temperatures a refrigerating system is required.



Schematic figure of the TC202 circulator.

The TC202 operating principle

The primary flow circuit is drawn with red lines. The secondary flow circuit is drawn with blue lines.
The only exposure of thermostating liquid against the air is via the free liquid surface in the expansion tank. The temperature in the expansion tank is close to the room temperature. The primary circuit is always completely filled. Any cold liquid pumped into this circuit will press out the corresponding amount to the cooling reservoir tank.
The heat exchanger arrangement is used to give a smooth and even cooling power. The cold liquid flow into the primary circuit is controlled via one of three different valves, i.e. the emergency cooling valve, the low temp. valve or the high temp. valve. The emergency cooling valve has an unrestricted flow while the two later valves have restricted flows.

The bench unit.

The bench unit holds the stirring motor in a vertical position above the reactor. Lowering down the vessel opens the reactor. A manually operated lifting device that is build into the bench unit supports this operation.
A separate wall mounted cabinet holds the frequency inverter and some associated components for the stirring motor control.
The bench unit is also prepared for the installation of a reflux condenser (optional equipment).

The bench unit with the 25 bars reactor.

The TC202 circulator.

The control unit

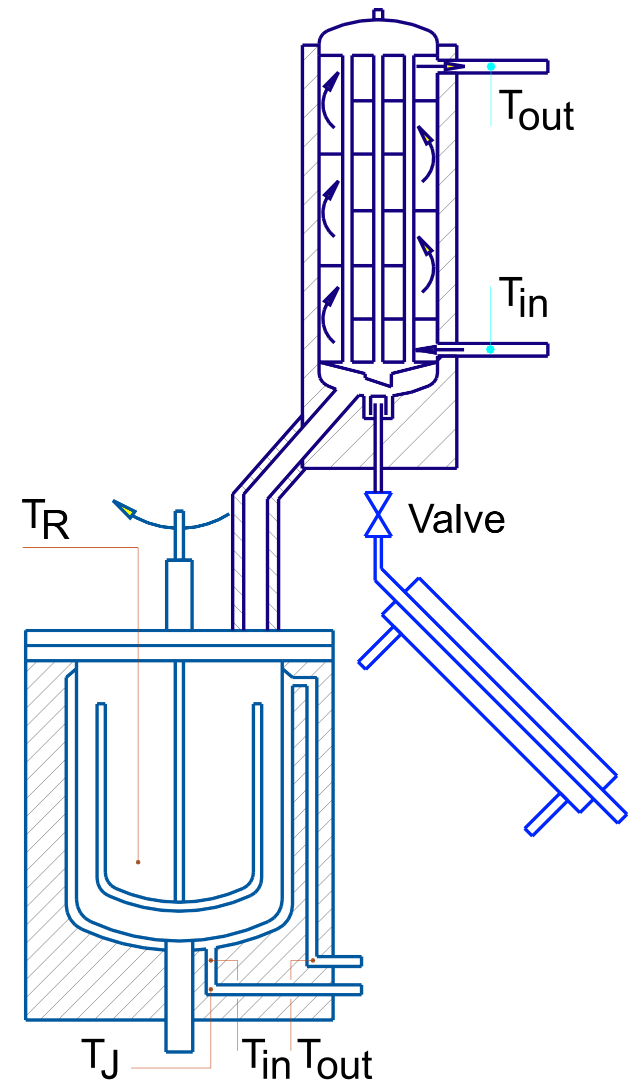
This is the interface between the operators PC and the calorimetric system and all its facilities.

It is a stand-alone unit to be placed at a distance up to 10 metres from the thermostating unit and the reactor. The unit holds all the interfacing electronics with its distributed computer system. The safety measures and the control loops and control functions that are time critical for the total system performance are located to the control unit.

It is a "black box", the only operator control is the power on/off switch. All cable connectors are located to the rear panel. A separate "panic button," to be placed at a distance from the control unit, can be pressed by the operator at any time to instantly activate emergency cooling.

Reflux/distillation

The CPA122 system also includes a reflux/distillation set for ambient pressure operation. The condenser is made from 316 SS and holds seven parallel tubes for high cooling efficiency. The total heat transfer area is 0.12 square meter. The condensation power is measured according to the heat balance technique. To compensate for heat-losses the condenser also includes separate sensors to measure the heat flow through the insulation of the condenser.



Schematic drawing of the tubular reflux condenser with Heat Balance measurement.

The schematic drawing illustrates the installation of the reflux condenser and the final cooler on the CPA122 reactor. In the lower section of the condenser the liquid split section is located. The condensed liquid can be split to any fraction between full distillation and full reflux. The valve controls this. A closed valve means that all the condensed liquid will return to the reactor while an open valve means that all condensed liquid will leave via the vapour trap. The power from the condenser is calculated according to the equation

Power = dm/dt*Cp*(T(out)-T(in))

where

dm/dt	=	**Flow rate of cooling media through the condenser.**
Cp	=	**Heat capacity of cooling media**
(Tout-Tin)	=	**Measured temperature difference**

The dosing controller VRC202

All type of dosing controlled by the system is handled via the VRC202. This is a dosing controller to be installed between the CPA122 control unit and almost any type of dosing device, pumps, valves, gas flow regulators etc. If balances are installed closed loop dosing can be used. VRC202 can besides these dosing lines also handle dosing from six other dosing lines, if precalibrated pumps are used.

The VRC202 is also used when auxiliary sensors as pressure, pH, gas flow meters, etc are needed. The versatility of the VRC202 can optionally be further increased by the installation of modules for control of additional specific pumps, reflux condenser, reflux/distillation set, etc.

Safety measures.

The CPA122 system is build to ensure high operator safety during all operational conditions.
The system includes both software controlled and hardware controlled safety functions. The basic idea is that the hardware functions are operating on a lower system level and can never be overruled by the computer system.

Maximum and minimum temperatures.

The operator must always specify the highest acceptable reactor temperature and the minimum temperature. The minimum temperature is a temperature that is considered as a safe temperature i.e. no reaction will take place.
If the reactor temperature during an experiment reaches the maximum temperature, the system will interrupt all dosing and use the maximum cooling power to reach the minimum temperature.

Hardware controlled maximum temperature.

This temperature is set directly on the circulator TC200 and refers to the temperature of the thermostating media. If this set temperature is exceeded, the heating is disabled and must be rearmed manually.

Watchdog.

A separate circuit – the watch dog – supervises the computer control of the CPA122 system.
If the communication between the CPA122 control unit and the operators PC is interrupted or the internal computer system in the control unit fails a hardware controlled emergency cooling is initiated.

Emergency cooling.

The operator always has direct access to the emergency cooling function by pressing a "panic button" which can be located at a convenient operator place.

Other parameters.

All measured parameters by the system can be used single or in any multiple combination to generate any action that is accessible by the present system configuration.

Internal safety measures.

All important internal functions of the system are also supervised and in case of critical failures automatically appropriate actions are taken.

Ex.:

- Reactor stirrer overload protection
- Supervision of thermostating media flow and level
- Protections against hazardous temperatures via separate circuits.
- Protection of calibration heater from internal over-heating
- Supervision of temperature sensor characteristics
- Supervision of critical electronic functions (A/D conversion etc.)
- Supervision of temperature of internal critical components
- Supervision of different dosing functions

Measured parameters.

The CPA122 system is run via a dedicated application of the InTouch software from Wonderware US. The ChemiSens application is called ChemiCall and offers some 50 measured parameters. All of the parameters are available on-line and most of them can be used on-line as test parameters for conditional jumps in automated, programmed experiments. The embedded graphic controller enables the possibility to manipulate any parameter to create user defined presentation of the result. All graphic captures, operator notes, events marks and event logs are stored for later use in the ChemiCall report generator. Raw-data can also be exported for use in spread sheet programs as well as the complete report can be exported to be included in other standard documents.

The Heat Balance power from the reactor
The stirring power (torque transducer)
The stirrer speed
The power from the internal cooling coil (opt. equipment)
The reactor temperature
The jacket temperature
The time derivative of the reactor temperature
The calibration power
The readings from two balances
The readings from two pH meters
The readings from two pressure transducers
The readings from four auxiliary sensors
The dosed amount of eight (or more) components.
The Heat Balance signal from the reflux condenser.
The control signal from two control loops.

CPA122 Technical specification

The reactor

Standard material:	Pressure reactors	316 SS
	Ambient pressure reactor	316 SS, Borosilicate glass, PTFE
Optional material:	Tantalum plated or corrosion resistant alloys for wetted parts.	
Total volume:	Two litres	
Useful volume:	0.3 to 1.8 litres. Less than 0.3 litre under special conditions.	
Pressure range:	Glass jacketed reactor	Vacuum to 0.05 Mpa or 0.5 bars.
	Metal jacketed reactors	Vacuum to 2.5 Mpa or 25 bars
		Vacuum to 6 Mpa or 60 bars
		Vacuum to 10 Mpa or 100 bars
	The given figures for pressure reactors refer to design pressures. Max. operating pressures are slightly lower.	
Fittings:	Lid fittings compatible with the Swagelok system.	
Thermal operating modes	Isothermal, isoperibolic, temperature scanning, temperature transport	
Measuring principle:	Heat Balance	
Temperature range:	Standard:	-20 °C to +250 °C
	Optional:	Extended down to -50 °C or up to +300 °C
Temperature resolution:	0.001 °C	
Temperature accuracy:	IEC 751 (1/3)	
Power measurements:	Baseline stability normal conditions	+/- 0.5 W (Absolute)
	Calorimetric sensitivity:	0.1 W
Calibration power:	Continuously 0 to 30 W. Resolution 0.01 W Accuracy min 99 %.	
Stirring speed:	Range 50 to 2000 rpm. Constant or any ramp.	
Max torque	Magnetic drive	1.5 Nm
	Mechanical shaft seal	2 Nm
Torque transducer:	Resolution:	0.04 Watt at 100 rpm.
		0.8 Watt at 2000 rpm.
	Max torque:	2 Nm

The bench unit

Physical dimensions:	Height	1250 mm (without reflux/dest. set)
	Width	400 mm
	Depth	400 mm

The circulator

Physical dimensions:	Height	700 mm
	Width	400 mm
	Depth	400 mm
Power:	Standard: 230 V AC 50 Hz, Max 11 A	

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