KEP Technologies

# OIL & GAS
## CHARACTERIZATION

## THERMAL ANALYSIS & CALORIMETRY SOLUTIONS

- GAS HYDRATES
- WAX APPEARANCE
- OIL & GAS SHALE
- CO2 CAPTURE AND SEQUESTRATION

setaram
KEP TECHNOLOGIES

## YOUR CHALLENGES

From the initial exploration phases to the delivery to the consumer, the oil and gas production process faces many challenges : technical challenges related to extraction, transportation, refining and delivery operations, but also environmental challenges linked to reducing greenhouse gas emissions.

## COMMON THERMAL ANALYSIS AND CALORIMETRY SOLUTIONS

This brochure presents some of our solutions in this field and we encourage you to contact us for more information.

Gas hydrates affect gas flow in pipelines at high pressure and low temperature. You can determine the stability of different gas hydrate + inhibitor systems thanks to DSC or calorimetry. High pressure and low temperature conditions are achievable with these techniques.

**Gas Hydrates**

Waxes affect gas flow in pipelines at high pressure and low temperature. You can determine the conditions of the appearance of waxes in these oils with DSC or calorimetry. Real-life high pressure and low temperature conditions are achievable with these techniques.

**Wax Appearance**

Carbon Capture & Sequestration processes aim at releasing less carbon dioxide into the environment. Most processes are based on the reversible sorption between the gas and a substrate. Characterizing the subtrate, which can be a solid or a liquid, is very important.

**CO Capture and Sequestration**

High pressure sorption analyzers can help estimating the natural gas (methane) content of a gas shale field. Simultaneous thermal analysis (STA) is used to study thermos-oxidative decomposition processes for the valorization of oil shale.

**Oil and Gas Shale**



## CUSTOMER TESTIMONIAL

*"Featuring the exclusive calvet three-dimensional sensor, the [MICROCALVET] microcalorimeter can be used for highly sensitive and precise calorimetric measurements. It is able to study samples in liquid, gel, powder and solid forms in both isothermal and temperature scanning mode, with the operating temperature from -45 to 120 °C […]. Gas tight high pressure cells and gas panel are specialized for gas hydrate application, which enable measurements with pressure up to 400 bar."*

**Linga lab, National University of Singapore**

*https://blog.nus.edu.sg/lingalab/facilities/*

## THE KEP TECHNOLOGIES ADVANTAGE

KEP Technologies is addressing it's offerings to the Oil & Gas market by making available the widest and most versatile choice of solutions. Now you can consult with one company, KEP Technologies, to address your challenges across the broadest number of battery studies on the market.

Each solution embodies our "Reimagine Material Characterization" value proposition by delivering the three core customer benefits of **Experimental Control, Instrument Versatility and Quality Results.**

We believe solutions that provide these benefits will deliver the highest value to our customers.

In addition to our core customer benefits, we are able to provide **customized solutions** by harnessing the engineering and project management of our highly skilled organization.




**CUSTOMIZED SOLUTIONS**

**Modular design allows for upgraded and tailored functionality**
**Access to all previous non-proprietary custom requests**
**Open access to our engineering development team**

## INSTRUMENT

### MICROCALVET


**HIGHEST HEAT MEASUREMENT ACCURACY**
Calvet 3D sensor based on Peltier elements with Joule effect calibration.

**MODIFIABLE TEMPERATURE CONDITIONS**
for increased flexibility and replication of real life conditions

**CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS**
to perform even the most demanding experiments using one instrument :
• high pressure (1000bar) and high vacuum, pressure measurement and control
• mixing experiment

**EXTERNAL COUPLING CAPABILITY**
Designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

## SPECIFICATIONS

| | |
|---|---|
| **Temperature range (°C)** | -45 to 120 |
| **Isothermal and temperature scanning (°C/min)** | 0.001 to 2 |
| **Pressure, measured and controlled (bar [psi])** | 400 [5,800]<br>1 000 [14,600] |
| **Cell and crucible volumes (ml)** | up to 1 |

**For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com**



## APPLICATION

### Characterization of gas hydrates formation dissociation using high pressure DSC

### INTRODUCTION

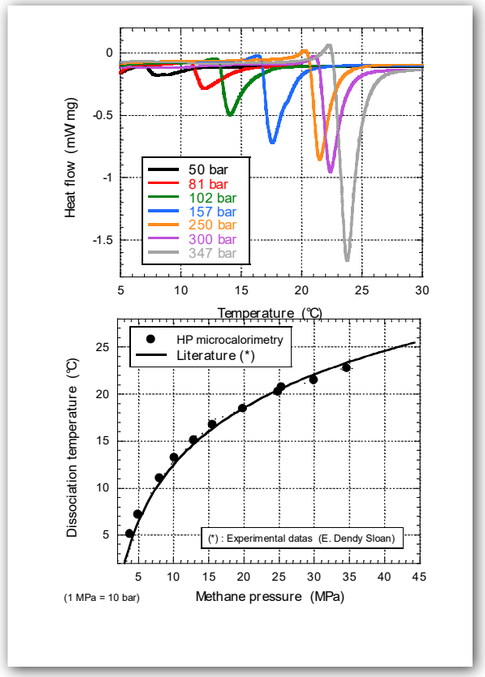
Calorimetry is a way to determine compositions, dissociation enthalpies and heat capacities of hydrates. In order to work under high pressure, an methodology (patent of the French Institute of Petroleum) has been developed using MICROCALVET up to high pressure to determine the thermodynamic properties and kinetics of gas hydrate formation. This technique allows the detection of phase transitions versus time, temperature and pressure.

### EXPERIMENT

MICROCALVET has a cell operating with a dedicated high pressure panel (FLEXI HP 1000) up to 1000 bar (14500 psi) and up to 120° C.
The high pressure microcalorimetry technique can be used to investigate gas hydrates in different situations
- formation of gas hydrates (especially methane)
- investigation of gas hydrates trapped in marine sediments
- plugging of annulars (offshore extraction) by hydrate formation in drilling muds
- storage and transportation of natural gas using gas hydrate
-gas hydrate formation and dissociation for cold storage

### RESULTS AND CONCLUSION

The charts below show methane hydrate dissociation after its formation in deionised water at different pressures of methane. The stability curve obtained from these data shows very good accordance with litterature.




*C. Dalmazzone et al., Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 165–172*

## INSTRUMENT

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Calvet 3D sensor based on Peltier elements with Joule effect calibration.

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## APPLICATION

### Effects of pressure on the Wax Appearance Temperature (WAT) of crude oils

### INTRODUCTION

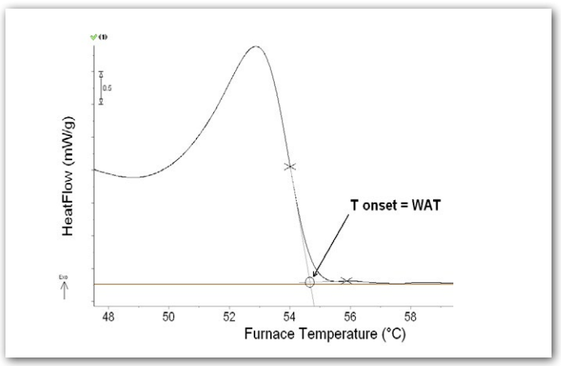
In the petroleum industry, waxes crystallization resulting from the precipitation of paraffins contained in oils, can occur in reservoirs, pipelines and process equipment. Many major issues can be related to these deposits, including a modification of the flow characteristics, a reduced production or even a blocked line in the worst cases. To evaluate the possible wax precipitation of a given fluid, the wax appearance temperature (WAT) has to be determined. It is defined as the temperature at which a crude oil first precipitates. Most of the studies about WAT are carried out under atmospheric pressure. However, WAT determination under experimental conditions close to real operating ones (particularly under pressure) is a key point to predict the crude oils behavior.

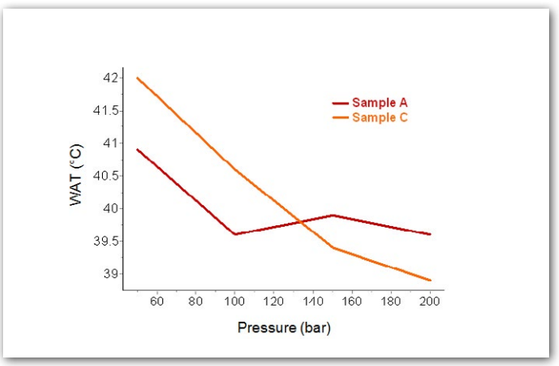
### EXPERIMENT

The high-pressure microcalorimetry analyses were carried out with the MICROCALVET, using two 330 µL Hastelloy C276 cells (sample and reference) designed to undergo pressures up to 400 bar. Two different crude oils, A and C, have been studied. They were preheated at 80°C for 1 hour to make sure waxes were solubilized. After cooling, about 100 mg of each sample were transfered to the MICROCALVETand analyzed using the following profile:
• heating from 30°C to 80°C and isotherm of 180 minutes at this temperature,
• cooling at 1°C/min until reaching a temperature of -10°C and isotherm of 15 minutes at this temperature
• heating at 1°C/min from -10°C to room temperature. The samples were pressurize under methane (99.995%)

### RESULTS AND CONCLUSION

Before pressurization, the experiments were run at amospheric conditions (1.01 bar). Two exothermic events were recorded for each sample during the cooling phase corresponding to two different paraffinic fractions that precipitate (high molar masses first then lower). The WAT, related to the first peak, was found at 44.6°C for the sample A and 44.2°C for the sample C.
Under methane, crystallization temperatures were reduced for both sample.
This tendency to see the WAT reduced under methane pressure was even more significant with the sample C. It can be explained by the fact that it contains a lower paraffin content and above all less linear paraffins above C34 than the sample A




*Lenise C. Vieira, Maria B. Buchuid, Elizabete F. Lucas, Effect of Pressure on the Crystallization of Crude Oil Waxes. Evaluation of Crude Oils and Condensate, Energy & Fuels (2009)*

## INSTRUMENT

### THEMYS TGA

**VARIETY OF ATMOSPHERE CONDITIONS**
multiple carrier and reactive gas options

**MODULAR ADAPTIONS ALLOWING**
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1750°C all in one instrument

**HIGH ACCURACY & VERSATILITY**
hang-down symmetrical beam balance, specifically designed for TGA applications

**EXTERNAL COUPLING CAPABILITY**
designed for evolved gas analyzers (FTIR, MS, GCMS, MS-FTIR,or FTIR-GCMS)

## SPECIFICATIONS

| | |
|---|---|
| **Temperature range (°C)** | room temperature to 1750 or to 2400 |
| **Isothermal and temperature scanning (°C/min)** | 0.01 to 100 |
| **Sample volume (µl)** | up to 2500 in TGA |
| **Optional protected DTA rods for enhanced corrosion resistance, tricouple DTA rods for enhanced sensitivity, protected tricouple for combined advantages** | |

**For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com**



## APPLICATIONS

### CO2 capture on aminated solid sorbents by thermogravimetry

## INTRODUCTION

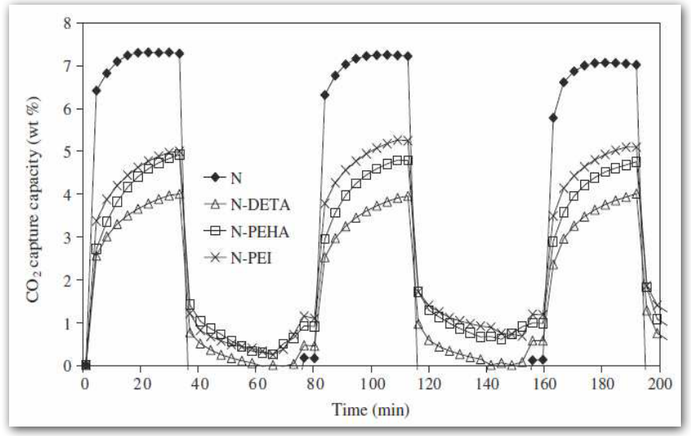
The leading contender for post-combustion carbon dioxide capture from coal-fired power plants is the use of amine solvents. Despite the advantages of solvent scrubbing, there are several disadvantages, especially the thermal efficiency losses due to the energy needed to regenerate the solvent by driving off the captured CO2. The use of solid sorbents impregnated with different amine solutions provides a new technological approach for CO2 capture with the absorption capacity of amines and the easy handling of solids without corrosion drawback. Thermogravimetry is very well adapted to investigate the adsorption and desorption performances of the sample and define the CO2 capture capacity of the corresponding aminated solid sorbents.

## EXPERIMENT

THEMYS TGA can be used for the investigation of the aminated solid sorbents. Commercial activated carbon Norit CGP Super (called N) is selected as the raw material. N is impregnated with different amine compounds: diethylentriamine (DETA), pentaethylenehexamine (PEHA) and polyethylenimine (PEI). Isothermal CO2 capture tests are run at 25 °C according to the Vacuum Swing Adsorption (VSA) technique. Each cycle includes a 30 min CO2 capture step followed by regeneration under vacuum for 30 min, and normal pressure recovery with an inert gas. The mass increase during the capture step is interpreted as the CO2 adsorption capacity of the solid sorbents.

## RESULTS AND CONCLUSION

While N reaches the plateau of maximum capture capacity in 20 min, the impregnated samples present a continual upward tendency for the 30 min of the capture step and attain no equilibrium capacity. Impregnation slows down the kinetics of the capture process, due to the diffusion of gaseous CO2 through the amine film. The CO2 capture capacities are also decreased after cycles 2 and 3. Impregnation with amines reduces the microporous volume of the activated carbon, thereby decreasing the capture capacity at room temperature.




*1- M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, Fuel 86 (2007) 2204–2212*

## INSTRUMENT

### GASPRO

**VARIETY OF MODES OF OPERATION**
ability to combine PCT, kinetics and cycle life modes to 200bar to determine the quantity and rate of sample gas interaction and its aging characteristics all in one instrument and operation

**PRECISION MEASUREMENT OF SMALL SAMPLES**
using the patented microdoser option to inject small doses of gas on the sample humidity controllers and gas panels.

**HIGH ACCURACY VERSION**
to reduce cumulative error across multiple measurements points

**EXTERNAL CALORIMETER COUPLING CAPABILITY**
to increase your research options

## SPECIFICATIONS

| | |
|---|---|
| **Temperature range (°C)** | -260 °C to 500 °C<br>with different sample holder options<br>Higher temperatures on request |
| **Calibrated reservoirs** | 5 high pressure calibrated volumes ranging from ~12 ml to ~1.2 l |
| **Sorption gas (Test gas)** | Carbon Dioxide, Methane, Nitrogen, Argon, Hydrogen, Deuterium, Helium, Neon, Ammonia, n-alcanes from C2 to C6, more on request. |
| **Operating pressure range** | From vacuum to 200 bar |
| **Sample pressure measurement** | 1 transducer for vacuum to 200 bar<br>Accuracy < 0.025% full scale<br>1 transducer for vacuum to 15 bar<br>Accuracy < 0.12% of the reading |
| **Maximum sensitivity** | 3 µmole of gas<br>(with the MicroDoser attachment) |

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## APPLICATION

### CO2 adsorption into zeolite 13X with GASPRO

### INTRODUCTION

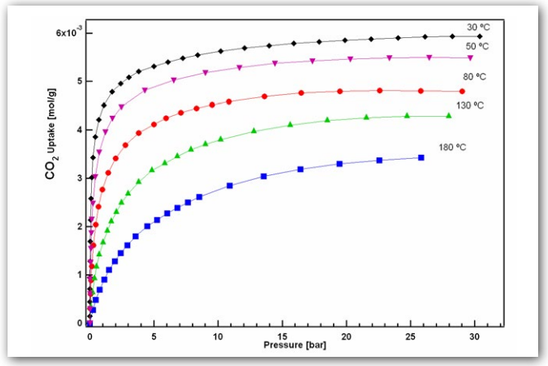
The rising level of CO2 in atmosphere has been linked to global warming. To mitigate the global warming, R&D is being directed towards understanding the relevant phenomena and foster innovation in the field of CO2 capture and sequestration (CCS). Due to their well-controlled pore structure and size, zeolites have been primary candidates in the gas separation (e.g. CO2 capture) in industry. Knowledge about the CO2 sorption properties of zeolites (adsorption capacity, pressure regimes and kinetics) is essential to the design of advanced materials capable of capturing CO2 in industrial settings. Among zeolites, 13X is known for its relatively high CO2 capacity. This application note highlights
precision measurements of the absorptive properties of a zeolite 13X over a wide range of temperatures.

### EXPERIMENT

CO2 adsorption into zeolite 13X was measured at various temperatures using a GASPRO Sievert's apparatus which was developed to study sorption of a variety of gases from vacuum up to 200 bar and from liquid He to 500 °C
Temperatures. Gas density temperature correction were done by measuring the apparent free gas volume at temperature.

### RESULTS AND CONCLUSION

The PCT isotherms for CO2 adsorption into zeolite 13X are shown in Figure 2. The zeolite capacity decreases with temperature reflecting the physisorption nature of the adsorption isotherms. The data are in good agreement with literature. For example, the CO2 capacity at 30 °C 20 bar is 5.7 moles/kg (5.0-6.4 moles/kg in the literature). The GASPRO is well-suited for the detailed characterization of materials used in CCS (adsorption of CO2 onto different solid sorbents). The ease of use and the temperature and pressure range are ideal for this type of materials application.




*R Siriwardane, M Shen, E Fisher, et al. NETL report,www.netl.doe.gov*

## INSTRUMENT

### THEMYS STA

**ACCURATE AND SENSITIVE ULTRA-HIGH TEMPERATURE**
heat flow measurement with Tri- Couple DTA technology

**ULTRA-HIGH TEMPERATURE CAPABILITY**
to 2400°C with a single furnace

**MODULAR ADAPTIONS ALLOWING**
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1750°C all in one instrument

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| **Sample volume (µl)** | up to 2500 in TGA |
| **Optional protected DTA rods for enhanced corrosion resistance, tricouple DTA rods for enhanced sensitivity, protected tricouple for combined advantages** | |

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## APPLICATIONS

### Thermooxidative decomposition of oil shales

## INTRODUCTION

Oil shales (OS) are sedimentary rocks with varying amounts of combustible organic matter in a mineral medium.
The quality of oil shale depends on the organic matter and mineral part amount and composition. They determine the possible applications of the shale as a raw material for chemical and/or power industry. The thermooxidative decomposition of oil shale samples in a thermal analyzer helps at determining these data.

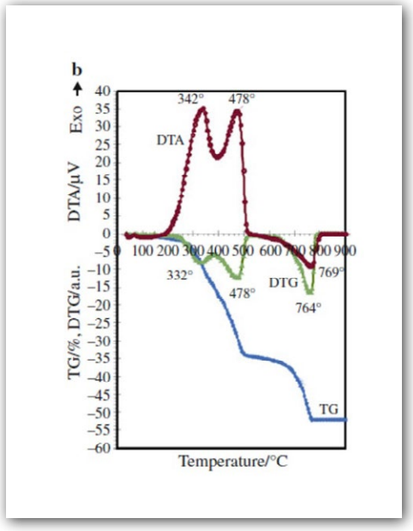
## EXPERIMENT

- 15±0.2 mg oil shale samples from Estonia, Jordan, Israel and Morocco
- THEMYS TG-DTA
- Heating rates from 1 to 20°C/min
- Coupled to a Nicolet 380 FTIR Spectrometer by a heated transfer line
- Atmosphere: 80% of Ar and 20% of O2

## RESULTS AND CONCLUSION

TG, DTG and DTA show:
- Emission of sorbed water 200–250°C (0.9–2.5% range)
- First, low temperature stage: exothermic thermooxidation of volatile organic compounds (exo)
- Mid temperature stage: exothermic thermooxidation of heavier organics
(kerogen) and fixed carbon as well as of pyrite (FeS2)
- High temperature: endothermic decomposition of carbonates

FTIR data show:
- Two major gaseous compounds, all fuels : CO2 and H2O
- All fuels, more minor gases: CO, acetic and formic acids, formaldehyde, acetaldehyde, ketones, SO2, ethane and chlorobenzene
- Israel and Morocco : emission of traces of ethylene, methanol and ethanol
- These differences can be explained by the differences in the content of organic matter




*Kaljuvee et al, J Therm Anal Calorim (2011) 105:395–403*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