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Visual and Raman spectroscopic observations using fused silica capillary reactor technique

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Outline

- ★ **Fused Silica Capillary Reactor (FSCR)**
- ★ **Measurement of solubilities in FSCR**
- ★ **Supercritical water oxidation in FSCR**
- ★ **Depolymerization of polyester**
- ★ **Determining the volume expansion**
- ★ **Summary**

FSCR?

What is

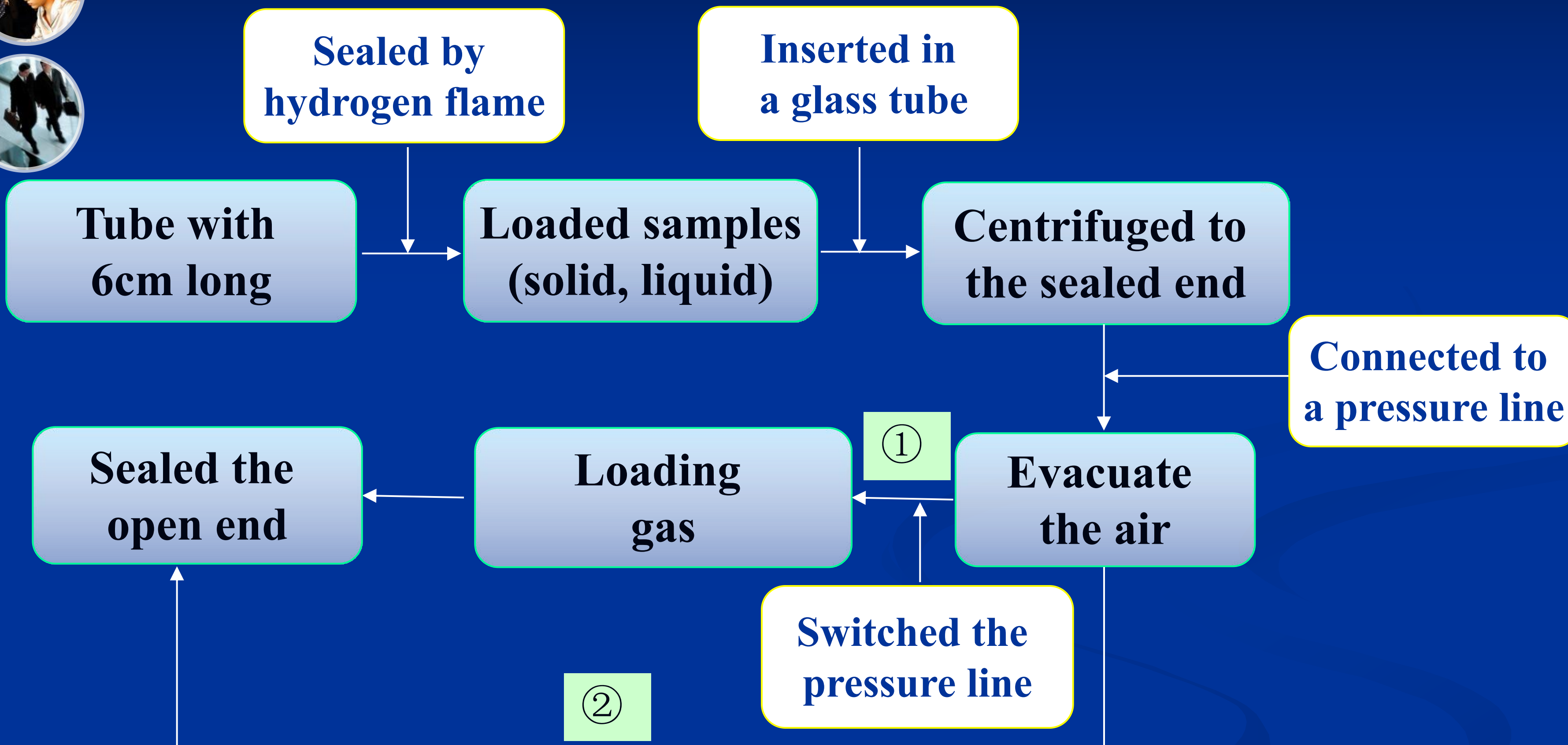
Fused **S**ilica
Capillary
Reactor?

Fused Silica Capillary Reactor (FSCR)

- Raw materials
- Manufacturing process
- Heating-cooling stage & Raman spectroscopy
- FSCR sample

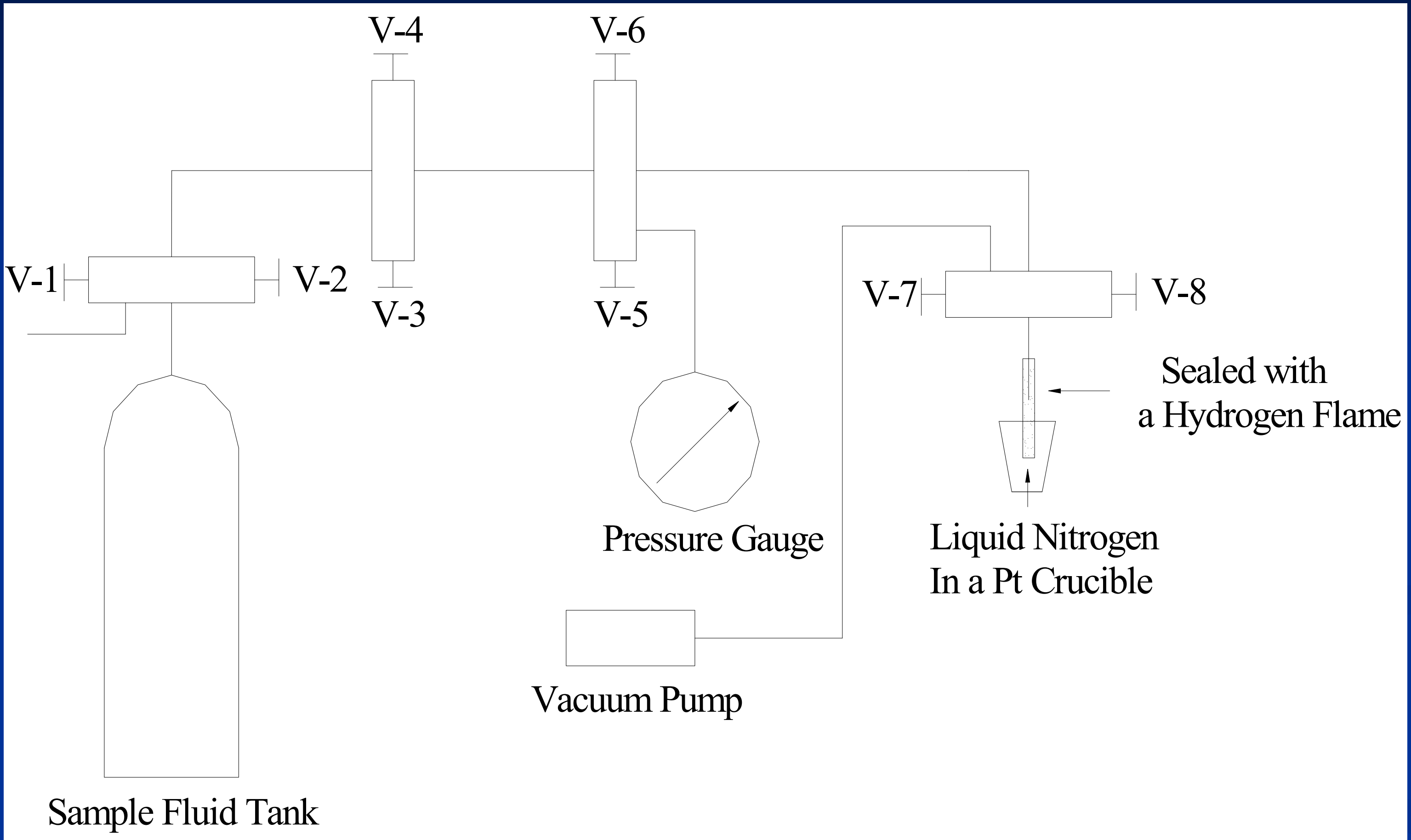
1.1 Raw materials

1.2 Manufacturing process



Schematic of Synthesizing of FSCR

Fused silica capillary reactor (FSCR) was constructed from capillary tube, which has a shape of round cross-section (OD 0.66 mm /ID 0.30 mm).

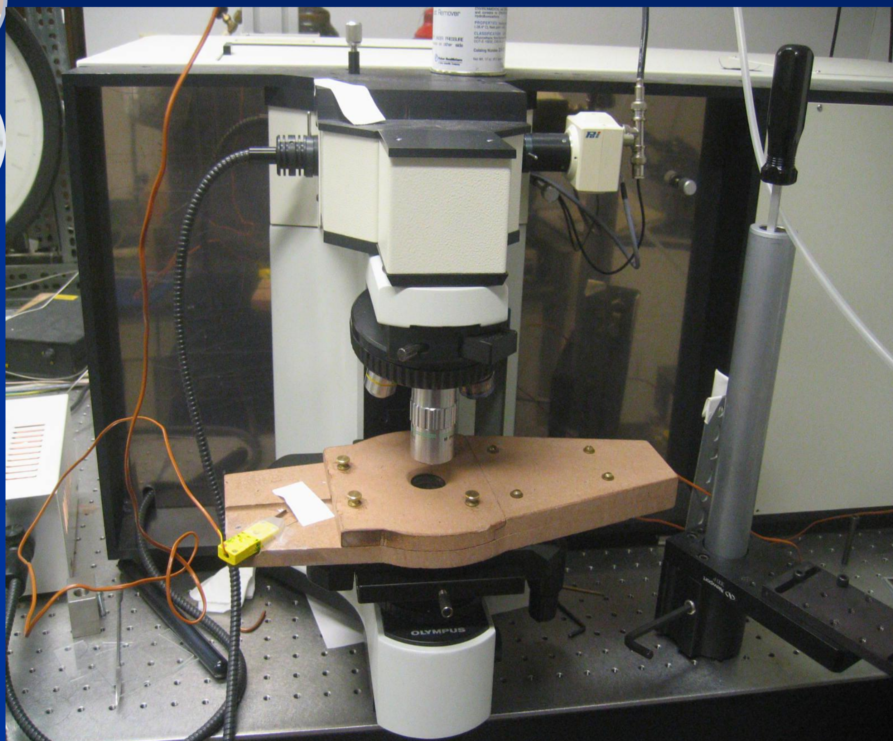


Schematic Diagram of the Vacuum and Sample Loading System

1.2 Manufacturing process

Photogram of the Vacuum and Sample Loading System

1.3 Heating–cooling stage

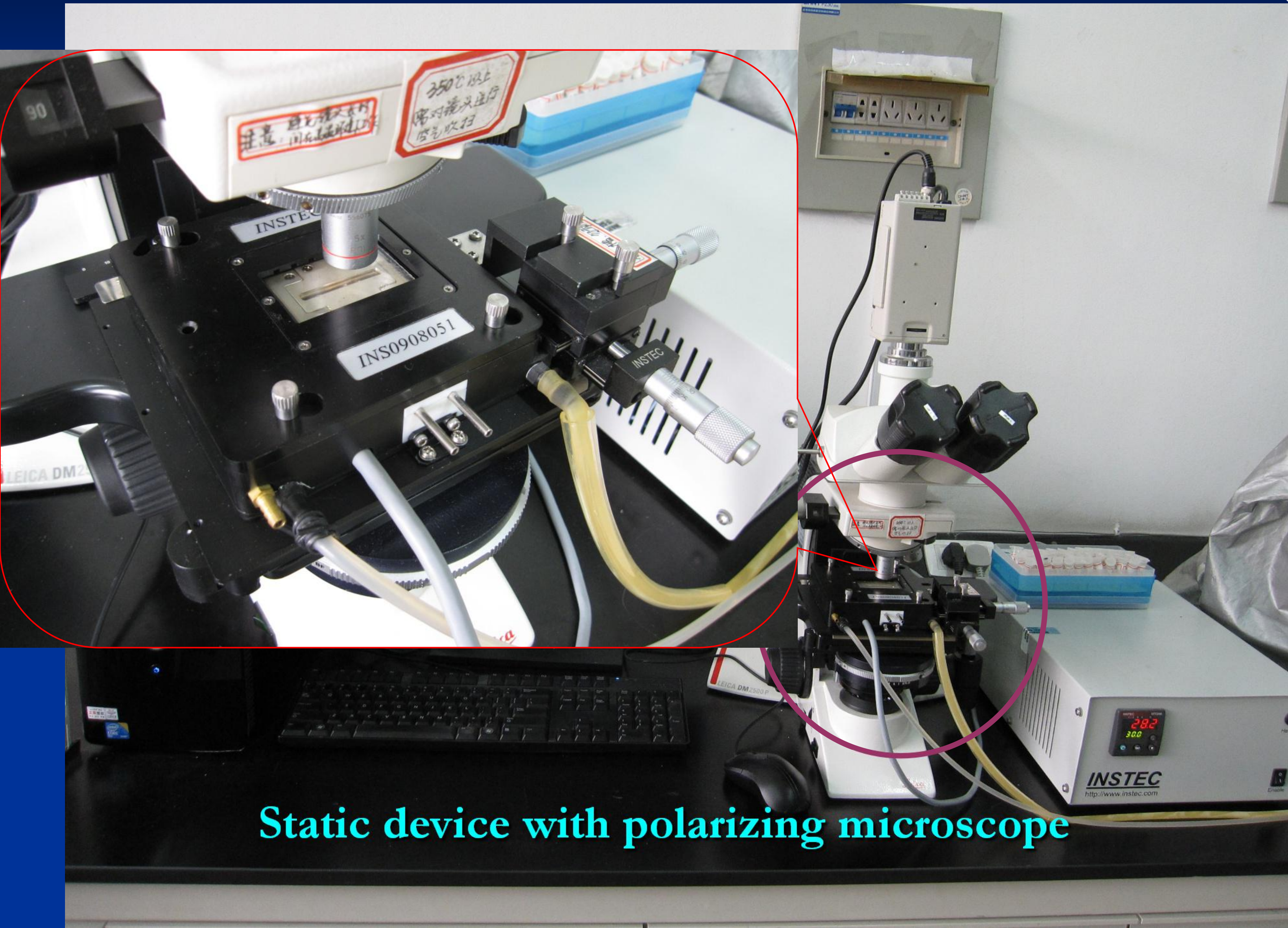


Heating–cooling stage of USGS

Raman Spectroscopy

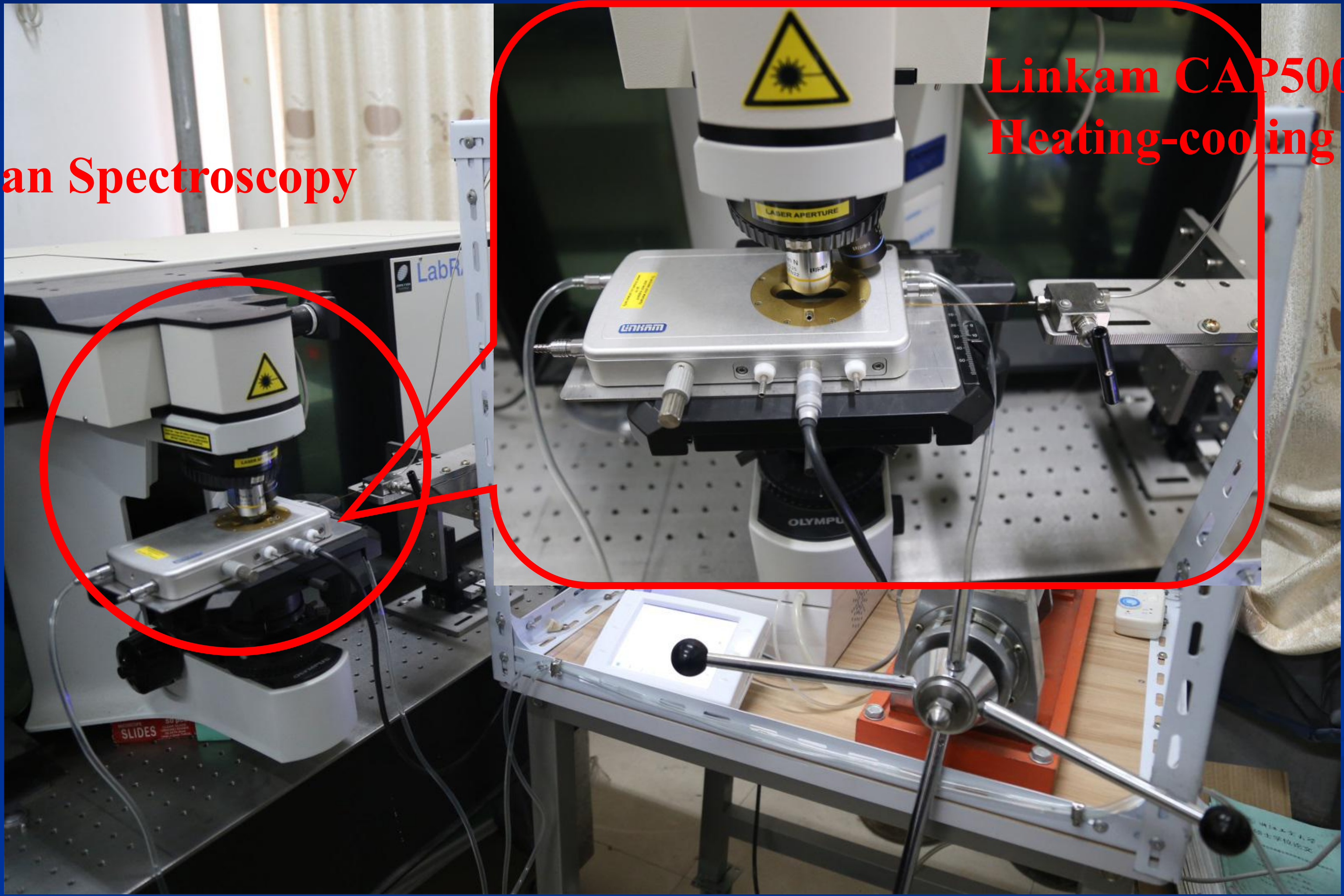
The FSCR prepared was inserted into the sample chamber of the USGS-type heating-cooling stage, where the temperature could be controlled and maintained by continuous flow of heated air, and read by a K-type thermocouple with an accuracy of ±0.2K.

INSTEC heating–cooling stage



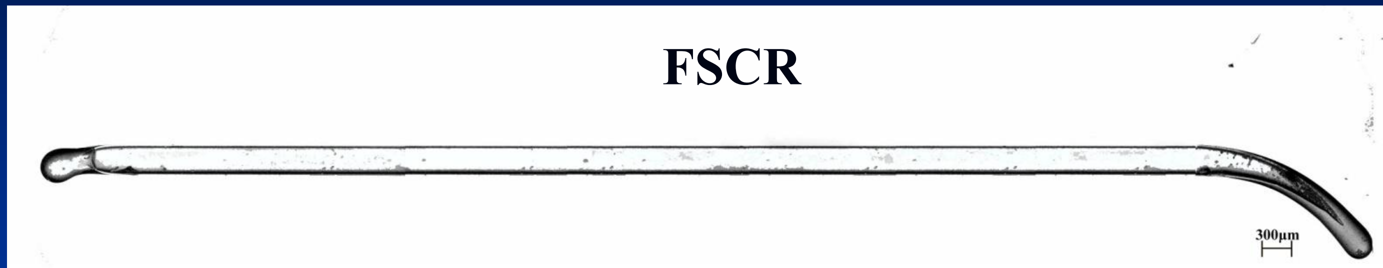
Static device with polarizing microscope

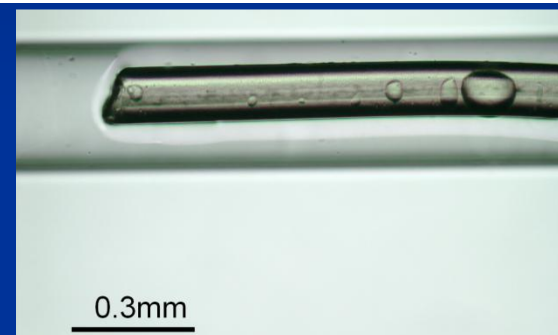
Linkam heating-cooling stage

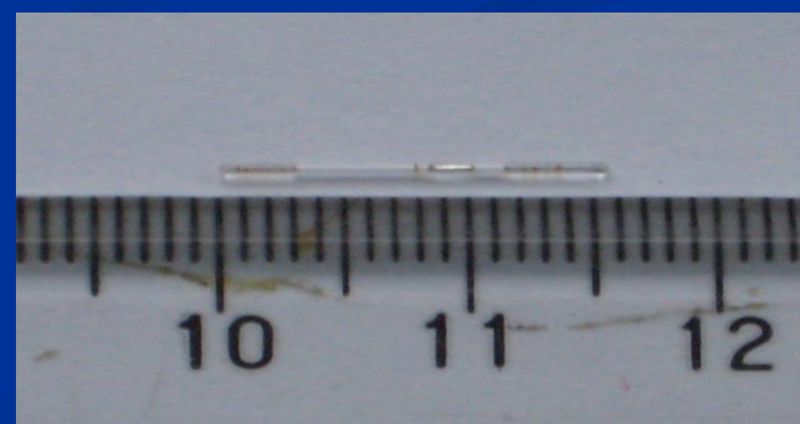


Raman Spectroscopy

1.4 FSCR sample

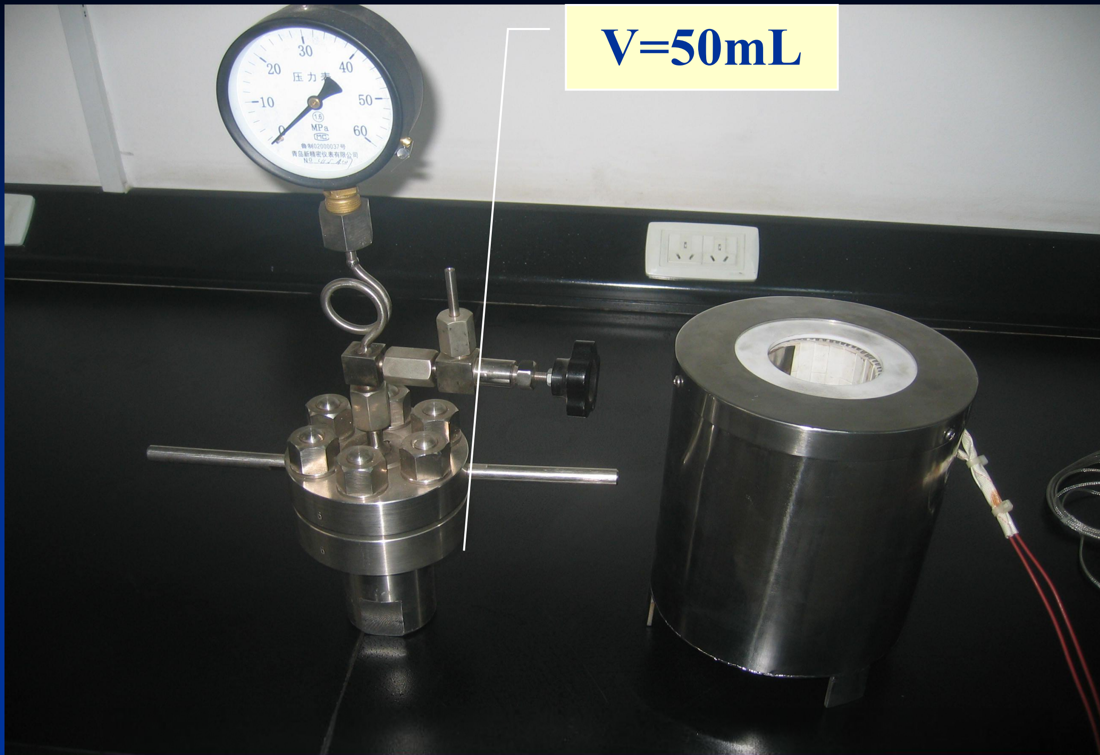






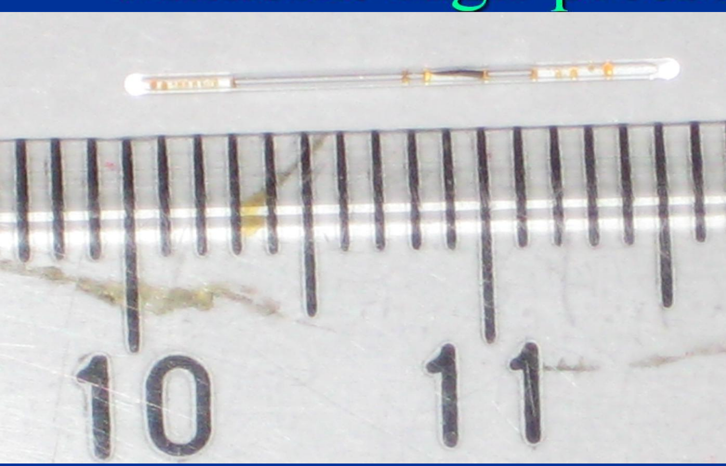
Photograph of the capillaries
(0.3mm ID, 0.66mm OD, and ~25mm long)

➢ *Green Chemistry*, 2009, 11: 1105-1107.



V=50mL

Minisize high-pressure reactor



V=0.001~0.005mL

Fused silica capillary reactor (FSCR)

V=500~5000mL

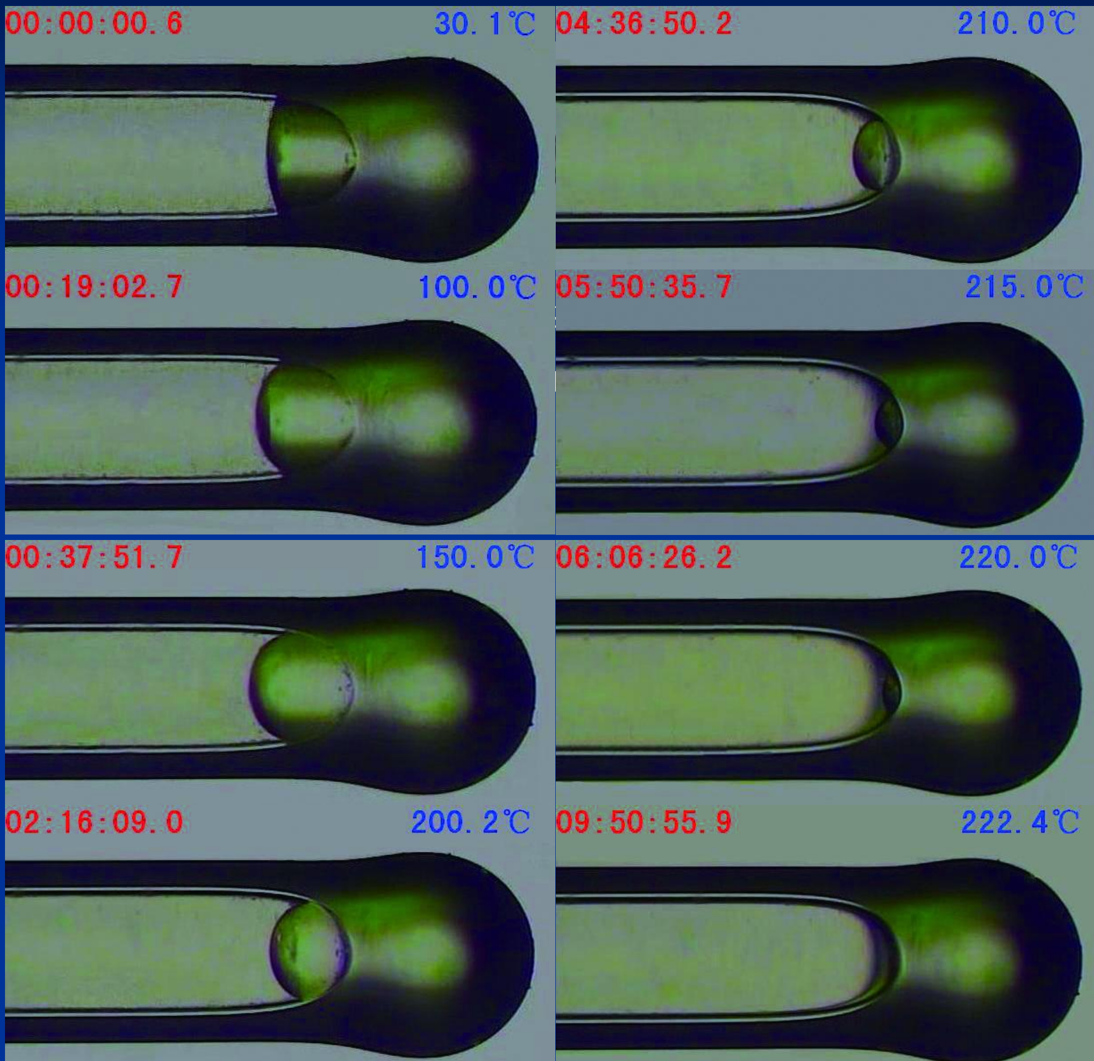
stainless steel autoclave

Measurement of solubilities in FSCR

2

- Solubility of chlorobenzene in hot compressed water (HCW)
- Solubility of 2,4-dichlorotoluene in HCW by in situ Raman spectroscopy
- Solubility of ethanol in SC-CO_2 with FSCR

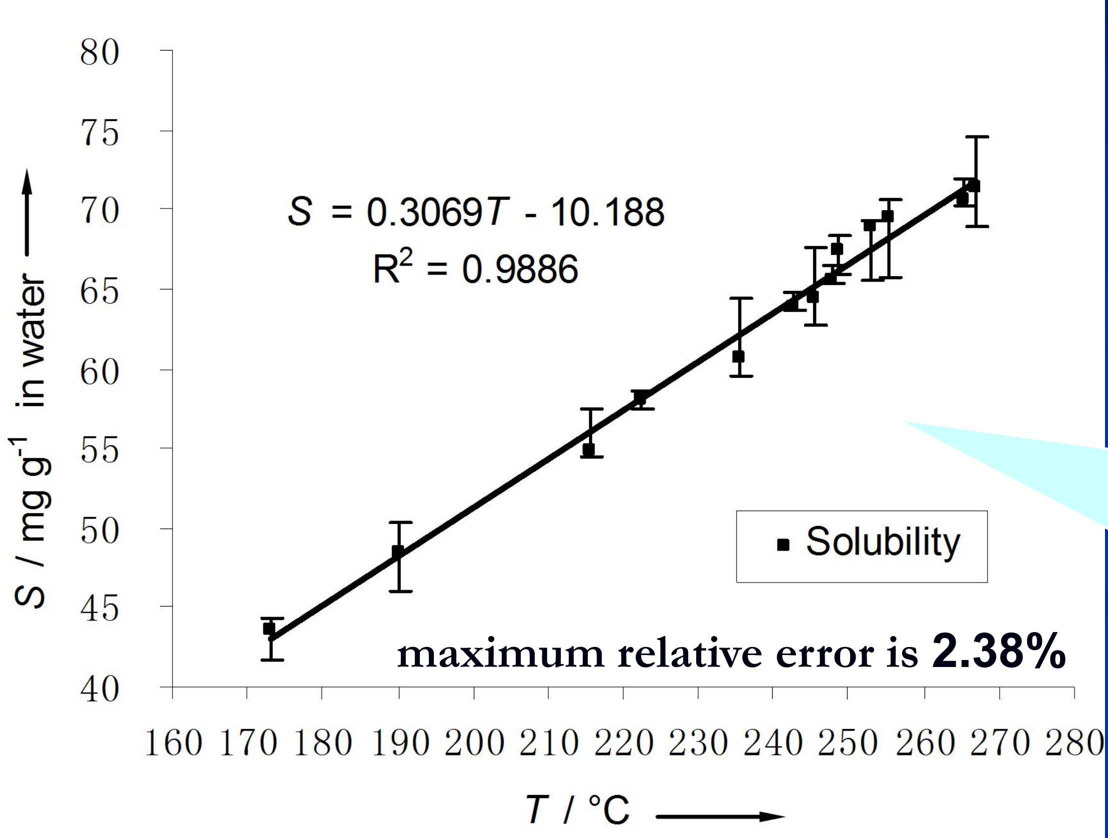
2.1 Solubility of chlorobenzene in HCW with FSCR



FSCR was heated to the preset temperature and allowed the sample to equilibrate for a period between 8 and 10h in the presence of a vapor phase. For example, the images of a sample containing 58.0 mg of C_6H_5Cl/g of H_2O, taken during heating from 30.1 to 222.4℃, they show the gradual dissolution of C_6H_5Cl during heating and its total disappearance at 222.4 ℃.

Dissolution of chlorobenzene in water during heating.
The C_6H_5Cl is shown at the right end of the FSCR. The FSCR is under the microscope

Temperature range（173.3～266.9 ℃）

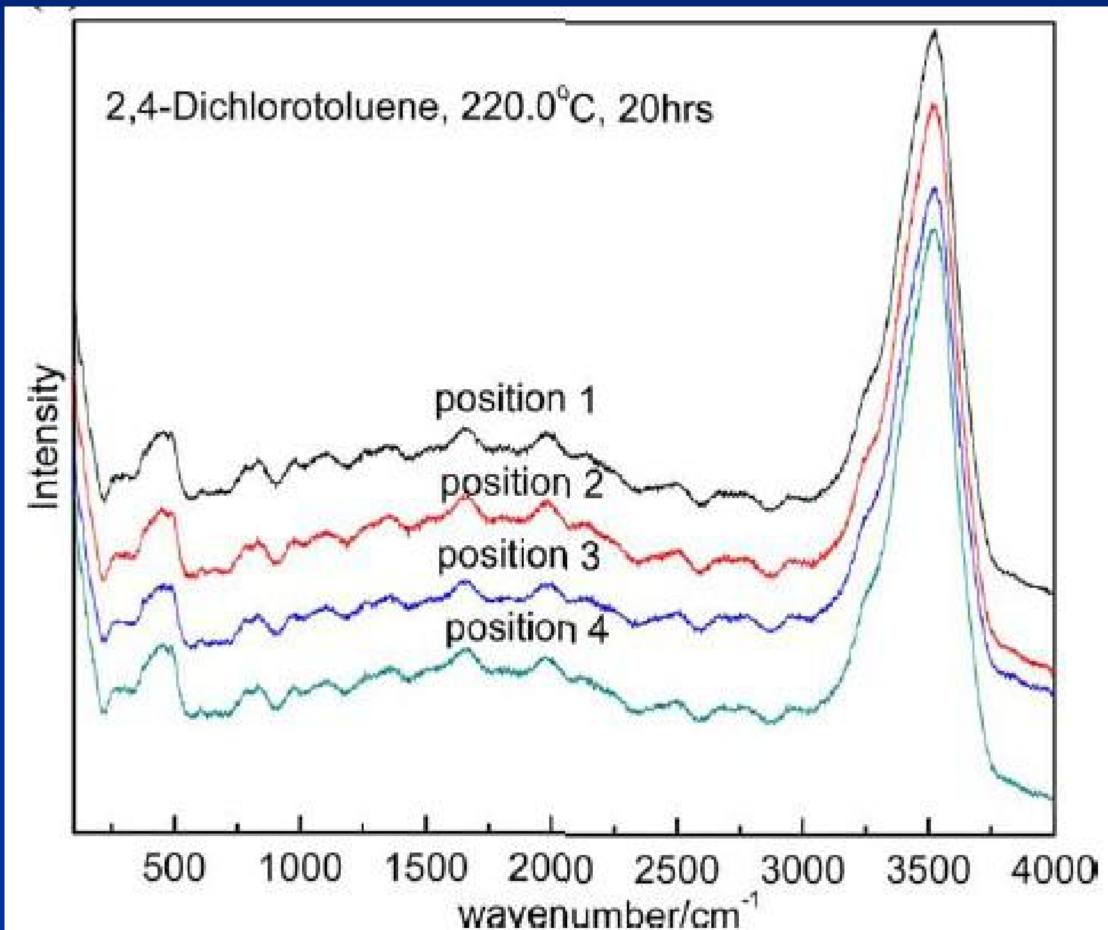


The results indicate the solubility of C_6H_5Cl increases with increasing temperature, and can be represented by the linear equation

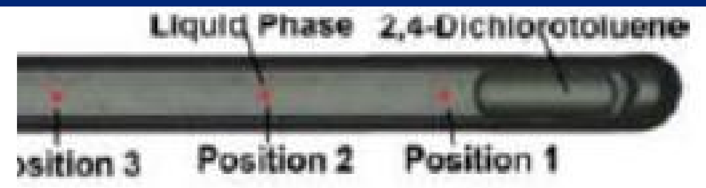
Solubility of C6H5Cl in pure water at temperatures between 173.3 and 266.9 ℃
■, experimental data; —, least-squares fit of the data

Industrial & Engineering Chemistry Research, 2011, 50 (20): 11724-11727.

2.2 Solubility of 2,4-Dichlorotoluene in HCW with FSCR by in Situ Raman spectroscopy



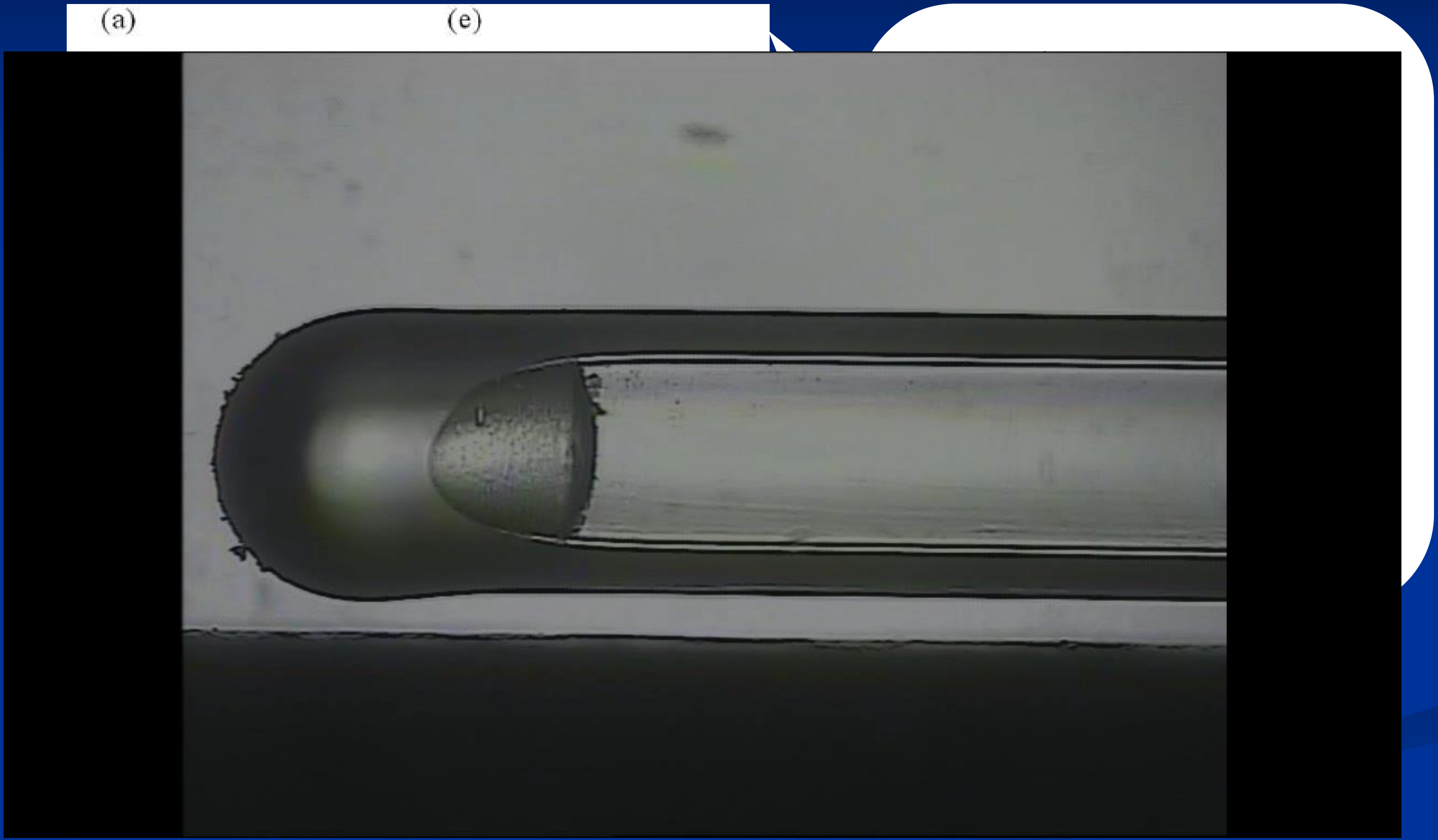
An image of Raman spectra of liquid phase in the FSCR at four spots, at 220.0C, 20 h.



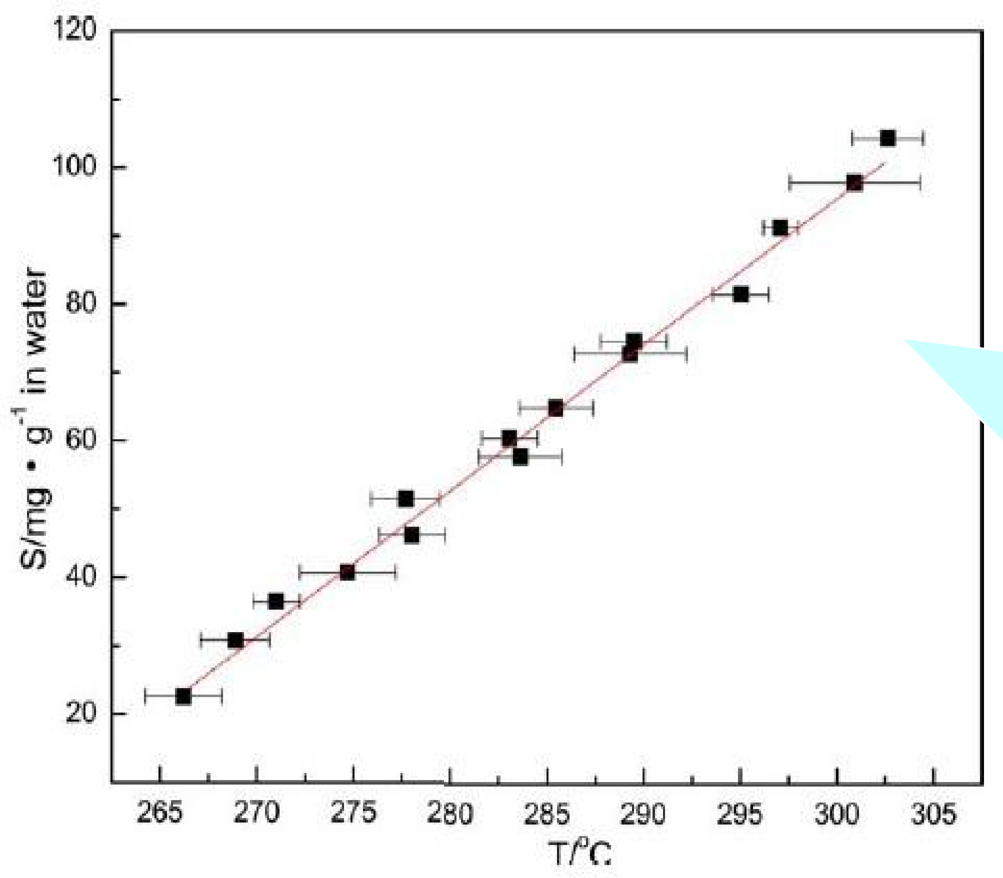
-dichlorotoluene, liquid phase,
ts fo

The Figure shows that the Raman spectra of 2,4-dichlorotoluene had bands with the same relative intensities at 457.04 cm^{-1} and 828.54 cm^{-1}. It can be concluded that the solute diffused uniformly and the system reached phase equilibrium within a certain time, proving that the apparatus is viable.

2.2 Solubility of 2,4-dichlorotoluene in HCW with FSCR by in Situ Raman spectroscopy



Dissolution of 2,4-dichlorotoluene in HCW during heating process. 2,4-Dichlorotoluene is at the left of the FSCR.

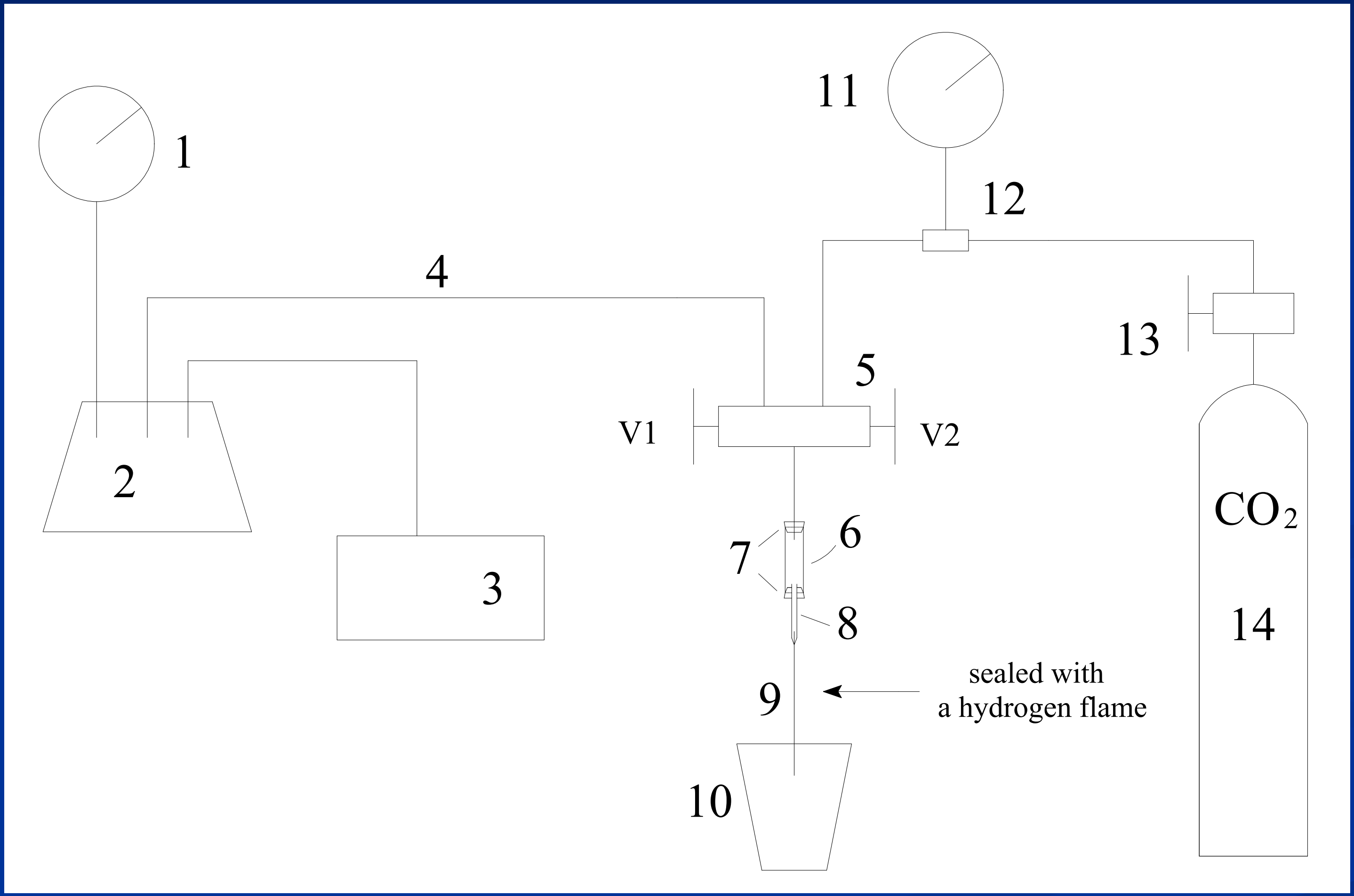


Solubility of 2,4-dichlorotoluene in water at temperatures between 266.3 and 302.4℃: (■) experimental data; (--) least-squares fit of the data.

The results indicate that the solubility of 2,4-dichlorotoluene increased from 22.6 to 104.2 mg/(gH_2O) when the temperature rose from 266.3 to 302.4℃

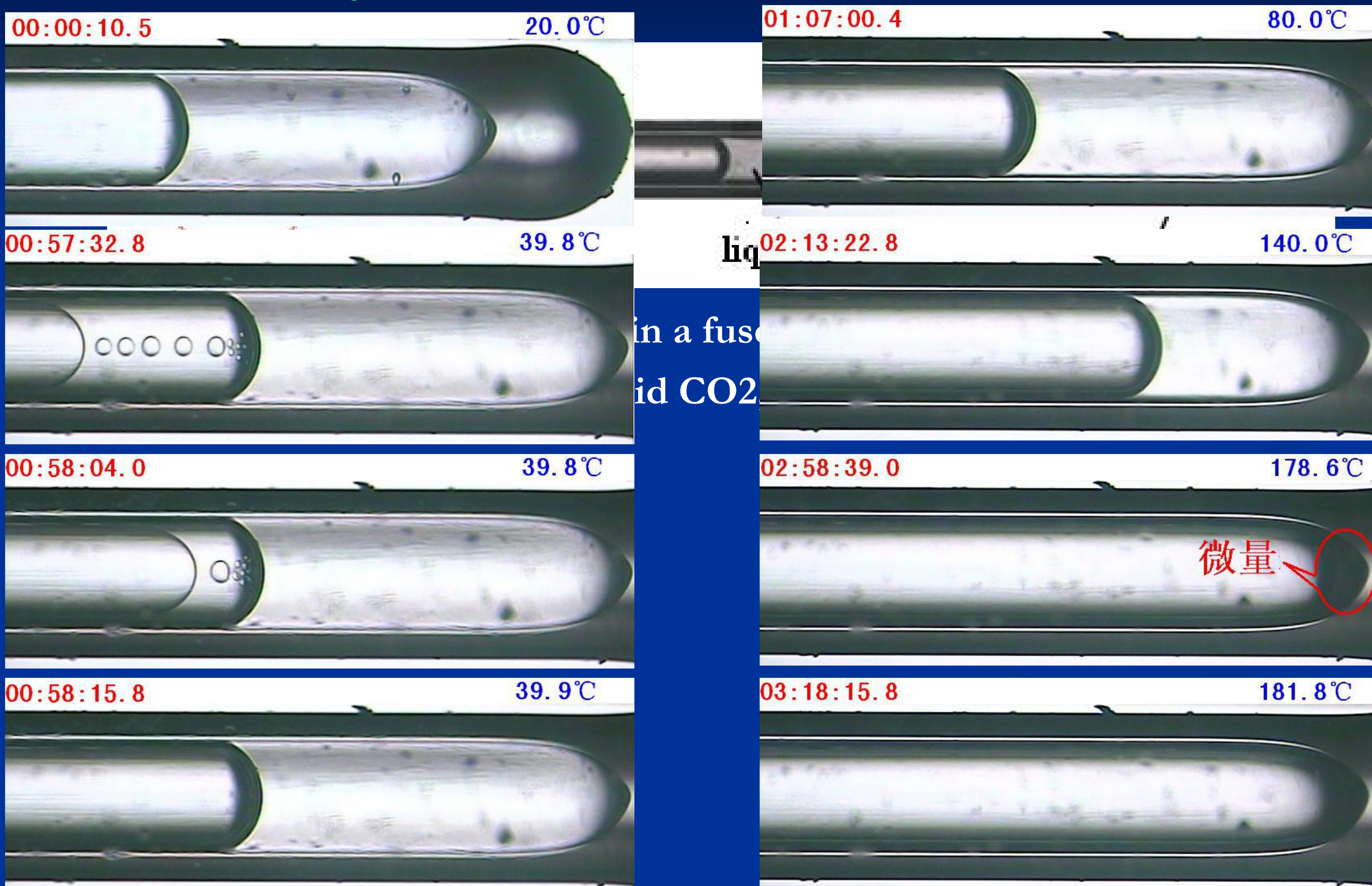
AIChE Journal, 2013, 59 (8):2721-2725.

2.3 Solubility of ethanol in SC-CO_2 with FSCR

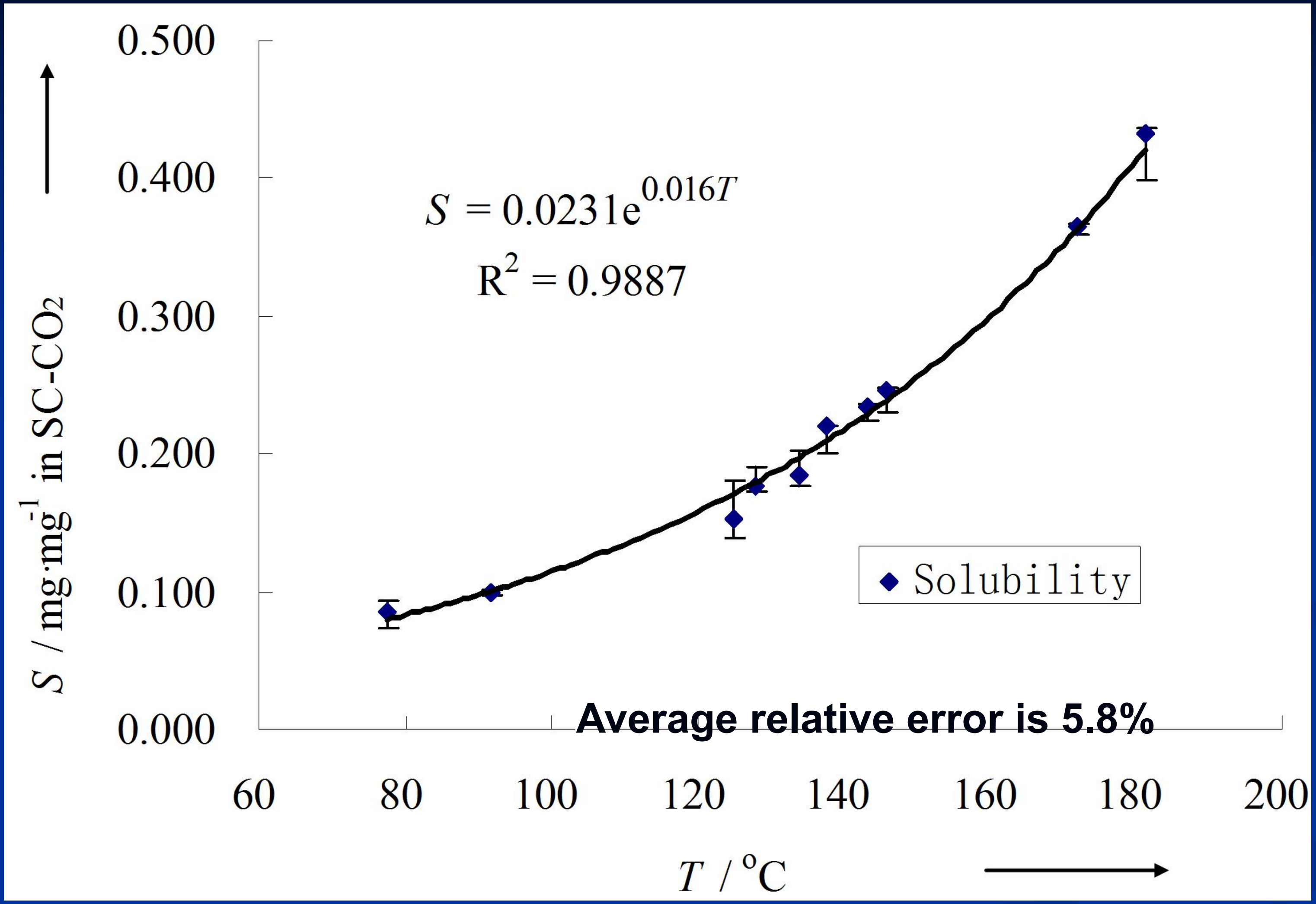


Schematic diagram of the experimental flow to determine the solubility of ethanol in SC-CO_2

2.3 Solubility of ethanol in SC-CO_2 with FSCR



Dissolution of ethanol in supercritical CO2 during heating.
The ethanol is shown at the right end of the FSCR, and the FSCR is under the microscope.



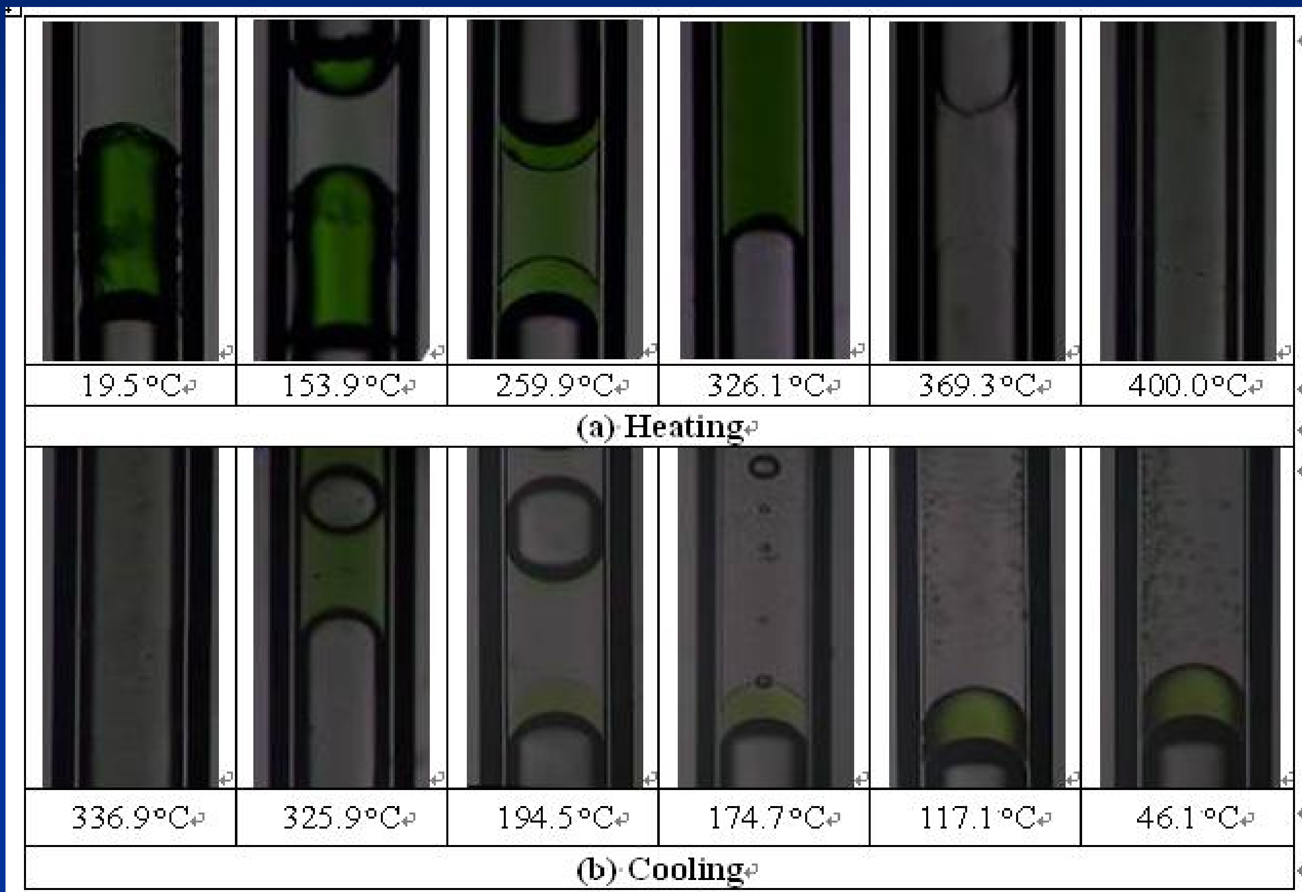
Solubility of ethanol in SC-CO2 at temperatures between 87.5 and 183.8℃
■, experimental data; —, least-squares fit of the data.

Supercritical water oxidation in FSCR

3

- Supercritical water oxidation of chlorobenzene (CB)
- Hydrolysis of CCl4 in HCW
- Decomposition of 1,1,1-trichloroethane (TAC) in HCW

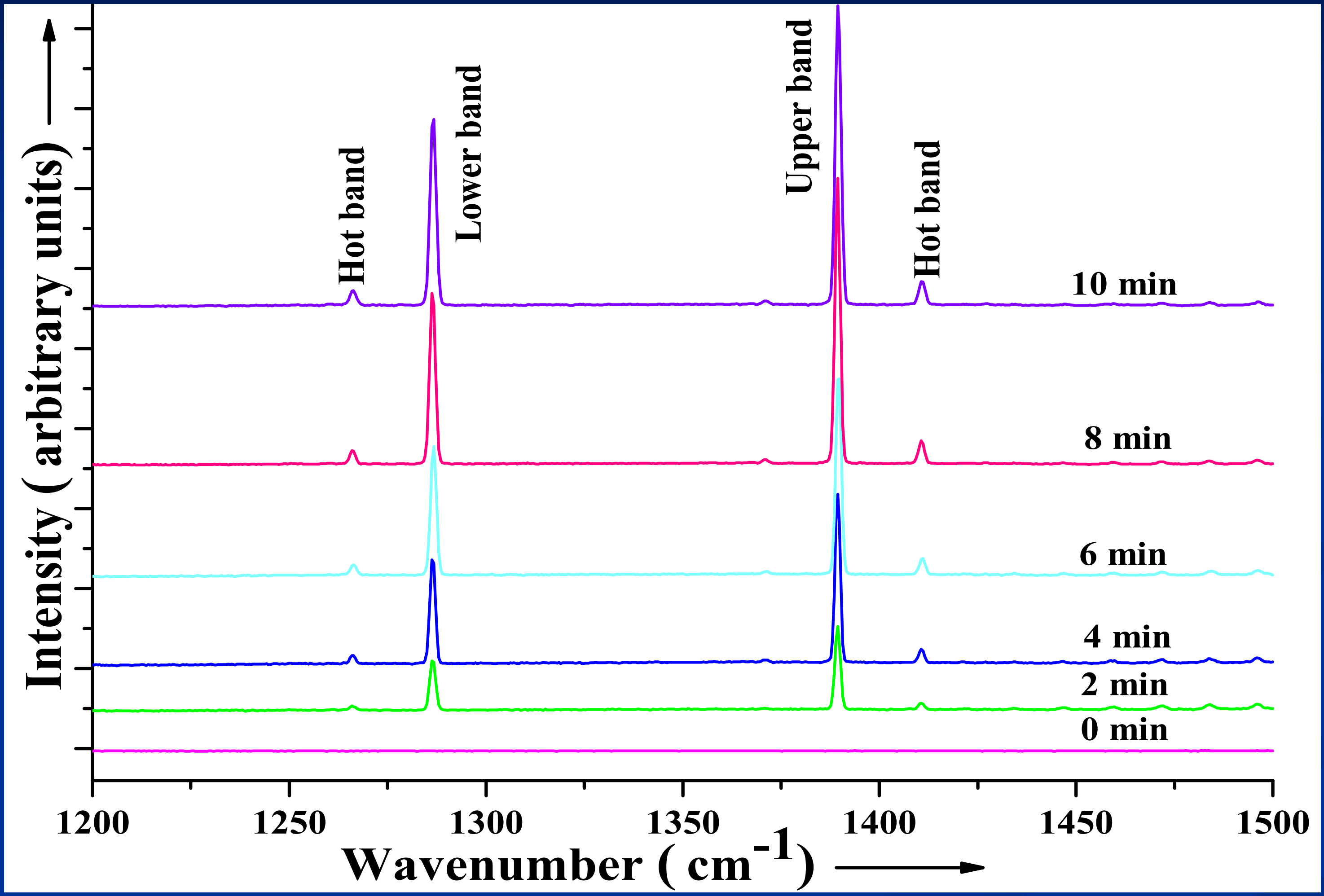
3.1 Phase-behavior changes of CB in the FSCR



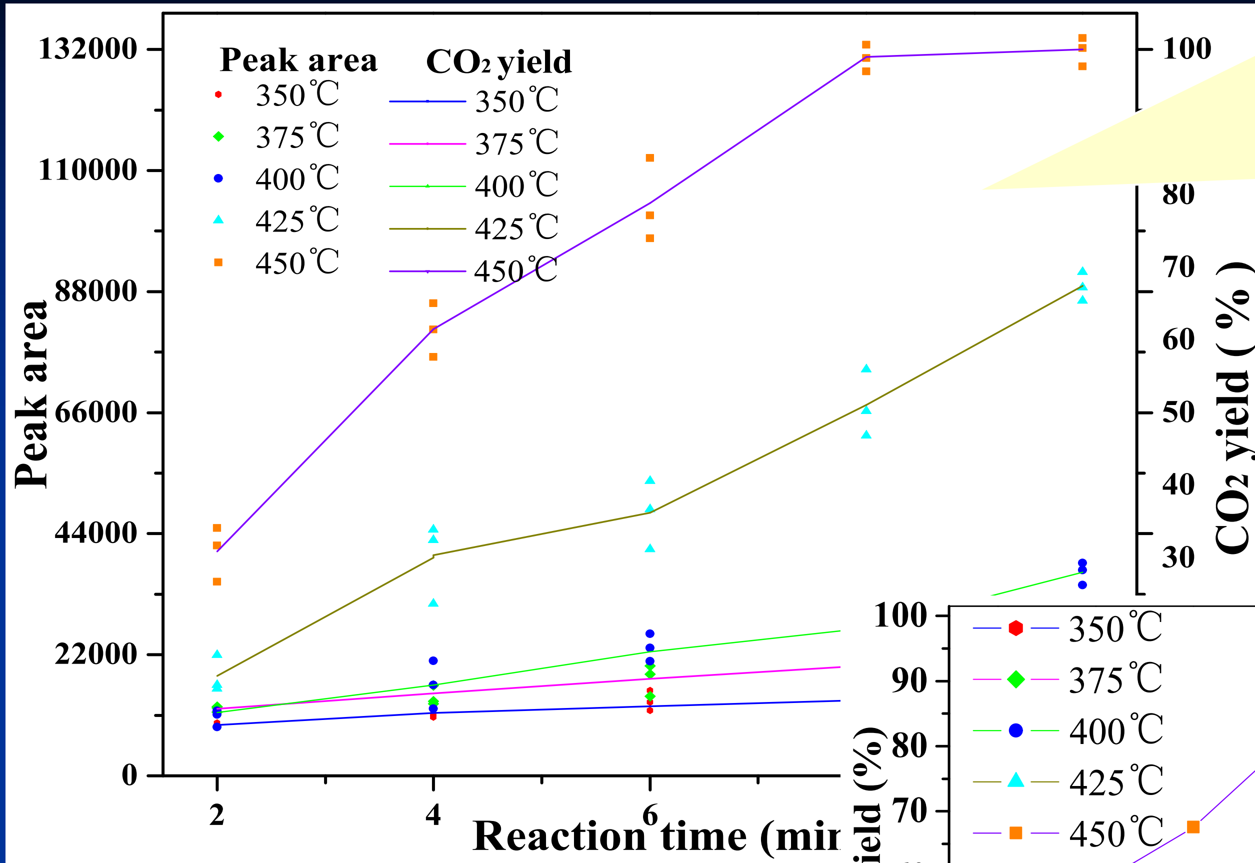
Photomicrographs of chlorobenzene in hydrogen peroxide (30 wt%) in a fused-silica capillary reactor during heating process (a), and cooling process (b).

- *Environmental Science & Technology*, 2012, 46 (6): 3384-3389.

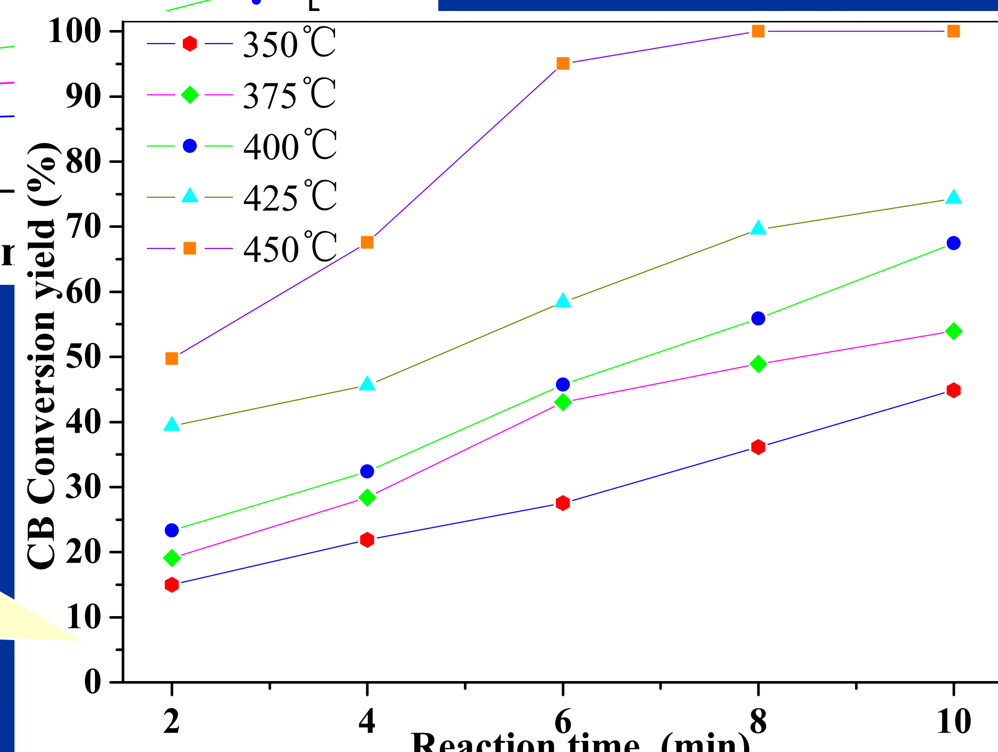
$$C_6H_5Cl + 14H_2O_2 \rightarrow 6CO_2 + 16H_2O + HCl$$



Raman spectra of CO_2 produced by oxidation of CB in supercritical water with 150% stoichiometric amounts of oxidizer at 450 ^OC at different reaction times.

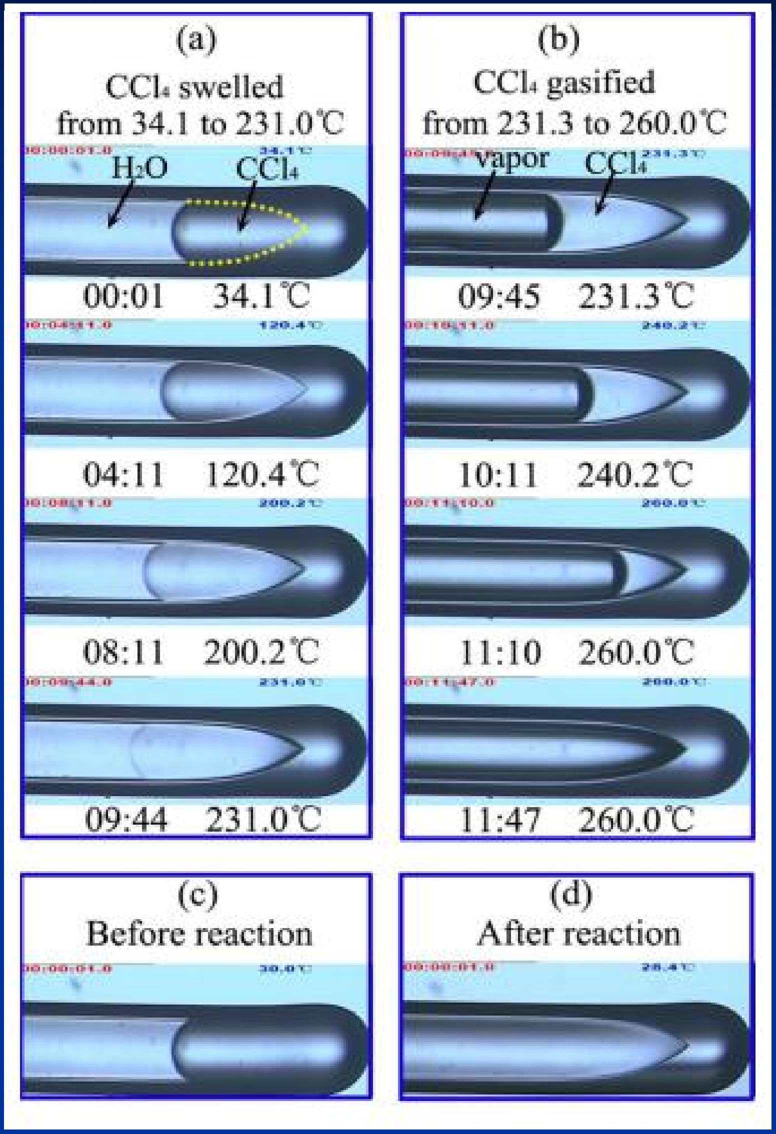


Raman peak area of CO_2 (scattered symbols) and CO_2 yield (lines) vs reaction time with 150% stoichiometric amount of oxidizer at different temperatures.



Effects of reaction time on CB conversion yield with 150% stoichiometric amount of oxidizer at different temperatures.

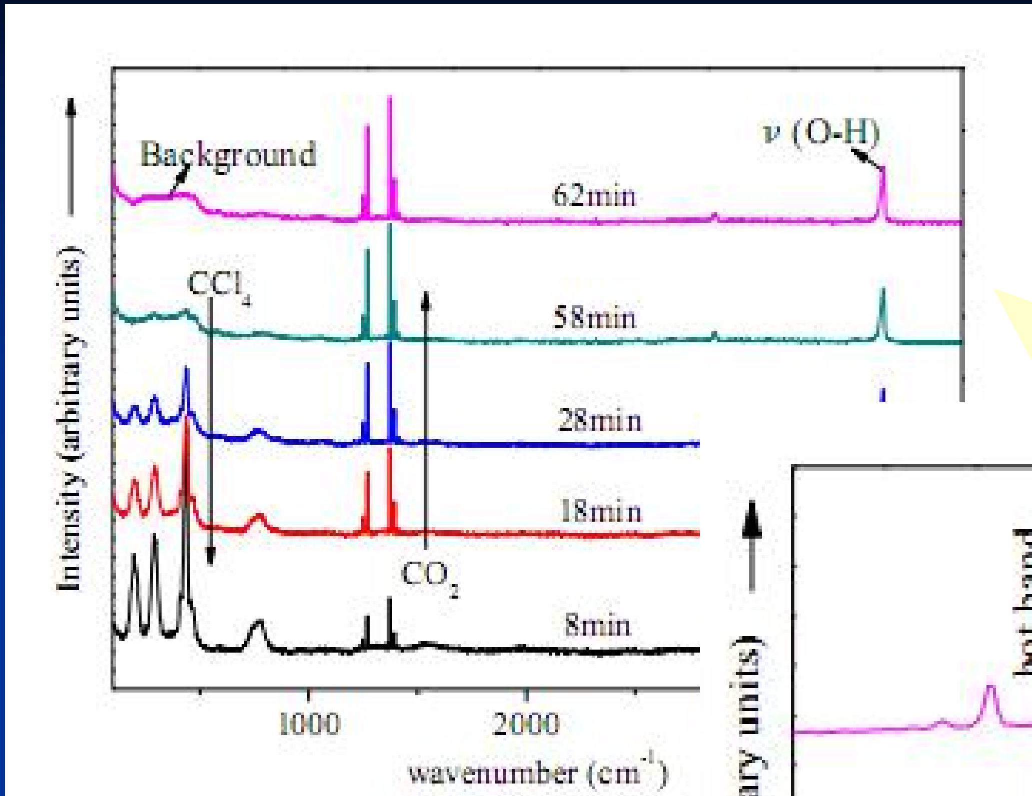
3.2 Hydrolysis of CCl_4 in FSCR



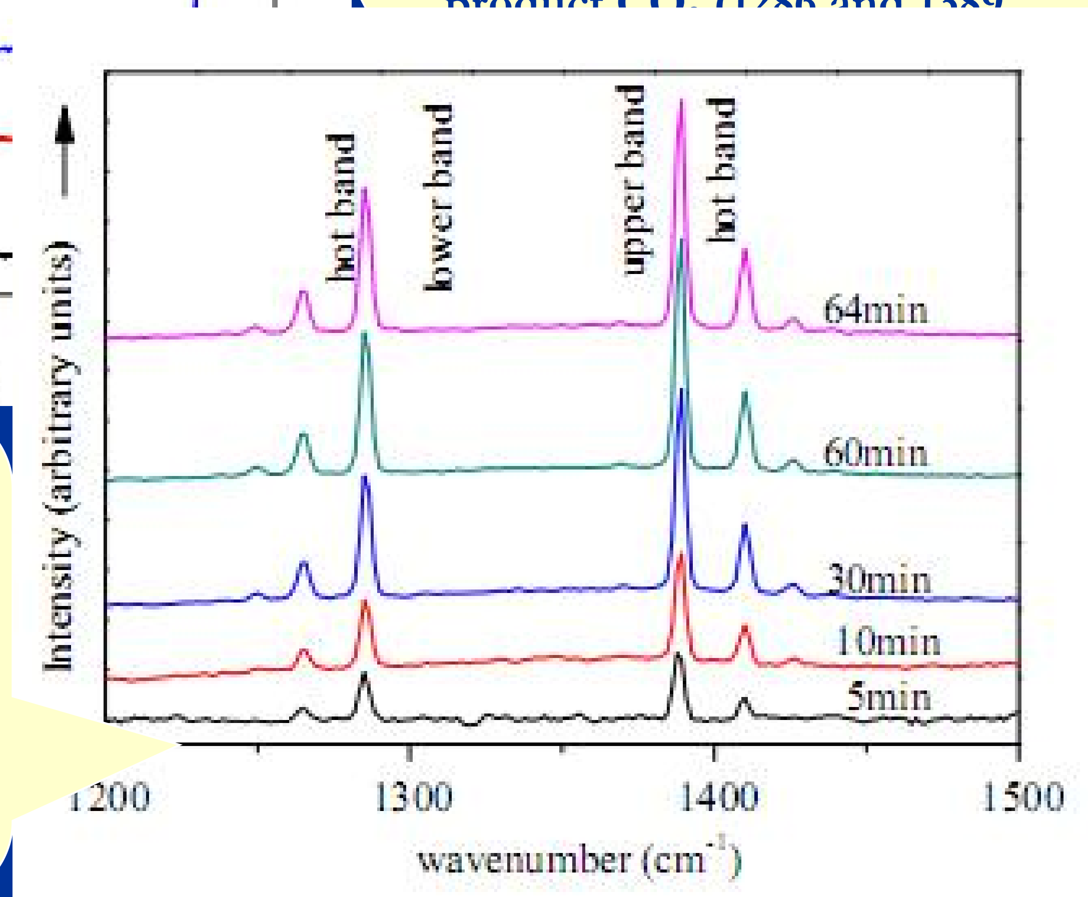
Photomicrographs of CCl_4 with water in FSCR during the heating process: (a) CCl_4 swells up between 34.1 and 231.0^{o}C and gasifies (b) between 231.3 and 260.0^{o}C. (c) Photomicrographs before and (d) after reaction taken at room temperature.

- In Situ Raman Spectroscopic Study of Hydrolysis of Carbon Terachloride in Hot Compressed Water in a Fused Silica Capillary Reactor

- *The Journal of Supercritical Fluids.* 2012, 72:22-27.

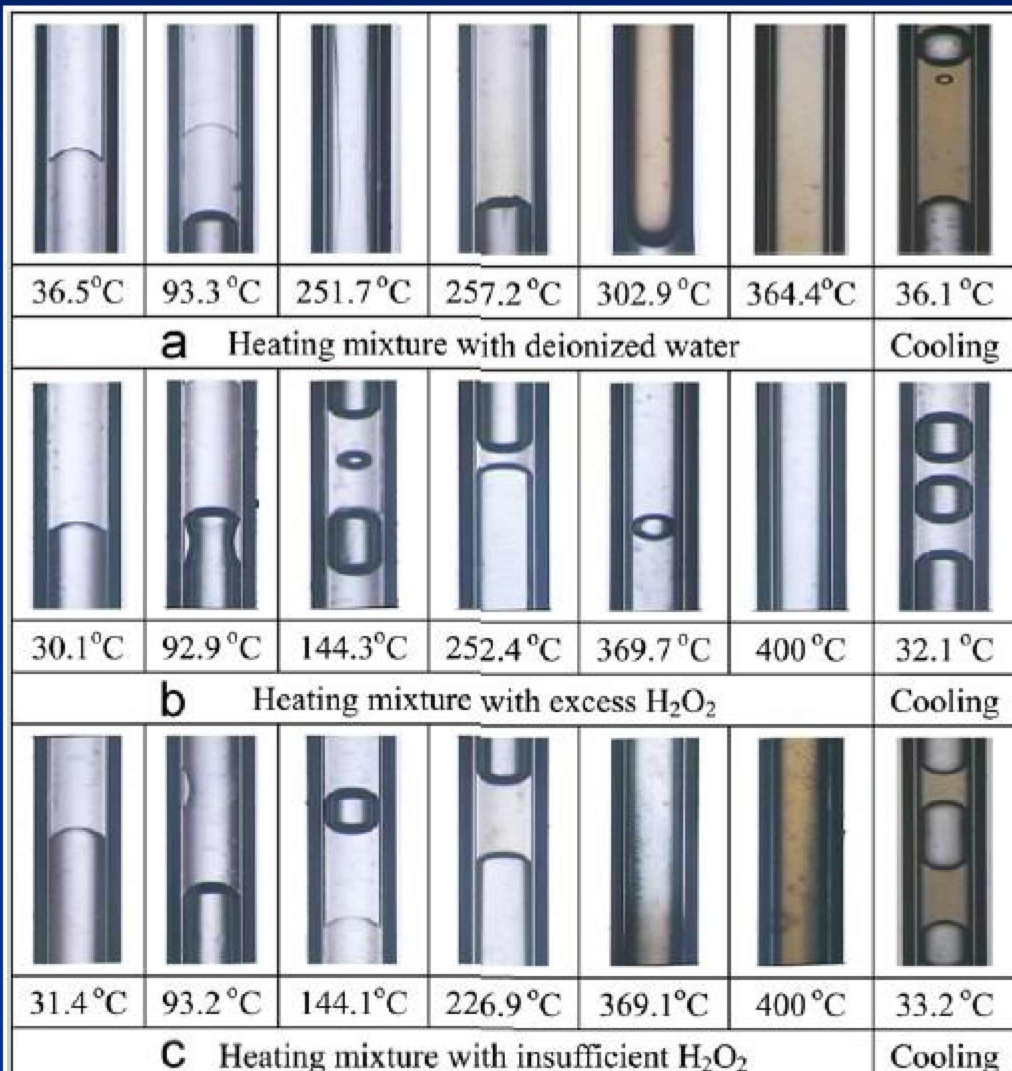


Raman spectra of the vapor phase in FSCR at 260°C collected at different reaction times showing bands for Carbon Tetrachloride (459, 314, and 218 cm^{-1}) and product CO_2 (1286 and 1389



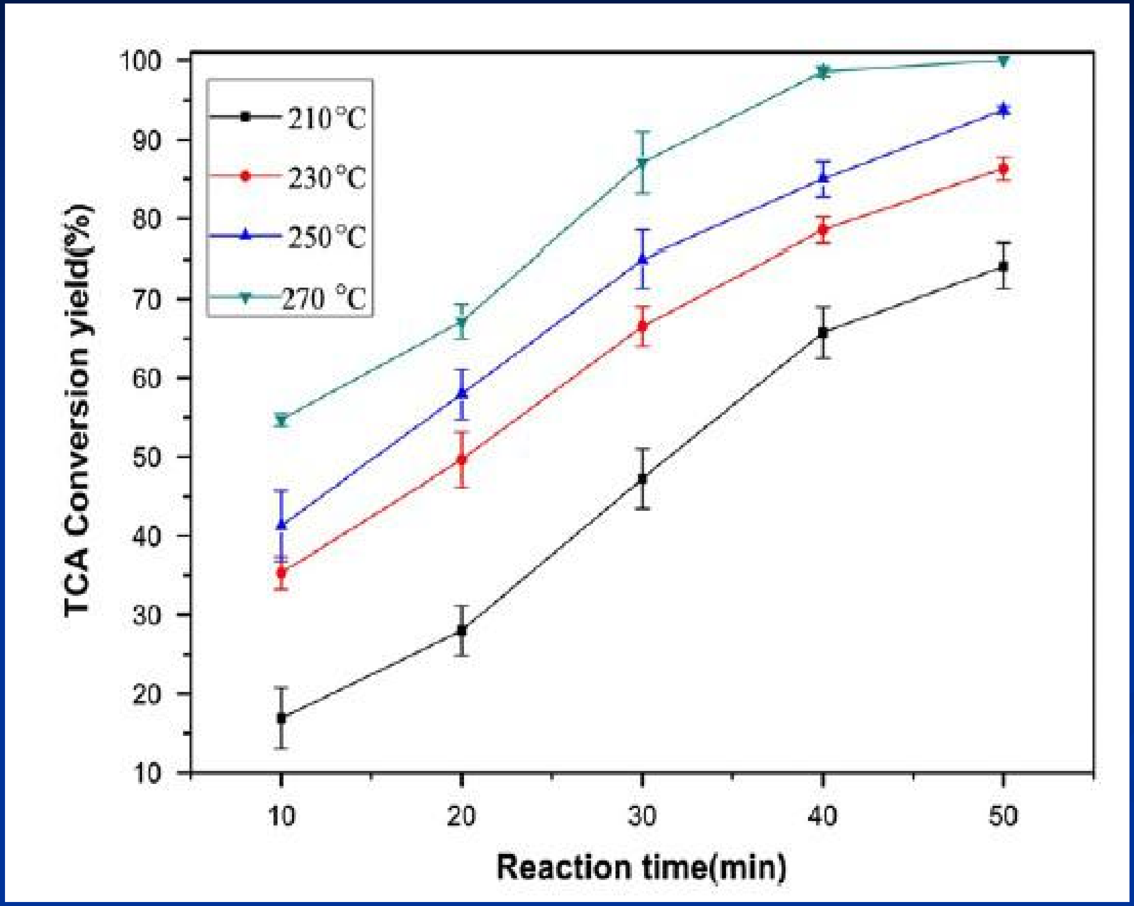
Raman spectra of the vapor phase produced by the hydrolysis of CCl_4 in HCW at 260°C at various reaction times, showing the CO_2 bands. and the increase of CO_2 signals indicates the progress of hydrolysis.

3.3 Decomposition of 1,1,1-trichloroethane(TCA) in HCW in FSCR



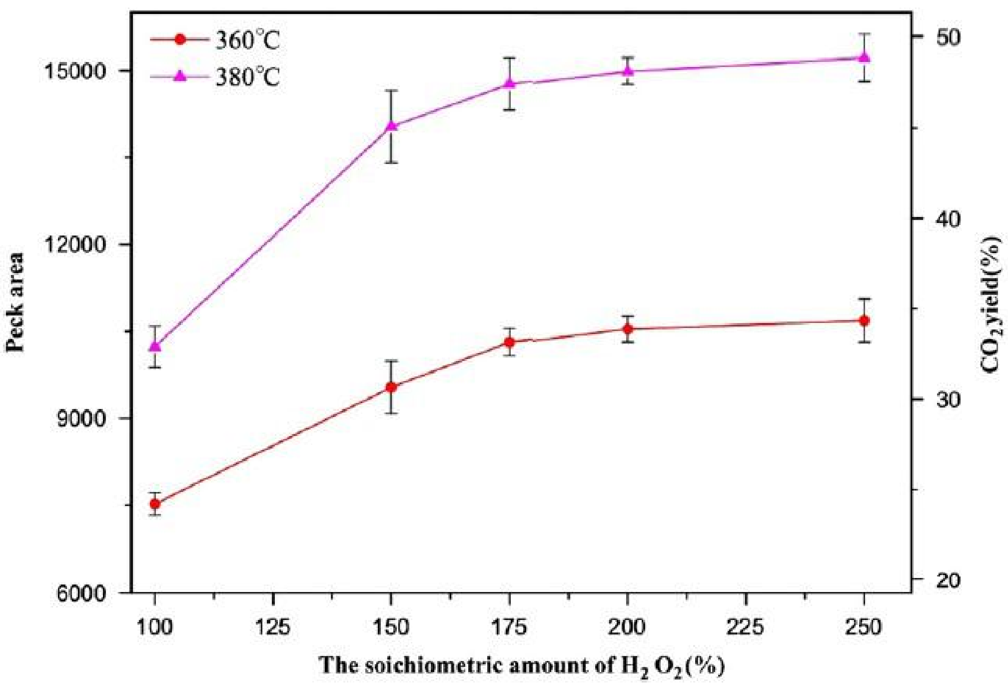
shows the hydrolysis of TCA in deionized water during the heating process.
B.P.=74-76

shows the phase behavior during the oxidation of TCA in H2O2 in the heating process.

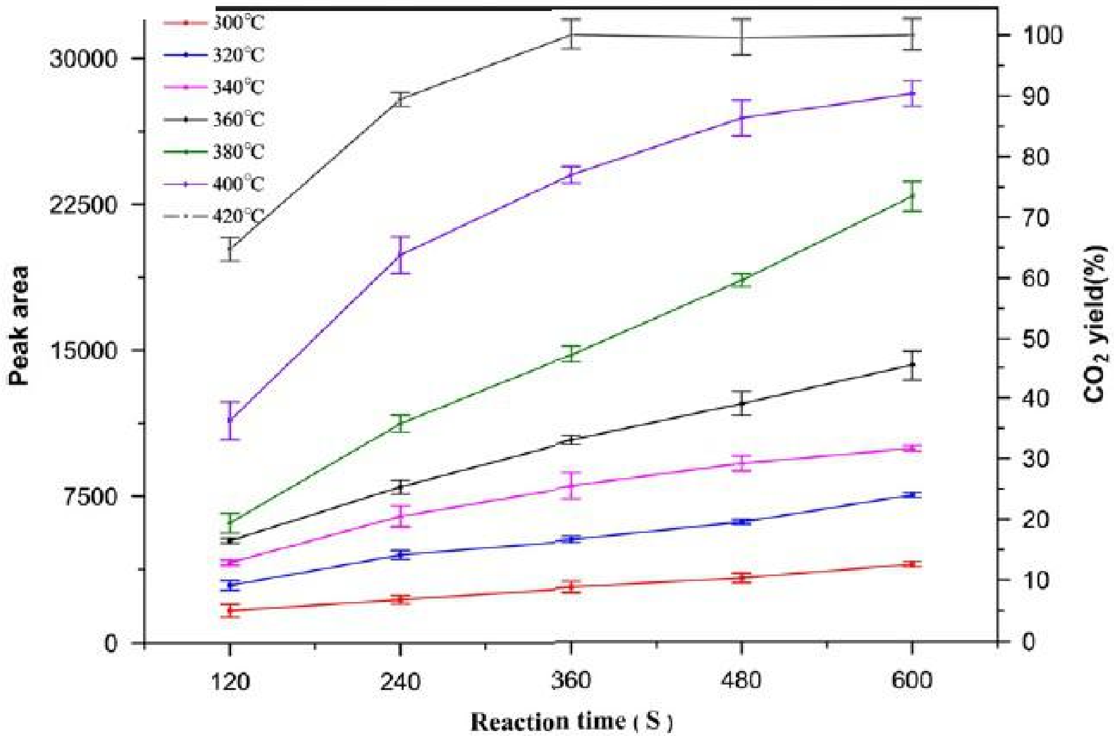


the conversion of TCA increased with increasing temperature in the range 10–50 min, reaching a peak value at 270.℃ for 50 min.

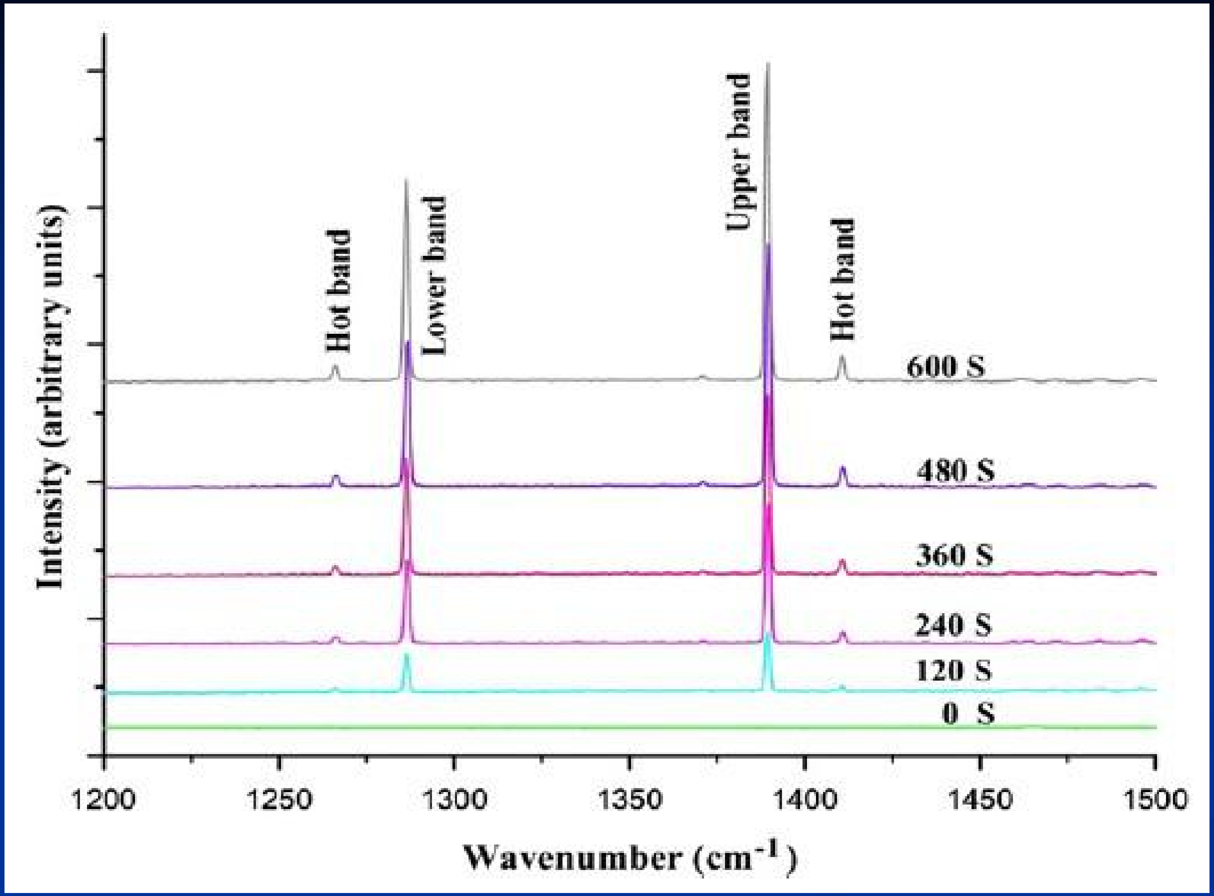
Effect of reaction time on TCA conversion at different temperatures in FSCR.



Effect of stoichiometric amount of H_2O_2 on Raman peak area of CO_2 yield from TCA (t=6 min).



Raman peak areas of CO_2 and CO_2 yields (lines) with 175% stoichiometric amount of oxidizer at different temperatures and reaction times.



Raman spectra of CO2 produced by oxidation of TCA in SCWO with 175% stoichiometric amount of oxidizer at 380 ℃ at different reaction times. The spectra were collected under similar conditions, and the increased CO2 signals indicate the progress of the oxidation.

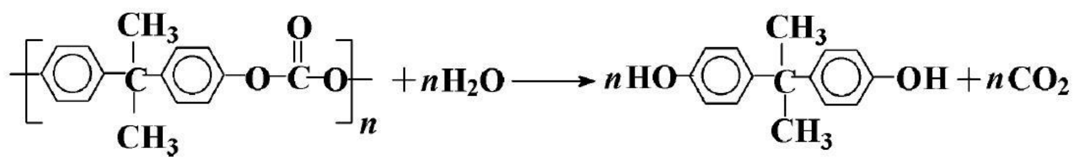
Chemical Engineering Science, 2013,94:185-191.

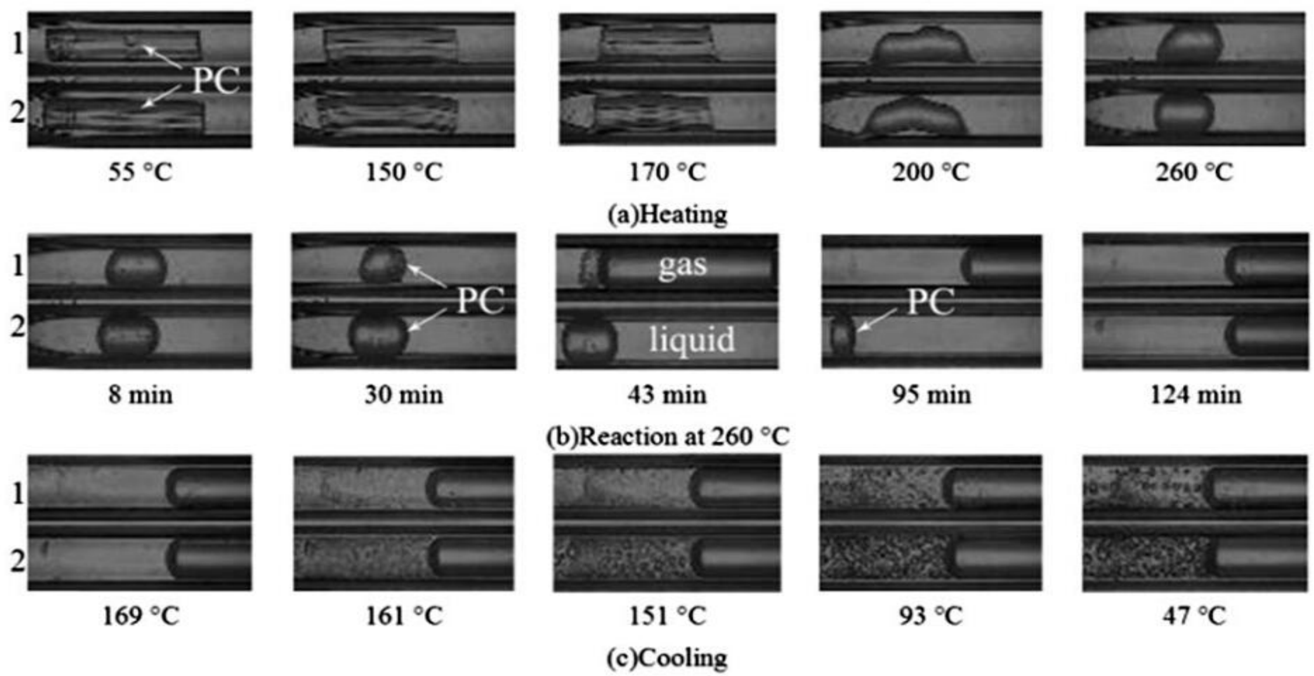
Depolymerization of polyester in FSCR

4

- Depolymerization of PC

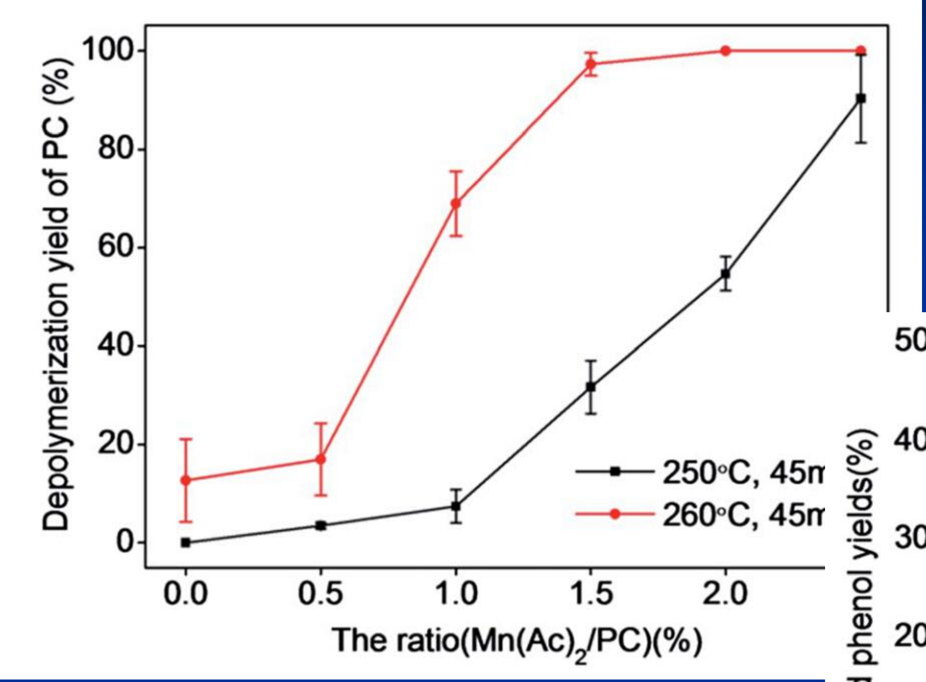
Depolymerization of polycarbonate(PC)



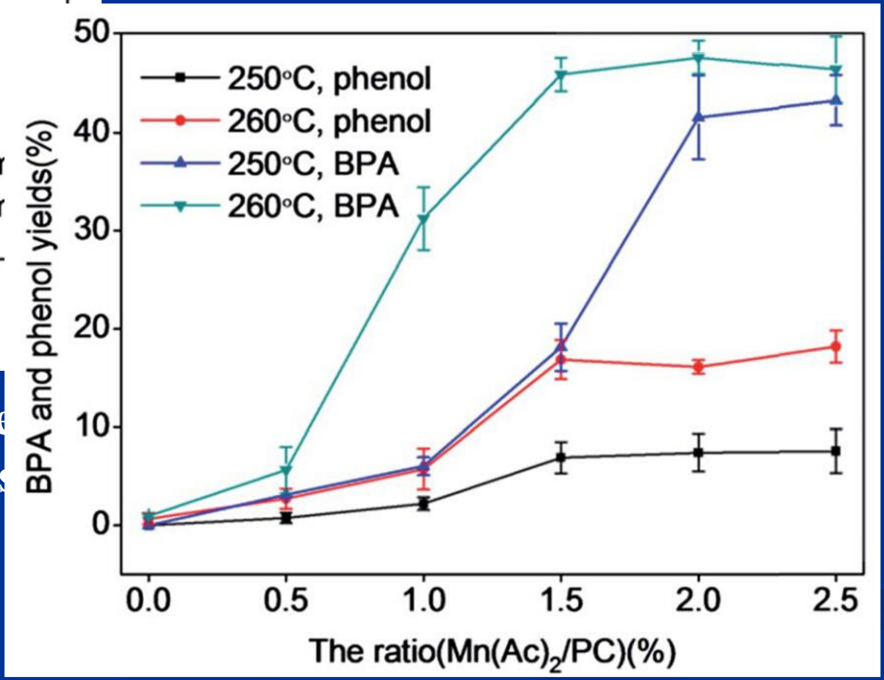


Photomicrographs of PC in water in FSCR1 and FSCR2. (a) heating process, (b) at diferent reaction times at 260 C, and (c) cooling process. $Mn(Ac)_2$ catalyst was present in FSCR1 and not in FSCR2. The heating/cooling/isothermal schedules were identical for the two FSCRs.

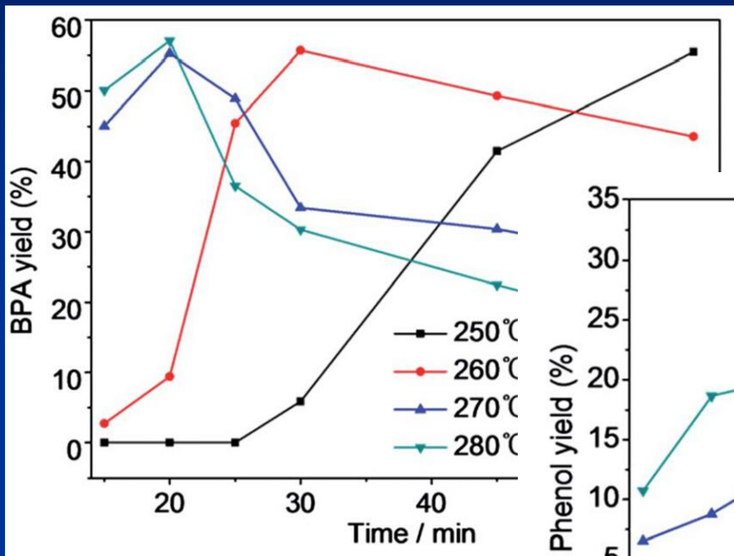
RSC Advance, 2014, 4: 19992-19998.



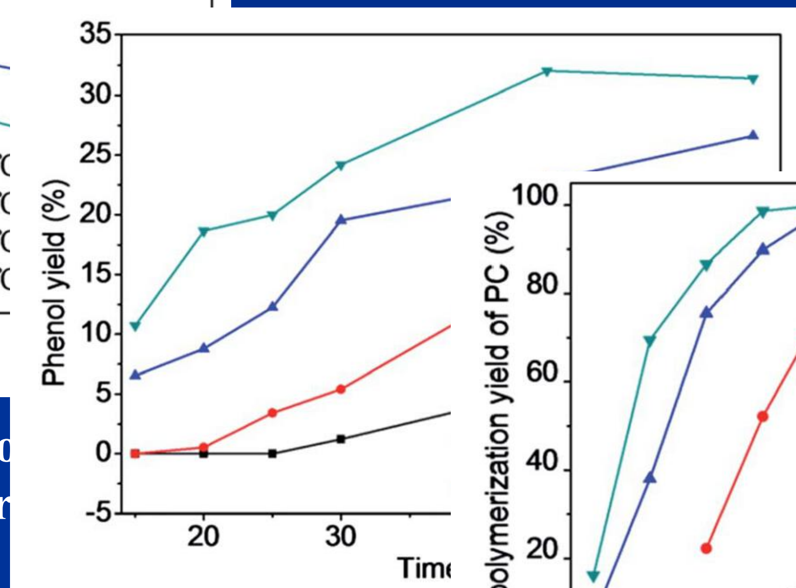
Efect of the $Mn(Ac)_2$/PC ratio on depolyme yield of PC at diferent temperatures



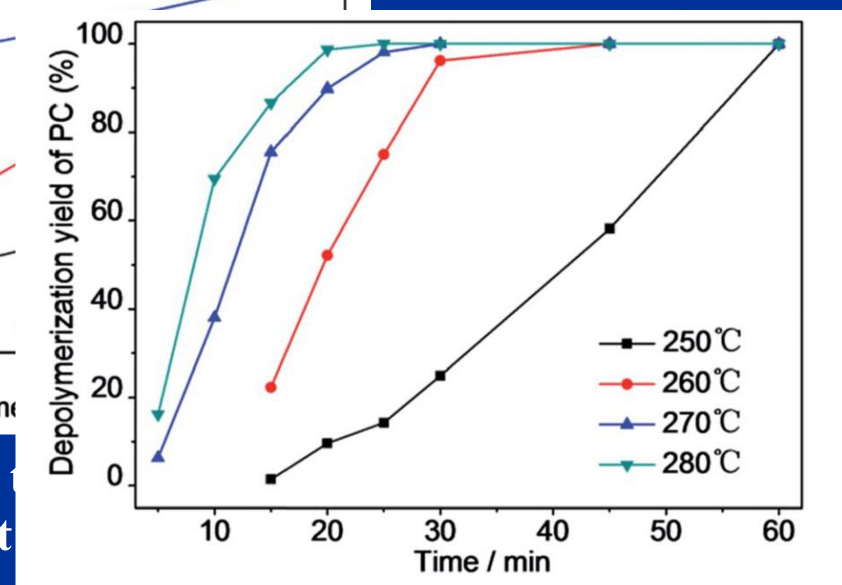
Efect of the $Mn(Ac)_2$/PC ratio on BPA and phenol yields at diferent temperatures



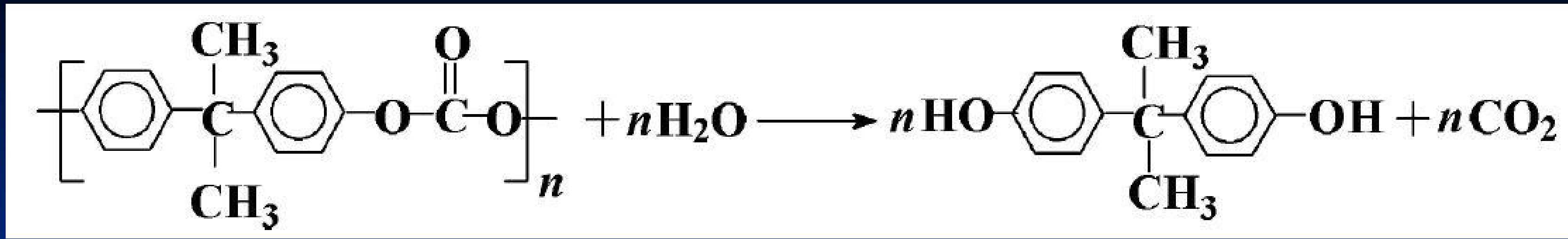
Efect of reaction time o
yield at diferent temper

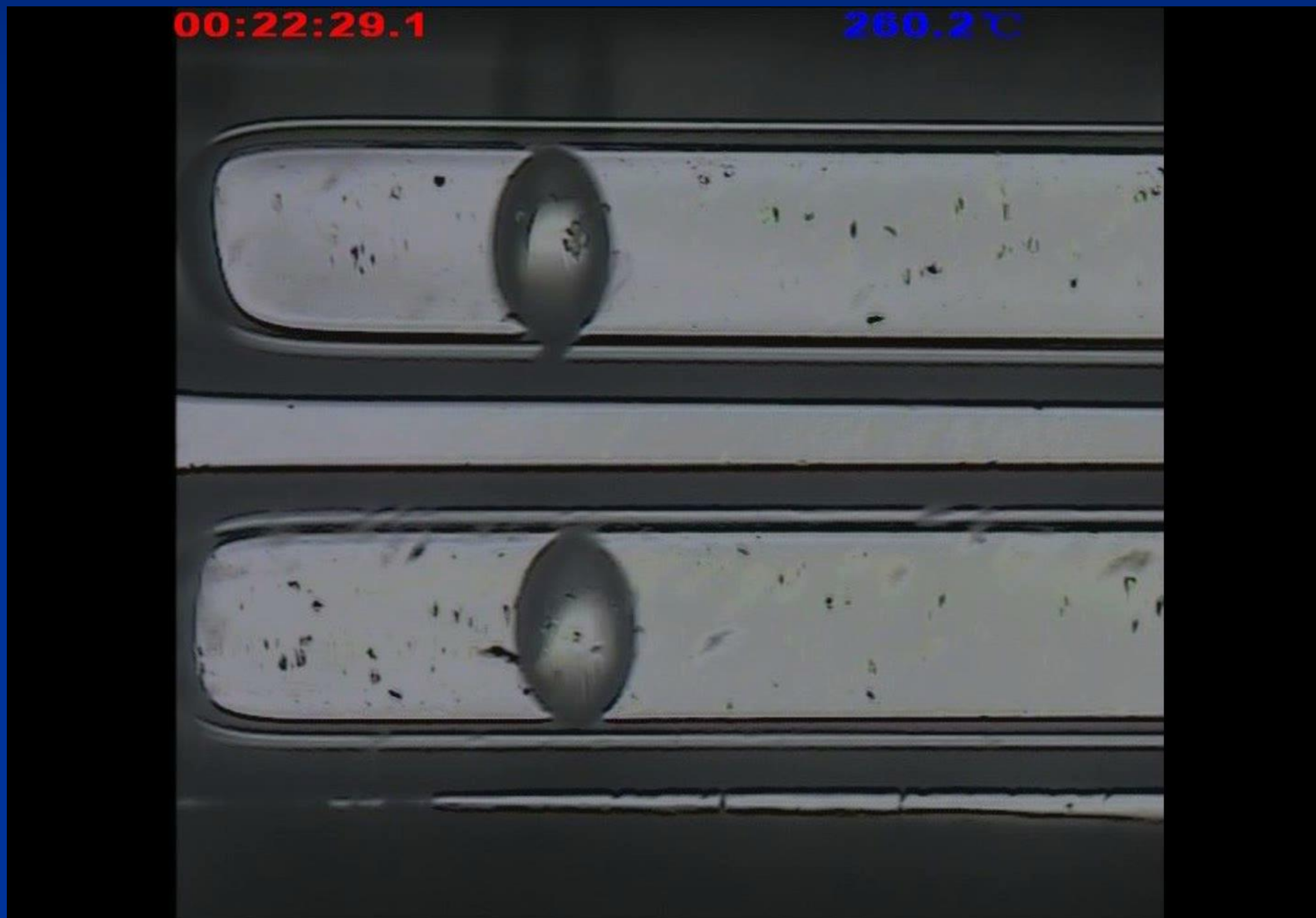


Efect of reaction t
yield at diferent



Efect of reaction time on depolymerization yield of PC at diferent temperatures




00:22:29.1
260.2℃

A new method for determining the volume expansion factor of CO_2 + petroleum model compounds

5

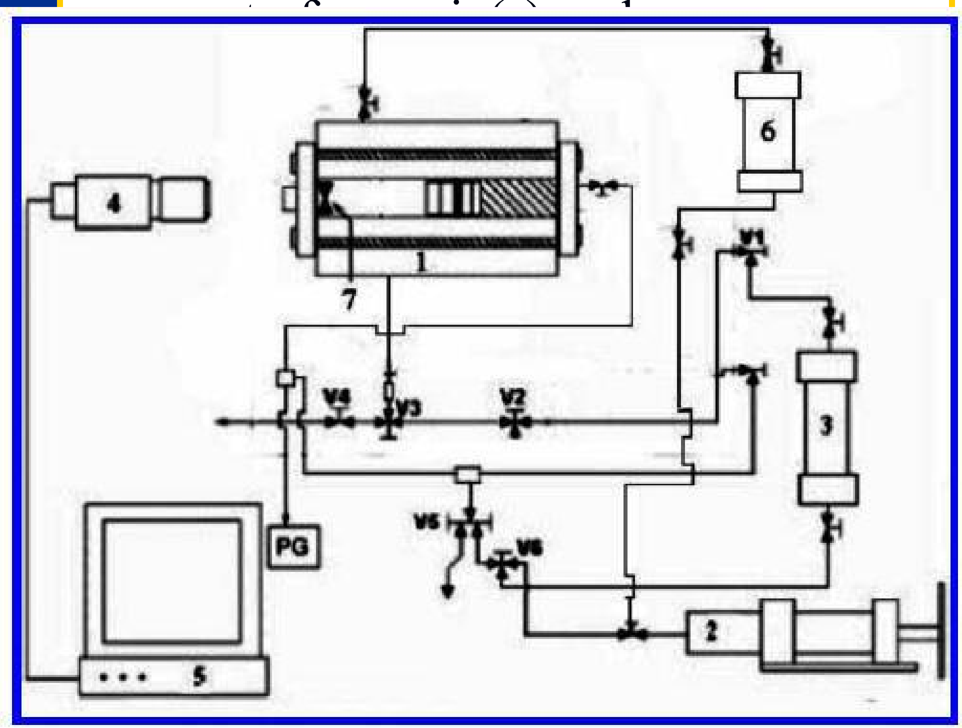
- The traditional methods for expansion
- A new method for determining volume expansion of CO_2 + petroleum model compounds

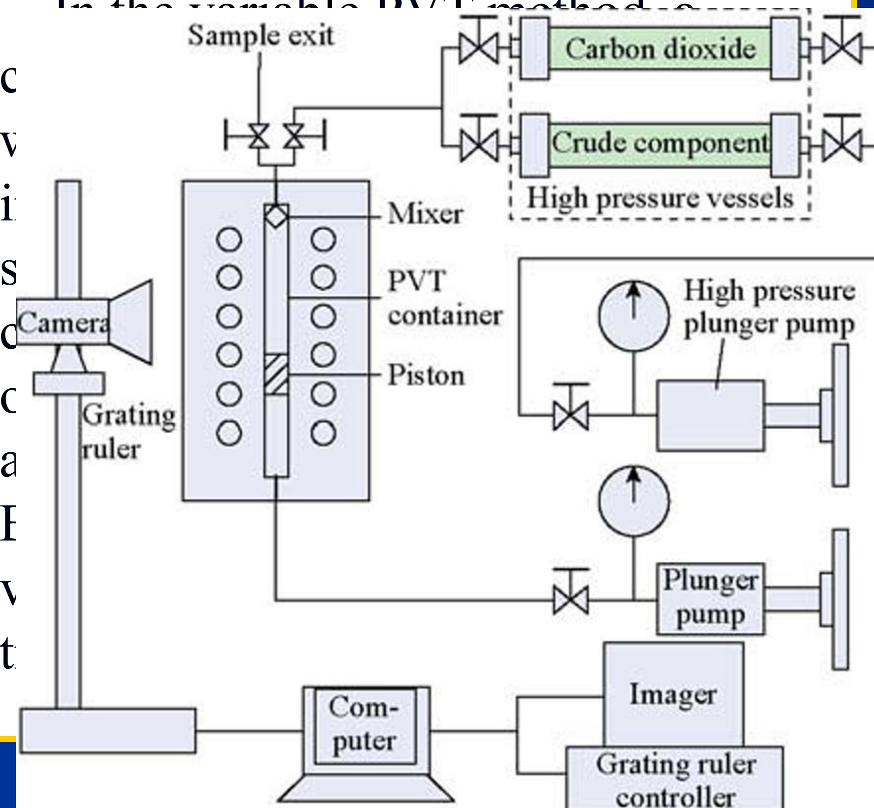
Enhanced oil recovery(EOR)

- CO_2 injection has been widely accepted as an effective technique for enhanced oil recovery (EOR) used by the oil industry since 1970s . Injection of CO_2 helps lower the viscosity of crude oil, reduce its interfacial tension, increase its mobility and cause oil swelling in the reservoirs which improves oil recovery. Meanwhile, this technique can effectively reduce greenhouse gas emission by permanent storage of CO_2 in geological formation . As the basic data of CO_2 - EOR, the volume expansion of CO_2 + organic(s) systems have been studied over the past decades with fixed or variable pressure - volume - temperature (PVT) methods.

5.1 The traditional methods for expansion

Fixed PVT method	Variable PVT method
In the fixed PVT method, certain	





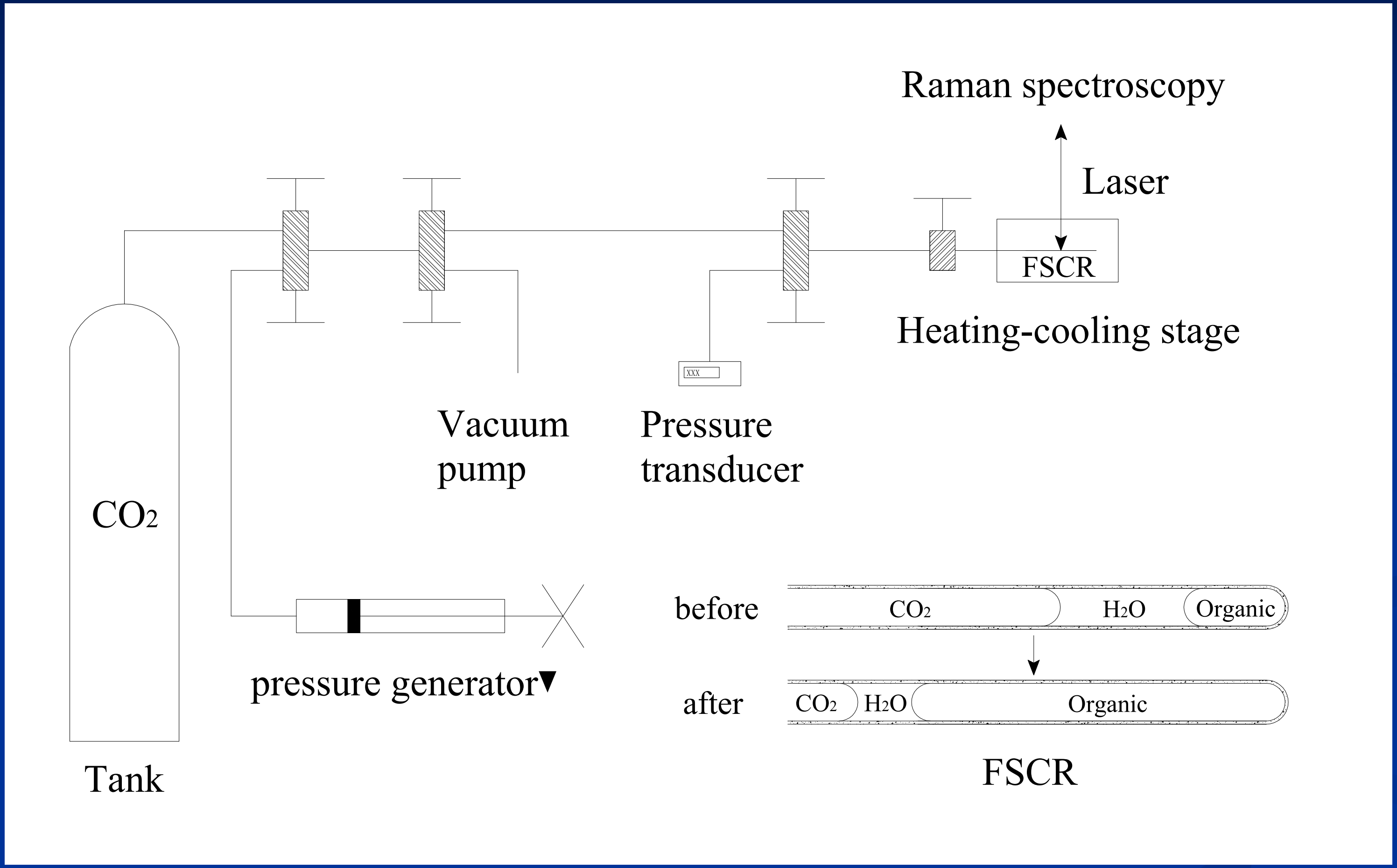
All of these traditional PVT methods had a high reagents consumption and temperature gradient.

The fixed PVT method was easy to cause the vaporization of organic(s) at higher temperatures.

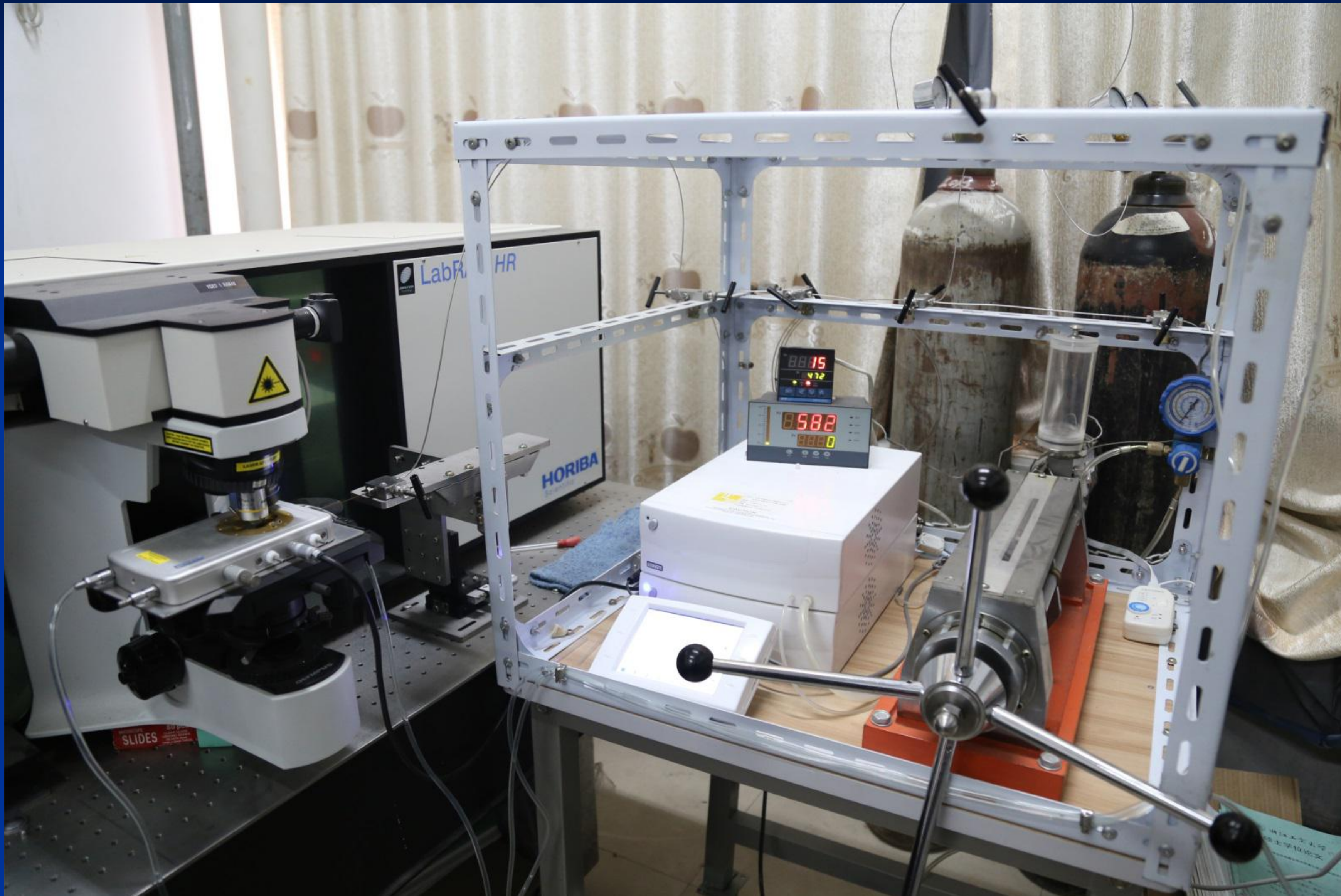
The variable PVT method was hard to determine the transitioning point at high CO_2 molar fraction and the CO_2 + organic(s) system was easy to oversaturation at low temperatures.

5.2 A new method for determining volume expansion of CO_2 + petroleum model compounds

A new method using a fused silica capillary reactor (FSCR), combined with heating-cooling stage, pressure generator, and co-focal Raman spectrometer has been applied to measuring the volume expansion of CO_2 + petroleum model compounds. This method using micrometer to measure the volume accurately, water seal to prevent the vaporization of organic(s), a microreactor to decrease the temperature gradient and Raman spectroscopy to ensure system reached phase equilibrium, which is shown to be efficient and generally better than the traditional PVT methods.



The schematic diagram of CO_2 + petroleum model compounds volume expansion measuring system.


HORIBA
SLIDES

Experimental section A

The procedure for measuring the volume expansion of organic with temperature at atmospheric pressure

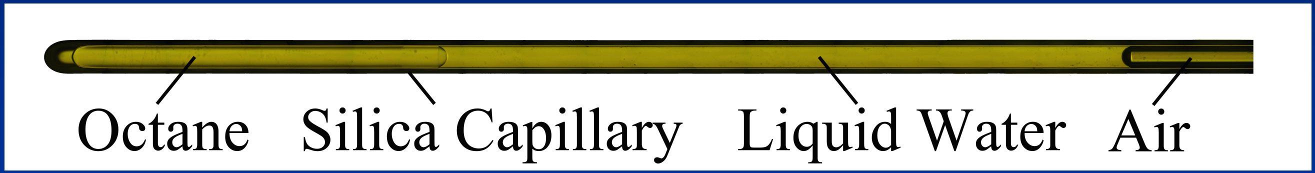
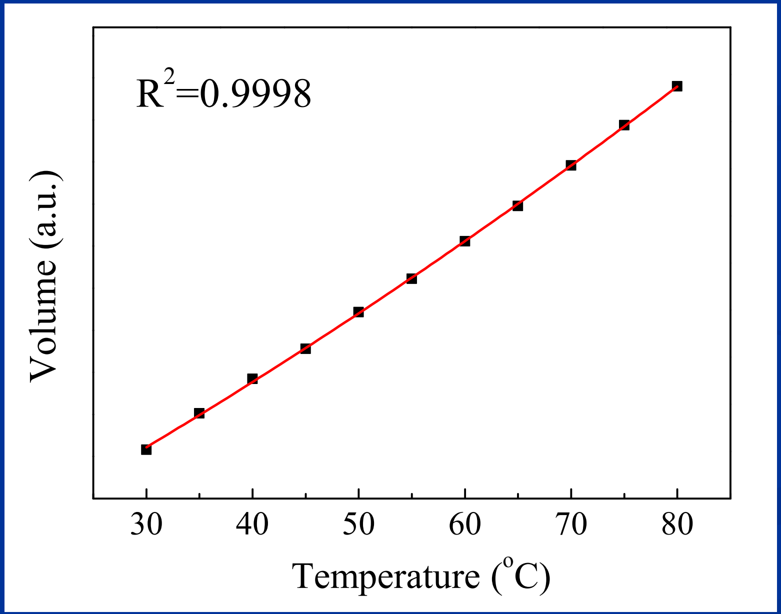


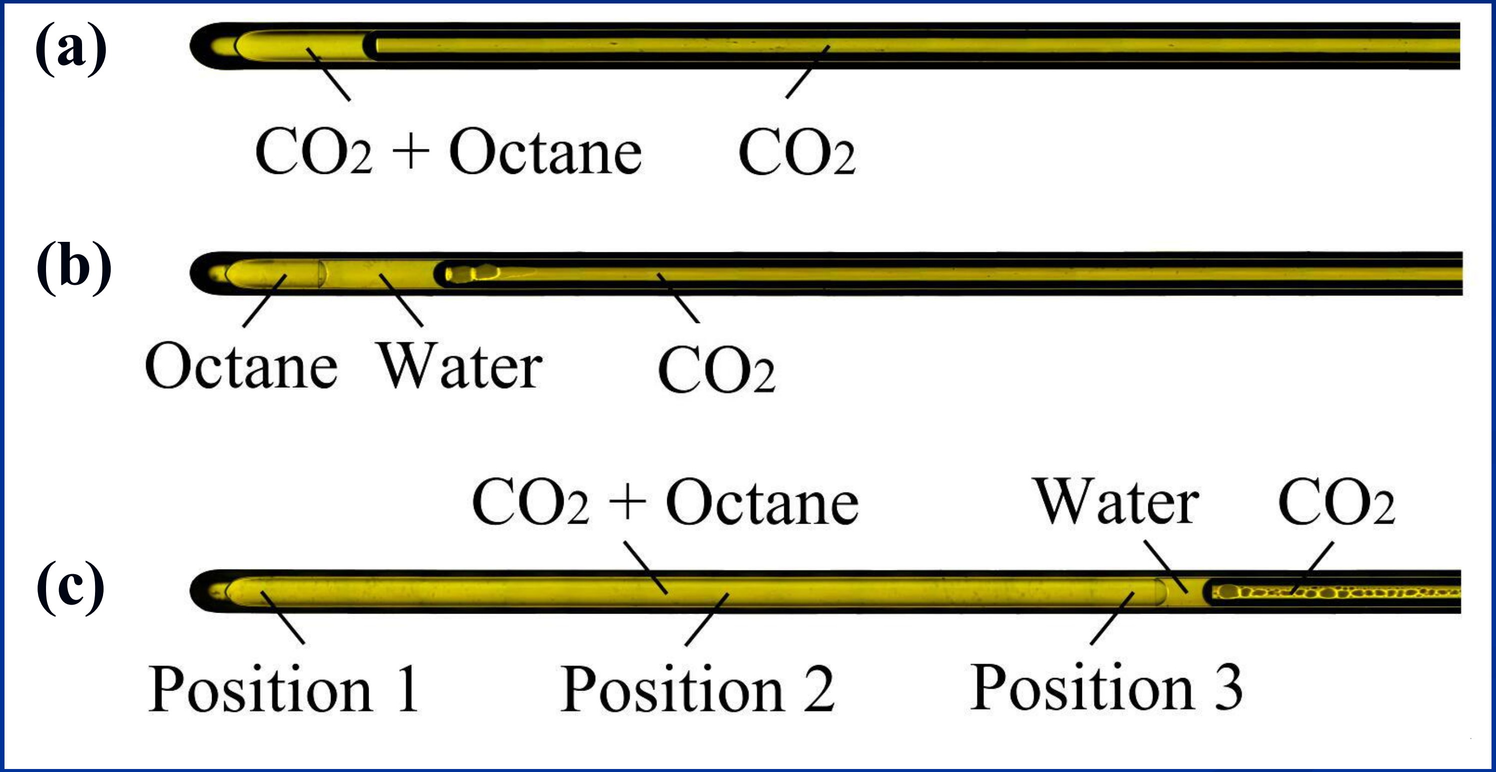
Image of octane in FSCR showing octane, liquid water and air



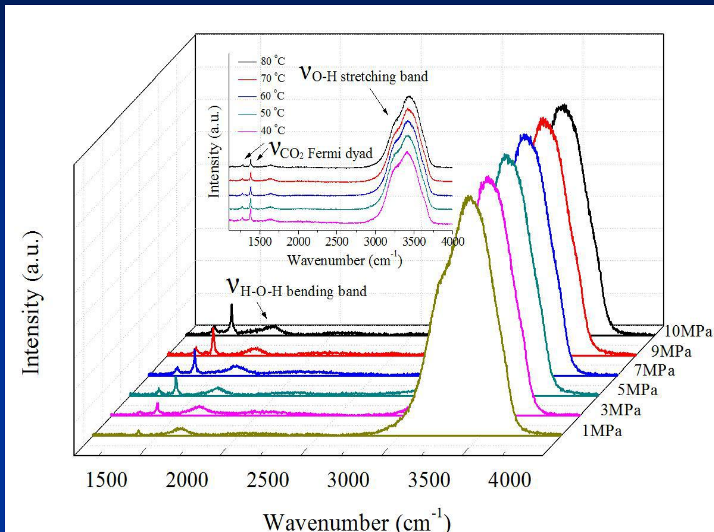
The volume expansion curve of octane from 30 to 80 ^{o}C at atmospheric pressure

Experimental section B

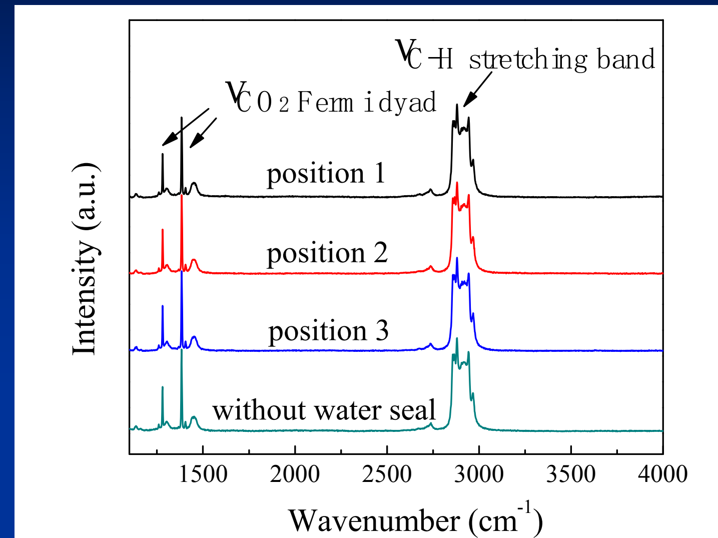
The procedure for measuring the volume expansion of CO_2 + octane system with temperature at diverse pressure



(a) Image of CO_2 + octane system without water seal in FSCR, showing octane and CO_2, (b) Image of CO_2 + octane system in FSCR before experiment, showing octane, water and CO2, (c) Image of CO_2 + octane system in FSCR after experiment, positions 1 to 3 indicate the spots for Raman spectroscopy analyses



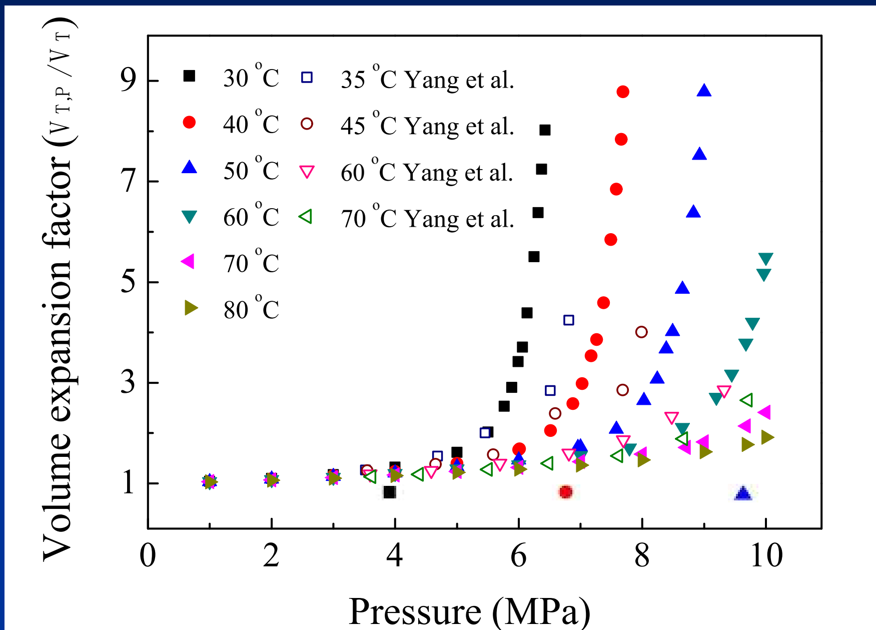
The Raman spectra of water in FSCR from 1 to 10 MPa at 80 °C and from 40 to 80 °C at 8 MPa.

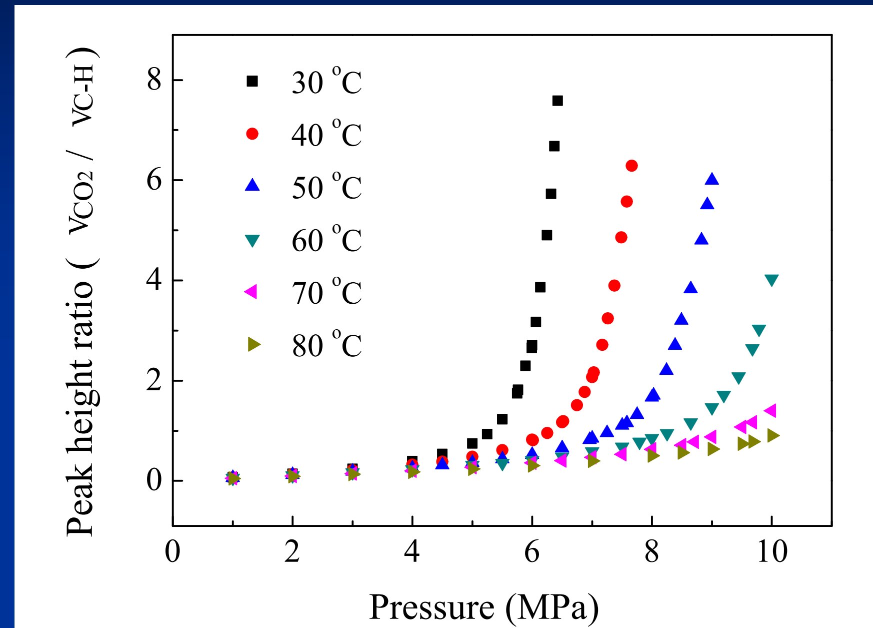


Raman spectra of CO_2 + octane system at 60 °C, 8 MPa

As shown in figure, the Raman spectra of water only contain the H–O–H bending band at 1629 cm^{-1}, the O–H stretching band in the region of 2800–3800 cm^{-1}, and the CO_2 Fermi dyad at 1280 cm^{-1} and 1385 cm^{-1} during the whole procedure, indicating that octane was not detected in water

The Raman spectra collected from three different positions in the FSCR showed the same relative band intensities between CO_2 Fermi dyad and the C–H stretching band of octane at 1280 cm^{-1}, 1385 cm^{-1} and 2800–3000 cm^{-1}, indicating that CO_2 + octane system reached phase equilibrium becomes a homogeneous solutions in FSCR

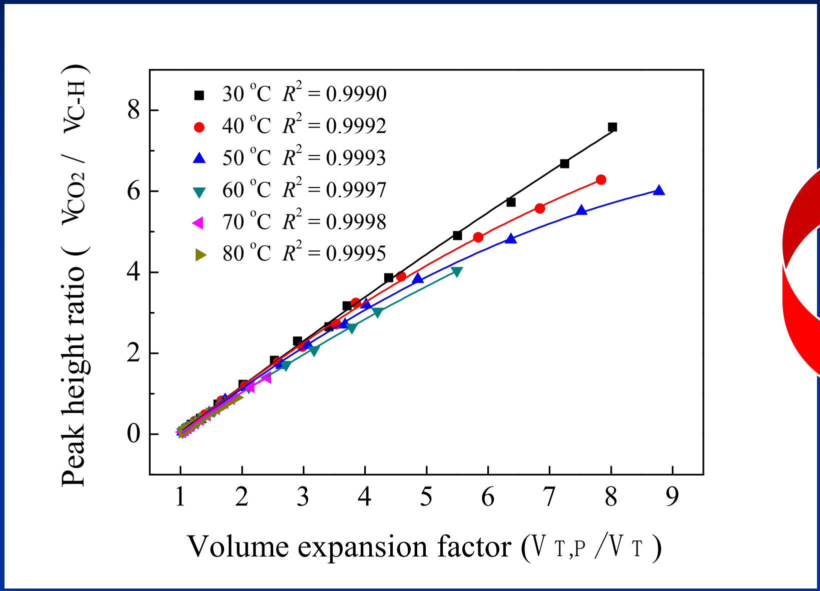




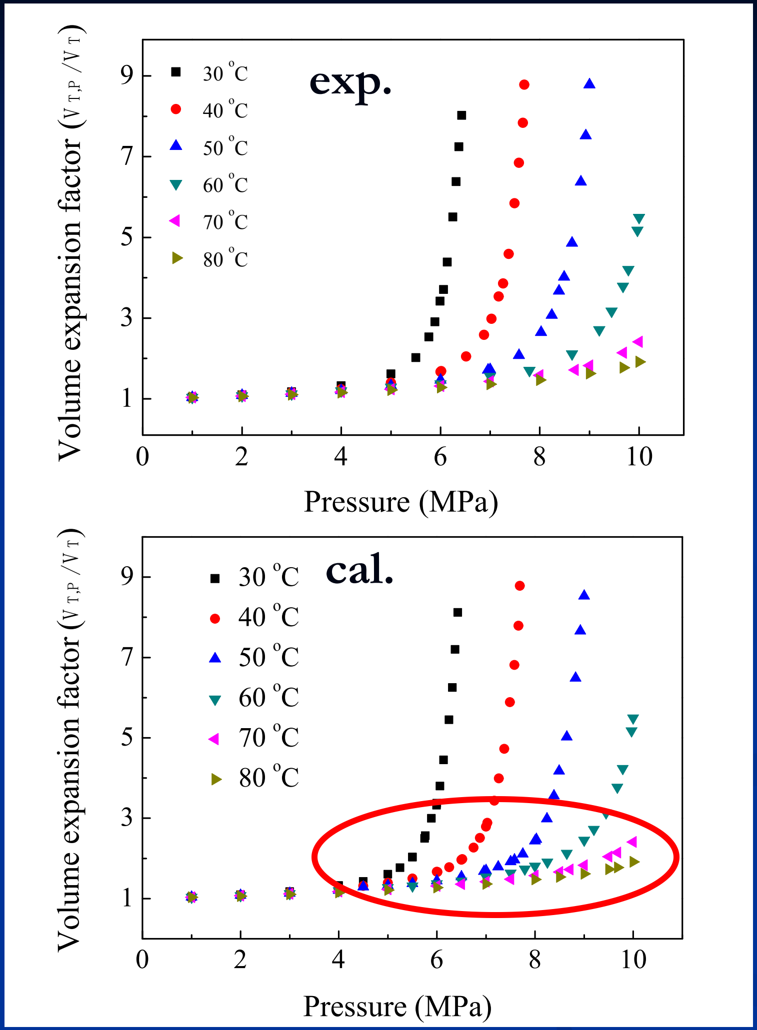
The volume expansion factor curve of CO_2 + octane system from 30 to 80 °C and 1 to 10 MPa

The peak height ratio curve of CO_2 + octane system from 30 to 80 °C and 1 to 10 MPa

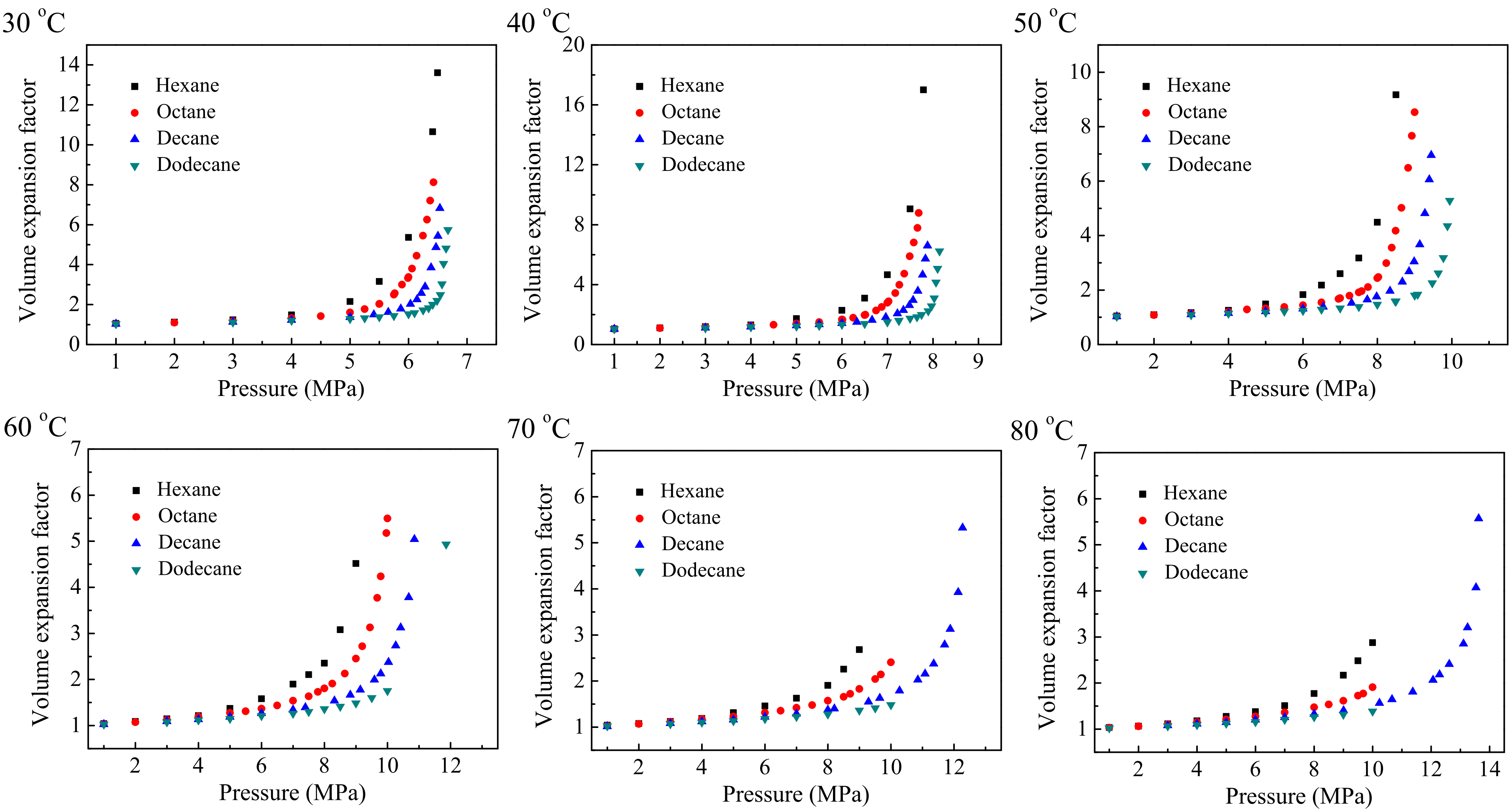
The peak height ratio of CO_2 Fermi dyad and C–H stretching band of octane had a similar tendency as the volume expansion factor of CO_2 + octane system



The relationship between the volume expansion factor and peak height ratio of CO_2 + octane system



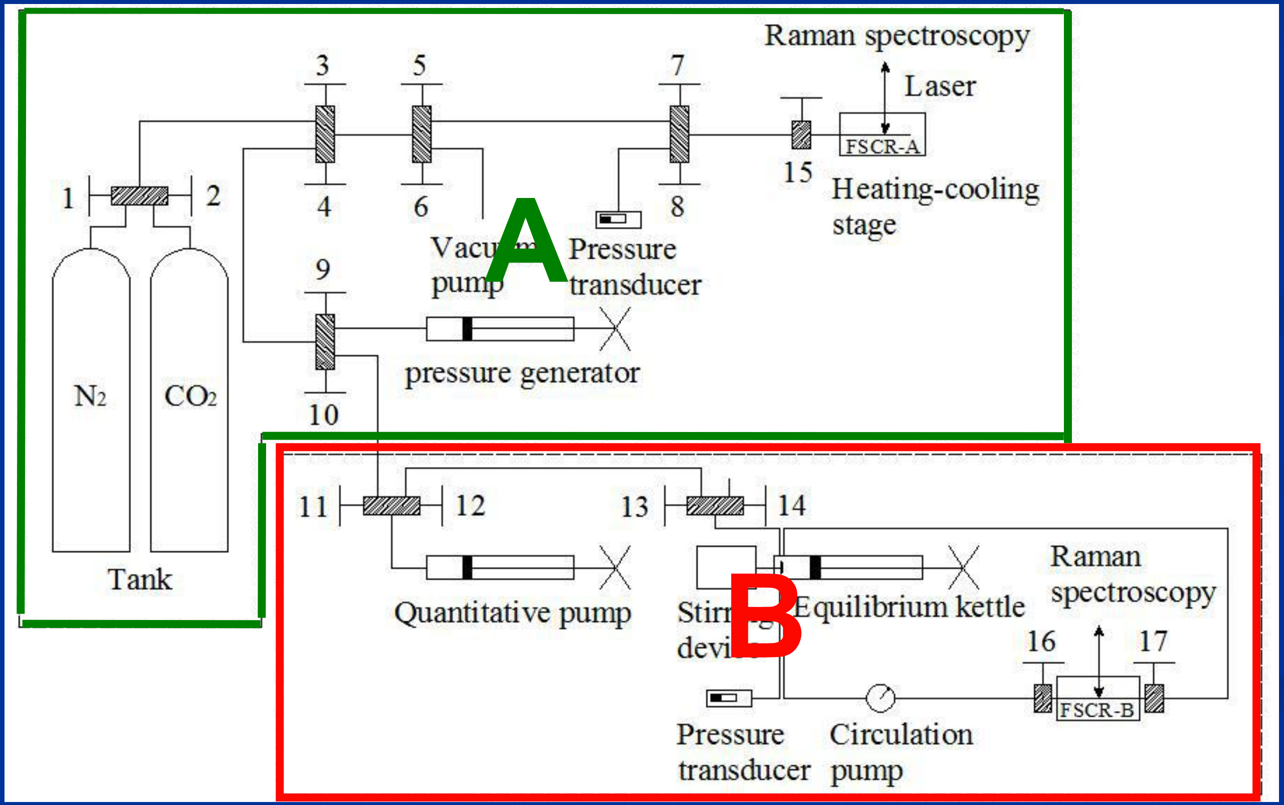
The relationship between volume expansion factor and peak height ratio can be represented by different quadratic equation at different temperature, with $R^2 \geq 0.999$. Indicating that peak height ratio could represent volume expansion factor indirectly.



The volume expansion factor curve of CO_2 + Hexane/Octane/Decane/Dodecane system

Future work

A new method using a fused silica capillary reactor (FSCR), combined with heating-cooling stage, pressure generator, equilibrium kettle and Raman spectroscopy has been applied to in-situ measuring CO_2 solubility in brines.



The schematic diagram of CO_2 solubility In-situ determine system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30.0
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搅拌
高压泵
加热
总电源
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Summary

- A new method for studying chemical reaction in sub- or super-critical water has been developed.
- Solubility of hydrophobic organic compounds in hot compressed water and SCWO were conducted in FSCR, and in situ Raman spectroscopy was used to analyze the products qualitatively and quantitatively. At the same time, the physical phenomenon was observed under a microscope and the images were recorded by a digital recorder continuously.
- The new method has a great potential for studying chemical reactions in fluids near their critical conditions.

Advantages of FSCR

★ The volume of FSCR is much smaller than that of the stainless autoclave, reducing from milliliter to microlitre:

It is environmental friendly because of the low amount of material consumed.

Resistance of mass transfer and heat transfer are reduced, and then the kinetics approach to the intrinsic kinetics.

Reactor is safe even if explosion happened.

★ Optically transparent capillary, what happened during reaction can be watched and recorded exactly with the help of microscope and digital recorder, which is much helpful to understand the reaction mechanism by Raman spectra in situ.

★ Round-sectioned FSCR with OD 0.3mm / ID 0.1mm can withstand H_2O pressures of at least 333 MPa at 600 ℃, and CO_2 pressures of at least 350 MPa at 600 ℃, respectively, which can not be done in ordinary reactors easily.

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- *感谢 国家自然科学基金委员会*

National Natural Science Foundation of China

THE END

THANKS

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