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Bao Nguyen Nhu **Application of acoustic levitation for the investigation of hydrogels**

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Application of acoustic levitation for the investigation of hydrogels

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PREFACE

This bachelor thesis entitled “Application of acoustic levitation for investigation of hydrogels” is the confidential information of research at the Ruhr University Bochum and the Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Oberhausen.

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ABSTRACT

This thesis is written as a requirement of the “Mechanical Engineering” Bachelor program at Vietnamese-German University. It reports the content of my working progress at the Ruhr University Bochum and the Fraunhofer UMSICHT during the last exchange semester of the program in Germany.

A lot of research has been carried out to investigate the sol-gel processing of hydrogel, but most of them are conducted in ambient condition. Thus, the studies about the transition under pressurized carbon dioxide are not broadly accessible. Moreover, the effect of different factors such as temperature, pH value of the solution, and type of catalyst, etc on gelation time under mentioned environment is not widely available. This thesis provides a possible method for the investigation of the gelation time in the sol-gel processing under high temperature and pressure CO_2 environment. The acoustic levitation technology can support the study; nonetheless, the investigation is unachievable with the current setup of the levitator at Ruhr University Bochum because of the gelation. To perform the determination of gelation point, a guideline is created to modify and improve the levitator. Then, this thesis creates a list of requirements and classifies the requirements according to the guideline. After that, possible solutions are generated with their disadvantages and advantages. Finally, the most optimal solution is chosen based on their pros and cons with explanation.

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NOMENCLATURE

Latin Symbols

Δz	distance between drop's centre and pressure node	m
R	radius of the oscillated drop	m
L_W	standing wave position	m
d_s	diameter of spherical sample	m
V_s	volume of spherical sample	m^3
k_0	wavenumber	$\frac{1}{m}$
c_0	speed of sound inside the gas medium	$\frac{m}{s}$
$\hat{v}$	sound velocity	$\frac{m}{s}$
k_0	static pressure distribution	$\frac{Ws}{m^3}$
F_{axial}	axial force	N
F_{AR}	acoustic radiation pressure	N
F_W	weight of the sample	N
F_R	Bernoulli negative pressure	N
g_0	gravitational force	$\frac{m}{s^2}$
$\hat{p}$	sound pressure	Pa
G'	storage modulus	Pa
G''	loss modulus	Pa
G	complex shear modulus	
l	oscillation mode	
f	frequency	Hz
f_M	low frequency signal	Hz
f_c	high frequency signal	kHz
U	levitation voltage	V_{pp}
U_0	initial amplitude	V_{pp}
$U(t)$	carrier signal amplitude	V_{pp}
Oh	Ohnesorge number	$dimensionless$

Greek Symbols

λ_0	wavelength	m
γ	amplitude	m
ω	frequency	Hz
ρ	density	$\frac{kg}{m^3}$
σ	surface tension	$\frac{N}{m}$
η	viscosity	$Pa \cdot s$
τ	damping constant	$\frac{1}{s}$
π	pi number	$dimensionless$
$\tan \delta$	loss tangent	$dimensionless$

LIST OF ABBREVIATIONS

CO_2	carbon dioxide
H_2O	water
HCl	hydrochloric acid
Si_2O	silicon dioxide
$Si(OH)_4$	silicic acid
$CaCO_3$	calcium carbonate
Na_2SiO_3	sodium silicate
$NaCl$	sodium chloride
Ca^{2+}	calcium ions
Mg^{2+}	magnesium ions
TEOS	tetraethyl orthosilicate
TMOS	tetramethyl orthosilicate
WG	waterglass
SCCD	supercritical carbon dioxide
SCD	supercritical drying
3D	three dimensional
FS model	Flory-Stockmayer model
LED	light-emitting diode
IFT	interfacial tension
AM	amplitude modulation

1 INTRODUCTION

Silica aerogel is a remarkable porous material which has more than 90 % air and less 10 % solid silica in cross-linked network structure form. Since it has extraordinary structural properties such as low density, high porosity, low thermal conductivity in air and low sound velocity [1], silica aerogel is being used both in technical and commercial fields such as thermal insulation for building and construction, aerospace, and super capacitor, etc [2]. Silica aerogel is produced by sol-gel processing where sol is a colloidal solution and hydrogel in the first step is a porous three-dimensional (3D) interconnected solid network. The sol is gelled by shifting the pH-value using acid or basic solution to obtain a solid hydrogel in the first step. Then, the liquid in the pores of solid gel is removed by supercritical drying (SCD) with carbon dioxide (CO_2) because CO_2 is a nontoxic and recyclable fluid. After these steps, silica aerogel can be obtained.

However, conventional aerogel processing is time consuming. Fraunhofer UMSICHT has developed a method to synthesize silica aerogel in granules form lately. Their method uses CO_2 at critical temperature and pressure which can be denoted by supercritical carbon dioxide (SCCD) to accelerate the whole production process. Moreover, this method can synthesize the whole aerogel production process which includes gelation, solvent exchange, and drying in the same system. As the result, the manufacturing process is shortening significantly.

However, the gelation under supercritical SCCD condition is happening very fast with Fraunhofer UMSICHT method. Therefore, the gelation process under this condition is still undetermined. Moreover, the investigation of gelation under pressurized CO_2 is not widely available and challenging because of the following five reasons:

1. The gelation occurs relatively fast during the sol-gel transition.
2. Traditional measurement methods are only possible for ambient condition.
3. The plant must withstand more than roughly 73 bar and 31°C to create SCCD condition.
4. The plant also needs to provide possibility to observe and analyse the transition.
5. The shape of the probe is spherical, and the plant must be able to float the probe.

With defining the gelation point parameters, it might be possible to optimize the aerogel production further. Besides the gelation time, there is still a lack of literature about physical properties of sodium silicate which are solution density, viscosity, and interfacial tension (IFT) in SCCD environment. Therefore, it is crucial to investigate the transition in sol-gel process and sodium silicate physical properties. An acoustic levitator at Ruhr-University Bochum is a suitable system for the investigation. However, with the current setup, the plant has some limitations for the study because of sol's unique behaviour. The goal of this project is to provide possible optimizations and improvements for the acoustic levitator based on theoretical approaches to investigate sodium silicate under high temperature and pressurized CO_2. To be more specific, the rework process will be:

- identifying and ranking requirements for the hydrogel investigation,
- stating the problem,
- developing different solution,
- discuss suggested solutions.

2 STATE OF THE ART

2.1 Hydrogel gelation

2.1.1 Definition of Hydrogel and Gelation

Hydrogels are networks of polymers which are meshed by using cross-linker. The cross-links between polymers can be strong chemical linkages, temporary entanglements, or weak chemical interaction. With the cross-linked structure, the gels can remain insoluble while absorbing aqueous solutions, physiological fluids, or water [3].

Since aerogel synthesis involves a sol-gel process, the formation of hydrogel is important for the whole process. The liquid pores inside the hydrogel then can be replaced by air without destroying the gel network structure [1]. Thus, aerogel is created with outstanding performance in many applications because of the unique 3D nanoscale network with open pores [4].

The transition from sol to hydrogel in sol -gel process involves 2 reactions which are hydrolysis and condensation. The first reaction replaces water molecules or hydroxyl groups with alkoxy groups in the precursor structure. Then, the condensation reaction takes place by expanding the molecule chain and releasing the water molecules derived from the hydroxyl group. Since the two reactions can occur continuously, an additional catalyst is introduced to control the rate and extend of each reaction.

To produce the sodium silicate precursor base sol, sodium ions must first be replaced by hydrogen ions to produce silicic acid. In addition, the sodium silicate precursor base sol can be called waterglass (WG). If the sodium ions remain in the gel network, dried gels will be translucent and weak because sodium ions do not dissolve in alcohol [5]. To replace sodium ions with hydrogen ions, there are 2 methods:

1) Ion exchange: sodium silicate will flow through an ion exchange column which contains string acidic cation resins. This method must be performed before the sol is changed to gel state. [6]
2) Vapour passing method: By using vapour oven, water inside the gel can be vaporized from the result temperature and pressure. Sodium ions will be removed during this process. [7]

Sodium silicate reacts with water and acid catalyst hydrochloric acid (HCl) to produce silicic acid $Si(OH)_4$ as demonstrated in the following reaction.

$$Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2NaCl$$

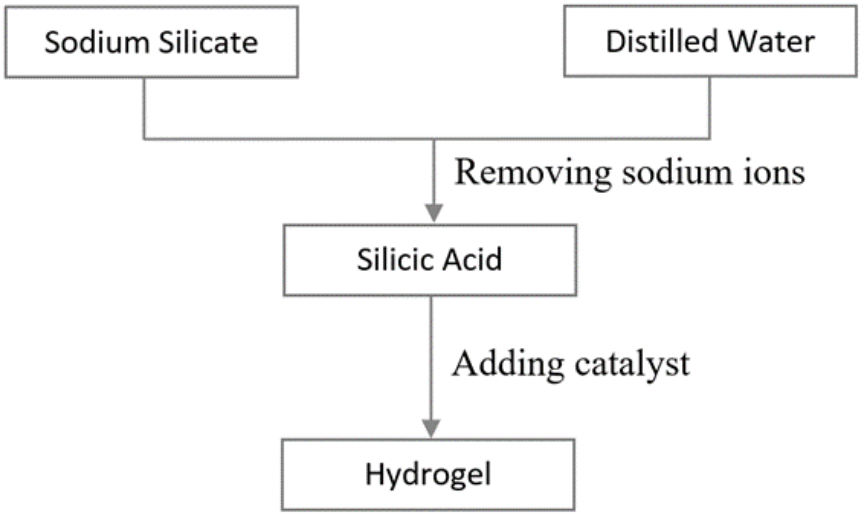


Figure 1: Hydrogel synthesis from sodium silicate

Sodium silicate hydrogel fabrication [8].

Gelation is defined to be a transition from sol to gel when the sol particles start to grow and collide with each other. Then the condensation appears and form macroparticles. The sol is classified as a gel when it has an elastic response to stress and sudden rise of viscosity. The duration of the transition is defined as gelation time and the start of the transition is defined as gelation point. In addition, there are many factors affecting the gelation time such as the pH-value of the solution, temperature, types of solvent, etc [9]. Throughout the decades, theoretical and experimental have been developed to determine the exact gelation time.

These are 2 typical theoretical approaches:

- The Flory-Stockmayer model (FS model) is the oldest thermodynamic description of gelation. The gelation indicates the transition of a liquid to solid by chemical reactions. However, the model focuses on general parameters which indicate a polymer solution such as an extent of reaction and a functionality instead of describing a local aggregate [10].
- The Percolation theory describes the formation of closed loops and predicts a divergent density for large cluster [11]. However, the Percolation theory cannot give analytical solutions for the percolation threshold which corresponds to the gelation point or the size of distribution of polymers.

Experimental approaches usually interested in the changes of viscosity [12]:

- The loss tangent ($\tan\delta$) method determines the gelation point by measuring the viscoelastic response of the gel.
- Dynamic modulus measurement method accesses the dynamic modulus with time curves to indicate the gelation time base on the loss tangent.
- Complex viscosity measurement method uses complex viscosity which is the derivative of storage modulus G' and loss modulus G'' to indicate the gelation time.
- Torque measurement method determines the gelation time from the curve of torque vs time.

Since most of the mentioned experimental approaches are based on the loss tangent method which is developed by Sacks and Sheu [13], this chapter gives more detail about this method. The gelation time is determined by measuring the viscoelastic response of the gel as a shear rate function. Sacks and Sheu used a viscometer with a narrow gap to measure the complex shear modulus G. The accurate shear rate is obtained when the viscometer piston oscillates in the sol at a frequency ω (in Hz) and small amplitude γ (in m).

The complex shear modulus has the form

$$G = G'(\omega) + iG''(\omega) \tag{16}$$

where G' (in Pa) is the storage modulus and G'' (in Pa) is the loss modulus. The storage modulus describes the elastic component of the sol-gel, while the loss modulus which can be called viscous energy obtains from the viscous component.

The loss tangent is defined by the loss of relative measurement between the viscous energy and the energy stored in the system.

$$\tan\delta = \frac{G''}{G'} \tag{17}$$

Recently, SCCD is used as sol-gel polymerisation solvent to shorten the gelation time beside the conventional gel processing which produces gel under ambient condition. In this method, precursor and hydrolysis solution are injected inside an autoclave surrounded by SCCD. Douglas A. Loy et al. [14] reports that SCCD can be used as solvent for creating high porous structure.

2.1.2 Previous research

Many investigations have been conducted about the structure and the gelation time of hydrogels with different catalysts, molar ratios, and pH values during the sol-gel transition, but most of them are limited by atmospheric pressure.

Acid catalysts such as sulfuric, nitric, and hydrochloric, etc can be used to shift the pH value. This catalysis class does not change the structure of the gel significantly [8].On the other hand, base catalysts such as ammonia, and ammonium hydroxide reduces the gelation time and produces uniform gels with large pores volume [15]. Moreover, both acid and base catalyst (acid-base) can be applied continuously in a two-step catalysis process. The results from Pradip B. Sarawade et al. [16] shows that the silica aerogel has high specific surface area and pore volume, and the gelation time is short (Table 2).

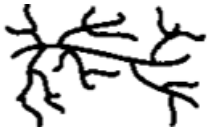
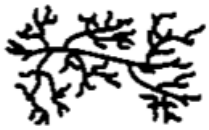
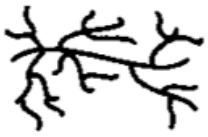
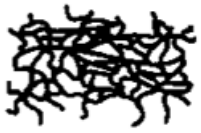
	Sol	Gel formation	Hydrogel
Acid catalysis			
Base catalysis			
Acid-Base catalysis		 	

Table 1: Hydrogel and gel formation

The influence of catalysis on the gel structure [11]

The pH value can be an indicator for the gelation, and it can be controlled by the amount and type of catalyst. As Pradip B. Sarawade et al. [5] stated, the gelation time of WG is different depend on the pH value. The following will expand the effect of different pH value on the gelation time and the structure of hydrogels.

- pH < 2, the sol has the longest gelation time. Moreover, a linear chain with low crosslink density is between silica particles at this high acidic pH value. Therefore, the resulting gel is a soft gel which is reversible and redispersed to solution form [9].
- pH ≈ 5, the viscosity starts to rapidly increase, and the gelation occurs due to the aggregation of silica monomer particles. Silica monomer is changed to particles at this point, and the particles begin to aggregate continuously into a gel network. In the pH value from four to five, the gelation time at this range is the shortest [5].
- pH >5, the aggregation of silica particles is slower at this high basic pH value. Therefore, the gelation time at this range increases. Moreover, there are more branched and the number of crosslinks between polymers [9].

Author	Catalyst	Gelation time
Fikret Kirkbir [17]	Acid	0.13 day - 2.5 days
Digambar Y. Nadargi [15]	Base	1 minute - 3 days
Luc Van Ginneken[18]	Acid/Base	~1 minute - 250 minutes
Pradip B. Sarawade [16]	Acid–Base	2 minutes - 15 minutes
A. Venkateswara Rao[19]	Acid–Base	1 minute - 10 minutes

Table 2: The gelation time of TEOS precursor in room temperature and atmospheric pressure

Salinity also affects the gelation time. Charge screening occurs after adding salt such as calcium ions (Ca^{2+}) or magnesium ions (Mg^{2+}) to an alkaline solution. Then, the gelation time is decrease [20].

Jurinak and Summers [21] found that temperature can affect the gelation time at fixed pH and salinity. The Arrhenius equation in their research shows that the gelation time decreases when the polymerization rate increases due the rise of temperature.

The influence of sodium silicate/water ratio on gelation time was investigated by Venkateswara Rao et al. [22]. The author stated that the gelation time decreases when the solid content in the solution increases.

Since most of the studies in the sol-gel process only preform under ambient pressure, there is a lack of literature research about the gelation time in high temperature and pressure environment especially compressed CO_2 [23]. Under pressurized CO_2 and room temperature, Preibisch et al. [23] observe a decline of gelation time of calcium carbonate ($CaCO_3$) when increasing the CO_2 pressure. Under SCCD condition, the tetramethyl orthosilicate (TMOS) gels in Douglas and Edward experiment [14] are similar the conventional gels. However, in their gels some cracking appears because of syneresis (aging). This problem can be avoided by producing granular gels. Then, the cracking is almost neglectable due to small diameters of the gel-particles. Moreover, Moner-Girona et al. [24] also used SCCD as an attractive medium and formic acid as condensation agent. However, the authors perform the whole process in one system and are interested in the resulting product which is silica aerogel.

2.1.3 Future possibility

A new parameter which is pressurized CO_2 also accelerates the gelation rate resulting more stable and homogeneous hydrogels with high porosities, surface area and strong pore connectivity [23]. Moreover, temperature also affects the gelation time under atmospheric pressure. By applying both temperature and pressure factors, the phase of CO_2 can be in liquid, gas, or supercritical form. As the result, the gelation time of homogeneous sols might vary. SCCD has already been proven that it accelerates the sol-gel process and produces an identical gel compared to the gel produced in the traditional way. Therefore, it might be scientific relevant to study correlation between levitated temperature and constant pressure in the future. However, the sol-gel processing under compressed CO_2 or supercritical CO_2 is usually performed in an autoclave with a limited possibility for a visual observation. Furthermore, the transition from sol to solid gel happens relatively fast. These are some of the many reasons that limit the investigation under mentioned conditions. Thus, the investigation cannot be proceeded because a plant with suitable technology and equipment is not available. Beside temperature and pressure, other parameters that are mentioned in section 2.1.2 also affect the gelation time under atmospheric pressure. Their influence on gelation time under high temperature and pressure is also worth to investigate. This thesis aims to provide a concept to determine the gelation time under high temperature and pressure as a foundation for future research.

2.2 Acoustic levitation

Since acoustic levitation provides contactless measurement and this technology can operate under high temperature and pressurized CO_2, acoustic levitation can be one possible option to determine the gelation time.

2.2.1 Overview about acoustic levitation

A transducer is emitting and generating ultrasonic waves with the wavelength λ_0 (in m):

$$\lambda_0 = \frac{2\pi}{k_0} = \frac{c_0}{f} \tag{1}$$

where k_0 (in $\frac{1}{m}$) is the wavenumber; c_0 (in $\frac{m}{s}$) is the speed of sound inside the gas medium; and f (in Hz) is the frequency. The ultrasonic waves are reflected from a coaxial, concave, or flat reflector which is mounted perpendicular to the direction of ultrasound emission (Figure 2).

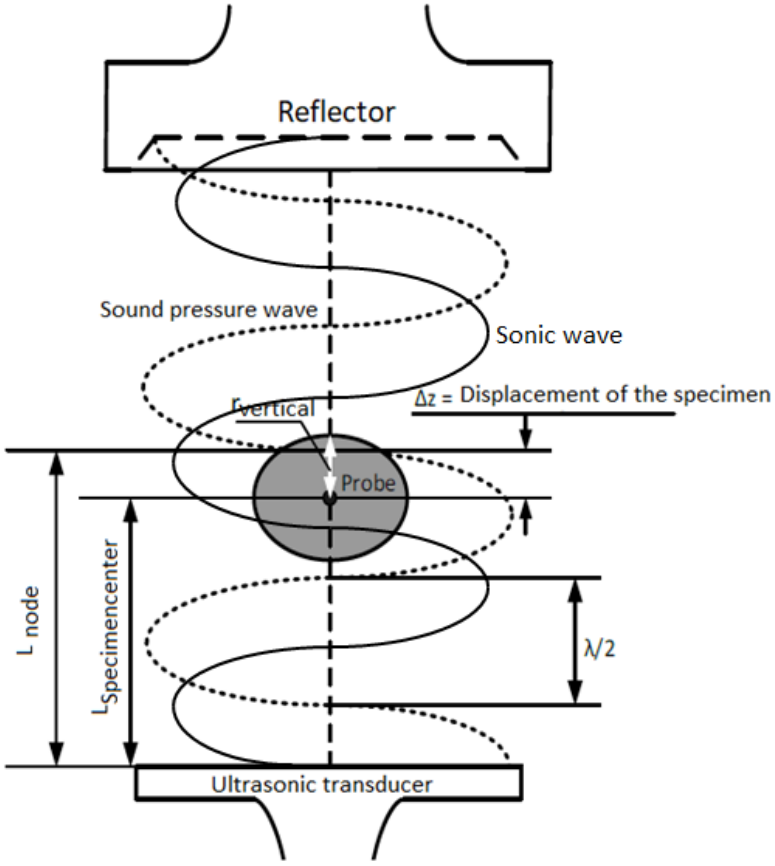


Figure 2: Schematic of an acoustic levitation principle

Standing ultra-sonic wave at the probe location [25]

A standing wave (standing ultrasonic field) forms when the distance L_W (in m) between the transducer and the surface of the reflector is equal to an integer n (n= 2, 3, 4...) multiplied with the half of the wavelength λ_0.

$$L_W = \left(n \times \frac{\lambda_0}{2}\right) \tag{2}$$

The standing wave consists of a sequence of sound pressure bumps and nodes. Liquid or solid probes can be positioned in these sound pressure nodes. At these nodes, probs are held axially because the maximum sound pressure locates above and below them (Figure 2). Furthermore, the maximum sound velocity is generated around the pressure nodes. The sound velocity is the speed of sound-transmitting particles moving back and forth in the acoustic field. Bernoulli forces are developed and held radially the sample, because the air molecules at this area move at a very high speed. This prevents the sample from lateral migration while levitating.

Since the standing wave consist of the sound velocity amplitudes ($\hat{p}_{max}, \hat{v}_{max}$), and sound velocity nodes $\hat{p}_z = \hat{v}_z = 0$, the following relationships of sound pressure $\hat{p}$ and sound velocity $\hat{v}$ (in $\frac{m}{s}$) is important for the kinetic and potential energy of the standing soundwave[26].

$$\hat{p} = \hat{p}_{max} \cdot cosk_0 z \tag{3}$$

and

$$\hat{v} = \hat{v}_{max} \cdot sink_0 z \tag{4}$$

where z (in m) is counted from the surface of the reflector (z=0).

The axial positioning forces (levitational force) F_{axial} (in N) can be calculated by the axial gradient integration of the pressure distribution over the entire sample area for a spherical and sonic sample with diameter d_s (in m), the volume V_s (in m^3), density ρ_s (in $\frac{kg}{m^3}$), the density of the carrier medium ρ_0 (in $\frac{kg}{m^3}$), and gravitational force g_0 (in $\frac{m}{s^2}$). [26]

$$F_{axial} = \frac{5}{8} k_0 \rho_0 \hat{v}_{max}^{\,2} \cdot V_s \cdot f_1(x) \cdot \sin(2k_0 \Delta z) = \rho_s \cdot V_s \cdot g_0 \tag{5}$$

With the geometric function

$$f_1(x) = \frac{3}{x^2}\left(\frac{\sin x}{x} - \cos x\right) \tag{6}$$

where $x = k_0 d_s$

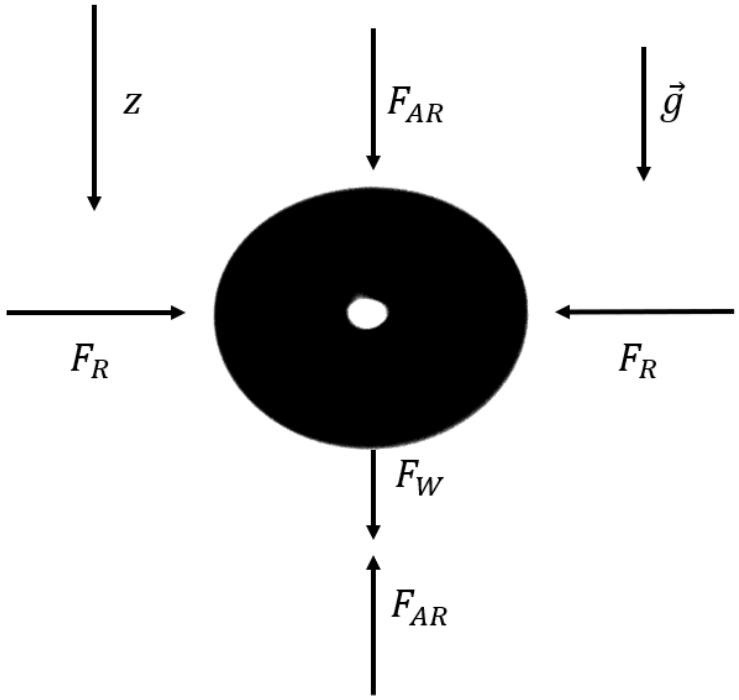


Figure 3: Schematically shows an acoustically levitated droplet with the force components

There are two forces help positioning the probes in the standing sound field. The acoustic radiation pressure is represented by F_{AR} (in N) and the Bernoulli negative pressure is described by F_R (in N). The axial force $F_{axial} = \sum F_{AR}$ compensates the weight of the sample $F_w = \rho_s \cdot V_s \cdot g_0$ (in N) while levitating. The radial force F_R prevent the probe from sliding out of the pressure node. Therefore, F_R is important to stabilize the levitated probe. In addition, the droplet is deformed into an oblate in axial direction because the axial force F_R is five times bigger than the radial force F_{AR} [26].

The location of probe's centre locates slightly below the pressure node because of the weight of the probe and the gravitational force in Figure 3. These forces are pulling the probe downward during levitating. The distance Δz (in m) is the distance between the nearest sound pressure node and the center of the leviated probe (Figure 2). It also can be approximated mathematically.

$$\Delta z = L_{node} - L_{probecenter} = \frac{1}{2k_0} \sin^{-1}\left(\frac{8}{5} \times \frac{\rho_s g_0}{\rho_0 \hat{v}_{max}{}^2 k_0 f_1(x)}\right) \tag{7}$$

2.2.2 Property measurement

Density of an unknown liquid

With relation between the axial levitation force and the gravity force, density of the droplet can be determined. If the droplets are levitated under the same conditions of sound field which are the wave number, sound velocity amplitudes, the distance Δz, gravitational forces, dimensionless geometry factor and especially the volume of the drop, the axial forces will only depend on the density of the droplet. Therefore, the density of an unknown liquid can be identified by decreasing the levitation voltage V_{pp}

Since the axial force can be manipulated by changing the levitation voltage input, the density of an unknown droplet can be found by determining the minimum levitation voltage of both reference and unknown droplets. The minimum levitation voltage U (in V_{pp}) is determined at the drop out point. During the process, the transducer frequency and the position of the reflector must remain the same. The density of an unknown droplet (in $\frac{kg}{m^3}$) can be calculate by using the minimum levitation voltage of a reference droplet with known density through the below relation [27]:

$$\frac{\rho_1}{\rho_2} = \left(\frac{U_1}{U_2}\right)^2 \tag{9}$$

where the reference is index 2 with known density and the unknown is index 1.

The measurement procedure of density under high pressure can be found in section 3.1.2 after a description about the acoustic levitator.

Viscosity and interfacial tension of an unknow liquid

Viscosity and interfacial tension are calculated when the droplet experience damped harmonic oscillation. The drop is oscillated by an amplitude modulation which is introduced from the transducer drive signal. The low frequency signal f_M (in Hz) is overlaying the high frequency signal f_c (in kHz) which is in sine wave. Moreover, the low frequency also sinusoidally changes the structure of the carrier signal amplitude $U(t)$ (in V_{pp}) with the initial amplitude U_0 (in V_{pp}).

$$U(t) = U_0 \cdot [1 + M \cdot \sin(2\pi \cdot f_M \cdot t) \cdot \sin(2\pi \cdot f_C \cdot t)] \tag{10}$$

M is denoted as the depth of the modulation which controls the amount of voltage.

The drop will experience a damped oscillation when the depth of the modulation is changed to 0. The surface tension σ (in $\frac{N}{m}$) of the drop determines the oscillation frequency, and the viscosity η (in $Pa \cdot s$) tells the duration of damped out. For a spherical drop, Rayleigh and Lamb gives the following equations with some assumptions [28]:

- Small amplitude oscillations,
- Incompressible and inviscid drop,
- Neglect density and viscosity of the host medium
- Neglect the effect of drop's viscosity on the oscillation frequency

$$\sigma = \frac{3\pi \times f^2 \times \rho \times V}{l(l-1)(l+2)} \tag{11}$$

$$\eta = \frac{\tau \times \rho \times R^2}{(l-1)(2l+1)} \tag{12}$$

Where f (in Hz) is the frequency of drop shape oscillation, l is the oscillation mode which can be axisymmetric oblate-prolate shape oscillation ($l = 2$) and running mode, ρ (in $\frac{kg}{m^3}$) is the density of the drop, V (in m^3) is the volume of the drop, and τ (in $\frac{1}{s}$) is the damping constant. R (in m) is the radius of the oscillated drop can be calculated:

$$R = \sqrt[3]{\frac{3V}{4\pi}} \tag{13}$$

Prosperetti stated that, the equations (11) and (12) only valid when the dimensionless Ohnesorge number (Oh) of the drop is less than 0.1 [29].

$$Oh = \frac{\eta}{\sqrt{\rho\sigma R}} \tag{14}$$

Due to the viscosity of the drop, the reduction of measured oscillation frequency is calculated by

$$f = \sqrt{{f_{measurement}}^2 + \left(\frac{2\pi}{\tau}\right)^{-2}} \tag{15}$$

The measurement procedure of viscosity and IFT under high pressure can be found in section 3.1.2 after a description about the acoustic levitator.

2.3 Research questionnaires

This thesis aims to implement acoustic levitation technology for the investigation of WG's properties and the gelation time under high temperature and pressure regarding section 2.1.3.

In order to do so, the following criteria are taken into account:

- Apply the acoustic levitation technology
- Pressurize the testing environment with CO_2
- Can operate under high pressure and high temperature conditions
- Adjust the testing environment' pressure and temperature
- Maintain a constant pressure while changing the temperature
- Insert the WG probe inside the testing environment
- Allow the operator to observe the WG probe while oscillating in the acoustic field
- Indicate the WG probe' temperature during levitation
- Can perform many experiments in one take
- Perform the experiment consistently
- Remove WG after and during an experiment.

The next chapter gives a description about the current setup of the plant. Then, a discussion about the problems which are caused by the missing features. Finally, requirements for the current setup are determined to satisfy with the mentioned criteria.

3 REQUIREMENT DEVELOPMENT

3.1 Current setup

3.1.1 Acoustic levitator for high pressure

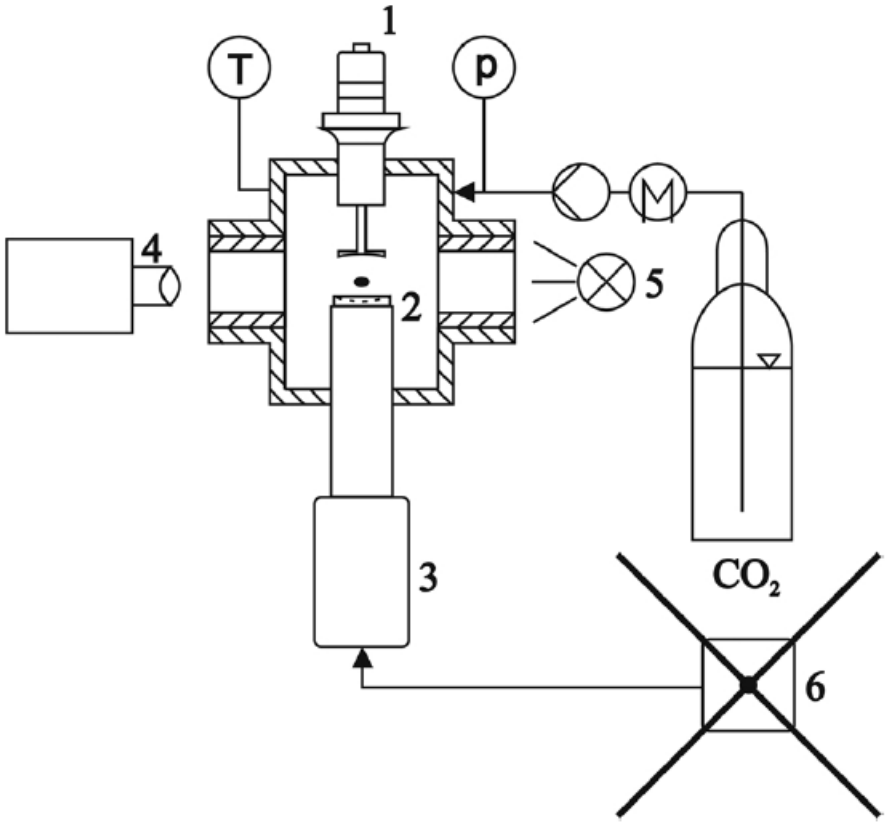


Figure 4: Acoustic levitator for high pressure systems

Components of the levitator: (1) sonotrode, (2) reflector, (3) swivel joint, (4) high speed camera, (5) LED light source and (6) screw press [30].

The following describes the setup of the acoustic levitator in Figure 4. The sonotrode (1), the reflector (2) and the CO_2 source are mounted in a high-pressure autoclave which can operate up to 200bar and 120°C. The sonotrode consists of an ultrasonic transducer and an ultrasonic horn. To generate ultrasonic wave, the sonotrode is excited by piezoceramics that are driven electrically. On the opposite side of the sonotrode, the concave reflector (2) is used to reflect sound wave from the transducer. Moreover, the reflector is installed on a magnetic coupling, which can vertically move the reflector.

In order to inject the droplet inside, a bore has been made on the reflector. Then, an injection syringe is located inside the magnetic coupling and able to move vertically to the pressure node through the bore. Then, the swivel joint (3) is used to connect the syringe and fixed pipe to the screw press (6).

Furthermore, image and video data of the droplet is captured by the high-speed camera (4) which is located outside the autoclave. To improve the quality of the image and video data, LED light source is installed opposite the camera.

3.1.2 Operation procedure

Firstly, the autoclave is heated to desired temperature by using the temperature controller (HTMC1/V 062071, Horst, Germany) before pressurizing the autoclave with CO_2. Then, an arbitrary function generator (AFG-2112, GW Instek, Taiwan) and a channel isolated amplifier (33502A, KEYSIGHT, American) is turned on and set to desired settings. With the help of the screw press (6) in Figure 4 and the injection syringe, a liquid drop is injected into the pressure node. After injection, the injection syringe must be carefully removed from the sound field using the swivel joint (3) in Figure 4 because the droplet might drop out of the sound field during this step. All of the real time data is recorded by the high-speed camera (4) in Figure 4 (CR3000x2, Optronis, Germany) equipped with a macro lens and a tele-converter (EX 2.8/105 DG Macro NAFD OS HSM and TC-2001, Sigma GmbH, Germany) by using Timebench software.

Density measurement

In order to perform density measurement under high pressure CO_2, the autoclave temperature is heated to the desired temperature. Then, the autoclave is pressurized by liquid CO_2 up to the required pressure. Because the temperature of CO_2 is lower than the autoclave temperature, the plant needs extra time to stabilize its pressure and temperature. After that, a frequency generator adjusts the transducer's eigen value. Then, the standing wave is created with by reaching the ideal distance between the reflector and transducer. A probe with known density is put to the pressure node by an injector. After that, the operator reduces the levitation voltage in steps of 0.01 V_{pp} until the probe fallout from the pressure node because the axial force cannot compensate the probe' weight. The procedure of the unknown density probes is the same as known probe. With the minimum levitation voltage, the density of the unknown probes can be calculated. However, the weight of a probe depends on its volume and the levitator cannot precisely inject a desired volume to the pressure node. Therefore, the result is not accurate.

Viscosity and interfacial tension measurement

The depth of modulation which can be called amplitude modulation (AM) is adjusted instead of the levitation voltage at the frequency generator. The probe is experiencing oscillations with axisymmetric prolate and oblate shape when AM is on. However, if the probe experiences rotation during this period, the operator must switch AM to 0 and turn it to 10 % again. Since the probe is in running mode which has an overlay rotation and resonance frequency, the measurement of viscosity and IFT are not possible with this mode. Then, the probe suffers damping after switching off the AM to 0. Additionally, the AM value depends on experiment liquids. With water base liquids, the value AM of 10 % is enough for the measurement. For liquids with higher viscosity a higher AM might be necessary. After turning off the AM, the probe suffers a damped harmonic oscillation. Then, the high-speed camera which has up to 2000 frame rate per second is used to record the damping of the probe. With the help of MATLAB codes, the viscosity and IFT value can be calculate from image processing toolbox.

3.2 Requirements

The current setup is not suitable for the investigation of gelation. The plant requires some modifications to execute the mentioned tasks in section 2.3. Some problems with the current plant setup are needed to address first (problem 1 to 3). Then, this thesis will discuss about the problems (4 and 5) causing by the missing additional features. After that, minor problems will also be mentioned (problem 6 to 8).

Current setup problem:

1. Adjust the testing environment' temperature.

Since the location of the temperature controller's sensor is not ideal, the senor cannot not receive and display the actual temperature of the autoclave correctly. Therefore, the temperature controller may receive inaccurate temperature of the environment and overheat the desired temperature. Thus, the heating elements require additional time to reach desired temperature when new liquid CO_2 is flushing inside the pre-heated autoclave.

2. Insert the WG probe inside the testing environment.

With the current setup, the operator can easily inject distilled water inside the pressure node because water partially diffuse in CO_2 environment. However, with WG, the operator needs to consider a new factor which is gelation. Therefore, the gelation behaviour of WG when contacting with CO_2 is causing 2 problems during the injection. WG might gelate at the tip of the syringe because the plastic tube and the liquid input pipe are partially heating up and contacting to CO_2 during the injection. Therefore, WG will not be put inside the acoustic field. Moreover, the gelation behaviour of WG also brings problem because the droplet might fall and start to gelate on the reflector surface during levitating. Thus, the gelated drop will block the reflected sound wave from the reflector back to the transducer.

3. Perform the experiment consistently.

With the current syringe position, it is also causing a problem when the operator is trying to levitate a droplet. While adjusting the syringe position in the sound field, the syringe gradually moves the reflector. Thus, the droplet might fall out from the pressure node. Moreover, the distance between the reflector and transducer is not constant between each injection. Additionally, the location of the CO_2 input pipe is also not ideal because it might blow the drop out of the pressure node when new CO_2 is introducing inside the system.

Missing features and reasons:

4. Maintain a constant pressure while changing the temperature

Since the temperature and pressure can directly affect each other in the testing environment, the current setup cannot automatically maintain constant pressure while adjusting the temperature. Consequently, the probe might drop out of the pressure node due to sudden change of pressure. The results are not consistent because it was determined at different pressure.

5. Indicate the WG probe' temperature during levitation

There is still a critical problem causing by the working principle of the acoustic levitation technology. As Tuckermann stated [31], the droplet is being heated up approximately 2-3°C more than the environment temperature while levitating.

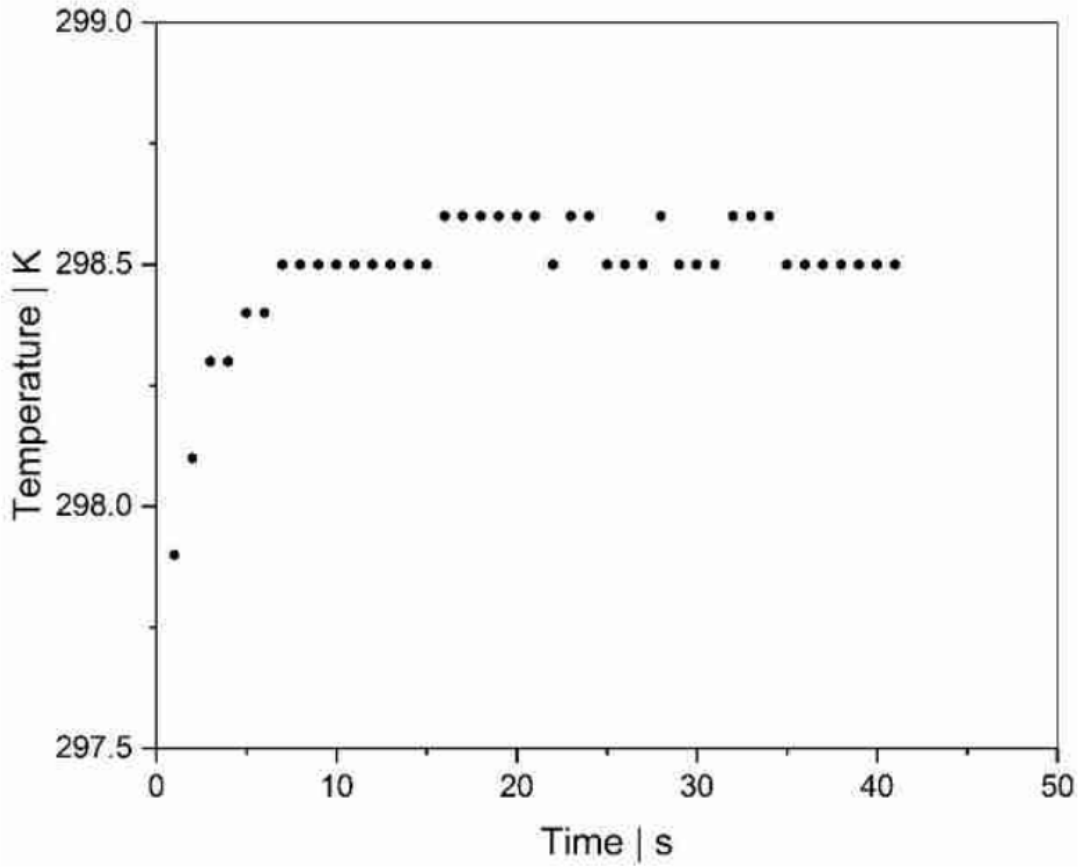


Figure 5: Temperature change while levitating

Temperature changes in empty sound field [28]

The diagram shows a temperature change after switching on the acoustic levitation. As soon as the acoustic is turned off, the temperature of the droplet drops to the environment temperature (ambient temperature in this experiment). This temperature change is causing by the energy input. Thus, the accurate temperature where the gelation occur is not available with the present setup (more detail at section).

Other problems

6. Cleaning the system after an experiment

Since WG can gelate in the syringe and on the reflector, the plant cannot continue with another experiment. In addition, the plant might need a cooling system around the testing environment so the operator can easily disassemble the testing area and start the cleaning process.

7. Measure the drop's properties

There is a problem with the provided MATLAB code. The code cannot execute the IFT, and viscosity measurement due to a software detection problem. It cannot determine the contour of the drop because the imported images which is a binary matrix do not store value 1. Thus, the following calculations fails and only 50 % of the data gives the result. The result data shows that the code only works with the drops which have the radius and volume more than 0.393 mm and 0.25 ml. Beside the viscosity and IFT measurement, the density measurement under high pressure also encounters an obstacle. As mentioned in section 3.1.2, the hand pump cannot

deliver the exact and constant drop's volume to the pressure node. Therefore, calculated density is not accurate.

8. Determine the gelation point by applying experimental approaches in section 2.1.1

Since the presented measurement methods for gelation time in section 2.1.1 mostly observe the sudden jump of viscosity, levitation technology might be a suitable way to detect the gelation point. However, the current setup of the plant cannot perform the investigation because the plant only able to do discreet measurement. As the result, it is nearly impossible to determine the sudden change of viscosity.

Apparatus:

The acoustic levitator should be used to study the transition between sol and gel by observing the oscillation frequency under high pressure and temperature. However, with the current setup, the plant needs some adjustment and modification to perform the investigation due to the mentioned problems.

Therefore, the plant must be improved in section 2.3 mentioned points in order to proceed the investigation of the gelation process of hydrogels in high temperature and pressurized CO_2. The requirement list is constructed based on this guideline with the following layout:

- Classification: The Roman numbers which denotes the needs in the guideline are stated in this column.
- Demand & Wish: Within this thesis scope, only the "Demand" class will be discussed in the next chapter.
- Number: Number of the requirement for better tracking.
- Requirements: Detail descriptions will be given at this column.
- Value: specific and detail parameters are provided in this column.
- Satisfaction: if the present requirement is labelled Y, this means that the current setup has already satisfied.

The guideline is stated again with Roman number:

I. Apply the acoustic levitation technology.
II. Pressurize the testing environment with CO_2.
III. Can operate under high pressure and high temperature conditions.
IV. Adjust the testing environment' pressure and temperature.
V. Maintain a constant pressure while changing the temperature.
VI. Insert the WG probe inside the testing environment.
VII. Allow the operator to observe and record the WG probe while oscillating in the acoustic field.
VIII. Indicate the WG probe' temperature during levitation.
IX. Can perform many experiments in one take.
X. Perform the experiment consistently.
XI. Remove WG after and during an experiment.

Number	Classification	Demand & Wish	Requirements	Value	Satisfaction
1	I, II, III	D	Acoustic levitation under high pressure and temperature		Y
2	VI	D	Put a WG probe inside the sound field		Y
3	I	W	Levitate the probe		
4	I	D	Excite the probe to oscillating state		Y
5	VII	D	Visually observe the process	120°C 150 bar	Y
6	VII	D	Record the process visually	Video or picture Color At least 10 minutes	
7	IV	D	Control temperature of the probe environment	25-120°C	
8	VIII	D	Measure the temperature of the environment of the probe	25-120°C	Y
9	II, IV	D	Input CO_2 pressure can be increase up to	150 bar	Y
10	IV	D	Manually depressurized the system		Y
11	X	D	Input CO_2 temperature can be adjusted before entering the environment	120°C	
12	X	D	Inlet and outlet of CO_2 must not interfere with levitation process		
13	VI	D	WG input at room temperature	20-25°C	Y
14	VI	W	WG input at different concentration		
15	VI	D	WG input at pressure	Maximum 150 bar	Y
16	VIII	D	Measure the probe temperature while levitating under high pressure		
17	V	D	Maintain constant pressure while increasing temperature during the process and vice versa		
18	X	D	Position of reflector must be stable during droplet input and levitation		
19	X	D	Indicate the distance between reflector and transducer		
20	IX	D	Prevent/Minimize the falling of drop onto the surface of the reflector		
21	VI	D	Avoid gelation at input source before oscillating (levitation)		
22	X	W	Determine frequency and amplitude at different temperature and pressure		

23	VI	D	Insert desire probe volume	Approx. 0.26 ml	
24	X	W	Automatic adjust the distance between the reflector and the sonotrode		
25	XI	W	Cooling system for the testing environment		
26	XI	D	Clean the WG input pipe		
27	XI	D	Clean the reflector surface		
28	IX	W	Remove the probe during the experiment		

Table 3: Requirement list

Requirement according to the mentioned criteria at the levitator.

As mentioned recently, only “Demand” requirements are discussed further in this work. Requirement 7 is addressed to give better temperature feedback from the sensor to the heat controller so the plant can meet up criteria IV. Regarding criteria V, requirement 17 suggests possible solutions to keep the pressure constant during the temperature adjustment. Since gelation might occur right inside the syringe, requirement 21 is created according to criteria VI. For criteria VIII, requirement 16 is needed to determine the exact temperature of the levitating probes. In order to satisfy criteria X, the requirements 11, 12, 18, 19, and 22 are going to significantly improve the experiment's consistency. About the criteria XI, the operator should be able to clean the WG after each experiment, so requirements 18, 25, 26 and 27 suggest possible solutions to keep the plant gelation free.

4 CONCEPT DESIGN

This thesis will concentrate on requirements 11, 16, 17, and 21 from section 3.2. The following is the reasons why they are crucial for the gelation investigation.

Requirement:

- 11: Since the CO_2 from the tank source has different temperature compared to the temperature of the autoclave, the autoclave takes a lot of time to stabilize the temperature before it can begin the testing. Moreover, the levitating probe can fall out from the pressure node because the volume of the autoclave is relatively small. Therefore, the temperature of CO_2 must be adjusted before entering the autoclave.
- 16: as mentioned in 3.2, the energy input from the transducer increases the temperature of the levitating probe roughly 2-3 °C. In order to determine the gelation time, temperature of the prob is one of the most important parameters.
- 17: During the levitation, if the operator wants to find the gelation respect with the temperature parameter, the sudden pressure increase (decrease) can affect the levitating probe.
- 21: this is the most important requirement because the investigation cannot proceed further if the plant does not able to inject the WG. Due to the unique behavior WG, the WG can terminate the whole experiment if gelation appears inside the syringe.

Possible solutions will be generated in section 4.1 according to the unsatisfied requirements which are stated in the requirement list.

4.1 Possible solutions

This section only discusses the “Demand” requirements and addresses their advantages and disadvantages.

6. Record the process visually

- A colour camera which can connect to a computer and use its software to record the experiment.

- Pros: The operator can easily observe the changes of WG from sol to gel form during the experiment.
- Cons: Modification is need at the previous camera location.

7. Control the environment temperature

- The position of the heat controller ‘sensor is located next the heating elements.

- Pros: The new position can greatly increase the accuracy of the feedback temperature data to the controller.
- Cons: However, the autoclave needs to have a new bore to install the sensor inside.

11. Input CO2 temperature can be adjusted before entering the environment

- One of the practical solutions is running the CO_2 pipe through a preheated distilled water inside a breaker. To increase the efficiency, the pipe is shaped in spiral structure.

- Pros: By using this approach, the optimization is relatively low and easy to modify. This setup can avoid the modification of the CO_2 tank source which will create more obstacles.
- Cons This method requires a heating magnetic stirrer to efficiently increase the temperature of the medium which is distilled water. Therefore, the plant location needs to have some adjustment, so there will be enough space for the heating magnetic stirrer. Moreover, the CO_2 input pipe must be reshaped in spiral form.

- Preheat the CO_2 tank

- Pros: The plant does not need addition optimizations or support gadgets to preheat the CO_2 because it will be done at the source. Furthermore, the plant will always have pre-heated CO_2.
- Cons: Since the CO_2 is stored as liquid in commercial tank and the CO_2 might expand when it is heated, a new special storage is needed. In addition, there are other plants which also use the same CO_2 and they do not require pre-heated CO_2 source. However, it might be more expensive and time consuming than the spiral pipe.

12. Inlet and Outlet of CO2 must not interfere with levitation process

- Reposition the inlet and outlet so that the input and output CO2 flow does not interfere or coincide with the pressure node.

- Pros: This setup creates a new solution for the requirements 20 and 29.
- Cons: However, the reposition is harder than adding a sheet method.

- Add a sheet right before the entering Co2 in order to block and redirect the incoming flow.

- Pros: With the sheet, the modification inside the autoclave is simpler.
- Cons: By contrast, all of the solutions for the requirements 20 and 29 are not possible.

- Using double piping system.

- Pros: The operator can freely choose which input pipe will be open.
- Cons: This method requires more modifications.

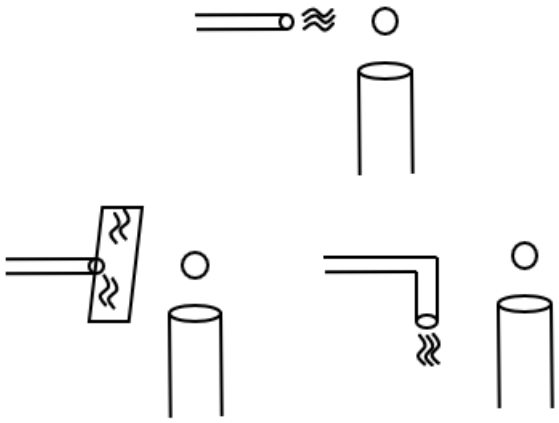


Figure 6: CO_2 inlet pipe adjustment

14. WG input at different concentration (sodium silicate/water)

- Dilute WG 7 %

- Pros: The gelation time of this concentration is shorter than WG 8 %
- Cons: The transition between sol to gel might be harder to observe.

- Dilute WG 8 %

- Pros: The transition between sol to gel is easier to observe because the gelation time is slower than WG 7 %.
- Cons: The operator needs to use more sodium silicate.

16. Measure the probe temperature while levitating under high pressure

- Using PID thermo camera.

- Pros: This is a contactless method, and it does not require any internal modification inside the autoclave.
- Cons: Since the CO_2 can experience the phase change during the experiment and visually block the PID camera. Therefore, the accuracy of the measure will be low. Another problem is the measured temperature might not the temperature of the probe, it can be the temperature of the view glass or the CO_2

- Attach sensor to the pressure node location

- Pros: The sensor can avoid measuring the temperature of the view glass.
- Cons: The autoclave needs some adjustments in order to implement the sensor in the pressure node. Moreover, since the sensor tip is located near or in the pressure node, it might be hard to levitate the drop at this node. This method also encounters the same problem as PID thermo camera. The measured temperature might be the temperature of the testing environment which is CO_2 if the position of the drop is not right on the sensor

17. Maintain constant pressure while increasing temperature during the process and vice versa

- Use a mechanical spring.

- Pros: The mechanical spring is simpler than the electric control value because it does not contain electric component.
- Cons: This tool only has one fix pressure. Therefore, the investigation only possible at a certain pressure. When the machinal spring is releasing CO_2, the pressure drops suddenly. As the result, the droplet might fallout from the pressure node

- Electric control value that can reduce pressure based on the operator's input.

- Pros: This valve can reduce the pressure inside the autoclave steadily without causing the droplet to drop out from the pressure node.
- Cons: This method needs to setup a self-written code.

18. Reflector must be stable during droplet injection and levitation

- Change the position of the injector to the side of the autoclave

- Pros: By changing the injector, the plant will have more room to develop and test.

- Cons: However, the whole injection system at the reflector needs to redesign again. Moreover, the injector is only able to put the droplet at a one location.

- Adjust the fitting around the reflector to reduce the shaking when removing the injector

- Pros: By doing this, the injection system can avoid the redesign.
- Cons: A suitable material is needed because the plant is running under high pressure and high temperature.

19. Indicate the distance between reflector and transducer

-Add a physical scaler inside the autoclave.

- Pros: The autoclave does not need any addition modification for the scaler.
- Cons: The accuracy of the distance is quite low.

20. Prevent/Minimize the falling of drop onto the surface of the reflector

- Using a mesh or foil on the reflector

- Pros: The cost of foil is relatively low and easy to obtain and remove. Moreover, the system does not need additional adjustments
- Cons: Since the effect of the foil to the reflected soundwave is still unknown, further testing is required.

- Using CO_2 inlet/outlet to blow out the drop from pressure node

- Pros: This method will limit the number of liquid drops or gelated drops on the reflector surface, so the operator can execute more attempts in one experiment set.
- Cons: The pressure inside the autoclave will increase and take additional time to stabilize the pressure, but it can be avoided by using requirement 17's solutions

- Using CO_2 inlet/outlet to blow out the drop from the reflector.

- Pros: Have the same advantage as the above method.
- Cons: The position of the CO_2 inlet pipe needs to readjust to the desired location. Moreover, more CO_2 is entering the system because the gelated WG drop on the reflector surface.

21. Avoid gelation at input source before oscillating (levitation).

- Using the electrical pump from a beaker instead of the hand pump to simultaneously pump squalene/oil – WG – squalene/oil (Figure 7).

- Pros: With the help of the electric pump, the separation of squalene and WG is possible because the operator just needs to change the liquid source at the pump input.
- Cons: Lack of data about the solubility and diffusion between WG and squalene (this thesis will address this problem later on).

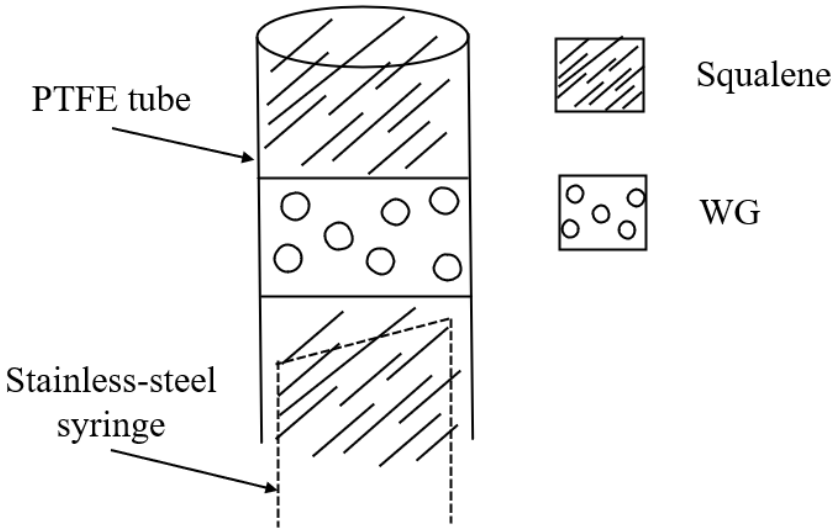


Figure 7: Separation of liquids at the plastic tube

- Pre-inject the WG in the PTFE tube before attach to the injector

- Pros: Since WG only injects inside the PTFE tube, the gelated WG is easy to remove.
- Cons: The injection must be done manually so the duration per experiment is much longer.

- Determine the maximum temperature and pressure before gelation occur by WG – squalene before phase change

- Pros: No adjustments and optimizations are needed.
- Cons: This approach requires a lot of time to determine the correct conditions. Moreover, the gelation will occur when operating under SCCD.

22. Determine frequency and amplitude at different temperature and pressure

- Establish a small databank for operators

- Pros: This will shorten the experiment duration for the operator in the future.
- Cons: A lot of trials and errors are needed to perform for this solution.

23. Insert desire probe volume

- Use electric pump

- Pros: This pump con precisely injects desired volume inside the system which is beneficial for the liquid property measurement and requirement 21.
- Cons: Since the plant is using the hand pump right now, a new electric pump which can adjust the flow rate and able to inject liquid inside 160 bar environment is needed. The input pipe also requires adjustments for the new pump.

26. Clean WG input pipe

- Wash it with water after an experiment.

- Pros: The electric pump from the solution in the requirement 23 can be used to push the gelated WG out.
- Cons: The operator needs to dry the autoclave afterward.

- Use air blower.

- Pros: The air blower can easily remove the gelated WG inside the pipe.
- Cons: The whole injecting system must be disassembled into small parts to use the air blower.

- Limit the WG in PTFE tube

- Pros: The operator just needs to change the PTFE tube.
- Cons: The whole injecting system must be disassembled.

27. Clean the reflector surface

- Using distilled water to clean the surface, with the help of cotton swab.

- Pros: Distilled water can clean the surface quite well.
- Cons: The operator might damage the reflector surface during the cleaning process

- From 19. mesh and foil are also a great help for the cleaning process.

28. Remove the probe during the experiment.

Only possible when combine with the first solution for requirement 12.

Right in the pressure node:

- The CO_2 inlet can be redirected to the pressure node. Therefore, the incoming CO_2 can push the probe out of the pressure node.

- Pros: This setup can limit the amount of gelated WG on the reflector surface.
- Cons: The operator cannot increase the pressure during levitation because the new CO_2 will push the drop out of the pressure node.

On the reflector

- With the above position of the CO_2 inlet, operator can adjust the position of the reflector near the pressure node. Thus, the CO_2 will blow out the probe on the reflector surface.

- Pros: The new CO_2 flow will not interfere the probes during levitation.
- Cons: This method might only be possible for the gelated probes on the reflector surface.

As stated in the first solution of requirement 21, the following part will discuss about the solubility and diffusion between WG and squalene.

A series of tests have been conducted at Ruhr University Bochum's pressure lab to observe the solubility and diffusion between WG and squalene. Squalene does not diffuse with high temperature and pressure CO_2 environment [30]. Moreover, it does not solute and diffuse with water and WG consists approximately 90% water. Squalene also available at the laboratory.

Solubility and diffusion a prove of concept

For the first test series, four experiments are conducted at a chemical workstation with 2 WG concentrations 7 % and 8 %. Regarding the first experiment, WG 7 % and squalene are put inside a beaker, respectively before capturing a picture as a reference. For the second experiment, WG 7 % and squalene are put in the same order as the previous experiment, but in this experiment WG 7 % and squalene are being mixed up continuously by a magnetic stirrer. The third and fourth experiment uses WG 8 % with the same procedure as the first and the second experiments, respectively. Then, the four tests are left inside the chemical workstation for approximately 24 hours. As the result, both WG 7 % and 8 % still stay separate from each other by looking with an unaided eye. Moreover, the position of the separate layer between WG and squalene remains the same when comparing the reference images from the first and the third experiments with the present pictures.

For the second test series, the author reproduces four experiments from the first test series. However, the new experiments stay inside the chemical workstation is 72 hours instead of 24 hours. After 72 hours, there are no changes between WG 7 % and 8 % and squalene when observing with an unaided eye. Therefore, solubility and diffusion between WG and squalene are assumed to be not significate in this thesis.

Colouring squalene and WG

Because they will be operated in an autoclave with limited visibility and squalene has the same colour as WG, one of them needs to be colourized for the observation with colouring chemicals.

1. Xylenol Orange $C_{31}H_{32}N_2O_{13}S$
- This colour does not react with squalene.
- WG 7 % is turned into purple.

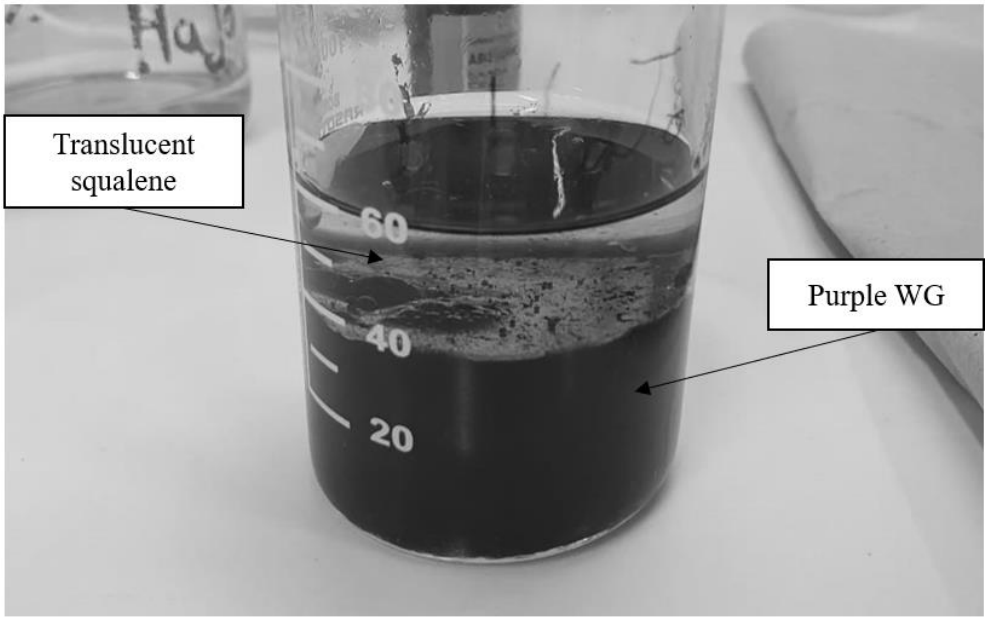


Figure 8: Testing with Xylenol Orange

2. Vivid red
- It turns squalene into red.
- The colour does not react with WG 7 %.

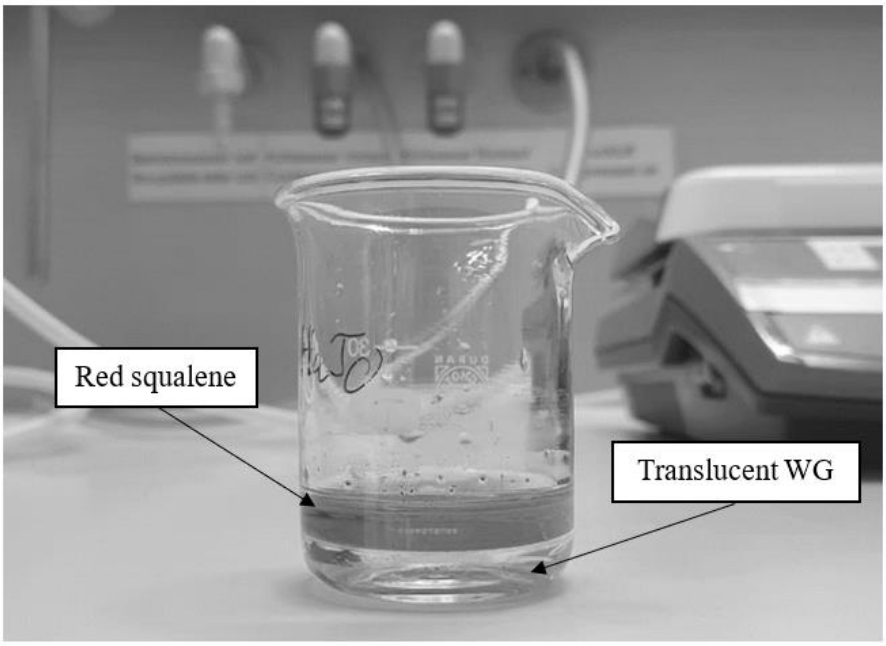


Figure 9: Testing with Vivid red

To maintain the chemical properties of WG after gelation, vivid red will be used in the future experiment inside the levitator instead of Xylenol Orange. Then, a small test is conducted with the vivid red squalene and WG to test the diffusion and solubility between them. WG 7 % and vivid red squalene are put in a beaker for observation. After a day, vivid red in squalene did not diffuse with the WG.

4.2 Solution selection

This section will discuss and justify the choice which is the most suitable for the plant and the high-pressure lab.

6. Record the process visually

The current high-speed camera is only able to record in black and white format. Moreover, the investigation does not require the experiment to be recorded with high framerate. Approximately 60 to100 frames per second are sufficient for the study.

7. Control the environment temperature

The Figure 12 shows the old location of the temperature controller senor. Since the heating elements locate in the opposite side, the sensor cannot send the accurate temperature feedback to the temperature controller. Thus, the temperature controller usually overheats the autoclave.

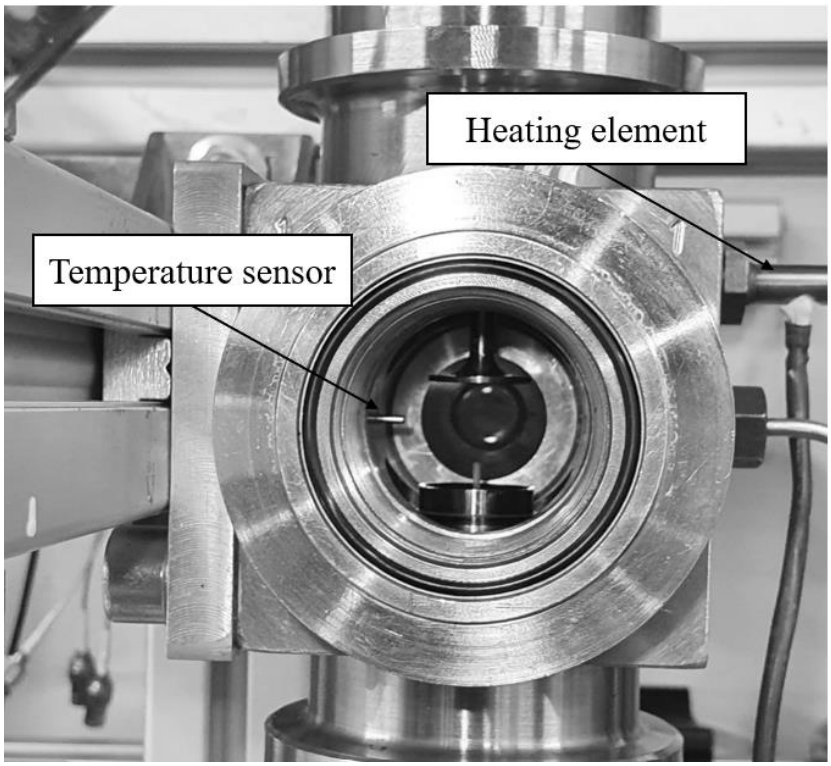


Figure 10: Old sensor location (front view of the autoclave)

Figure 11 shows the new position of the temperature controller's sensor. This new position locates near to the 4 heating elements which will give the better signal back to the controller. As the result, the controller can avoid overheating.

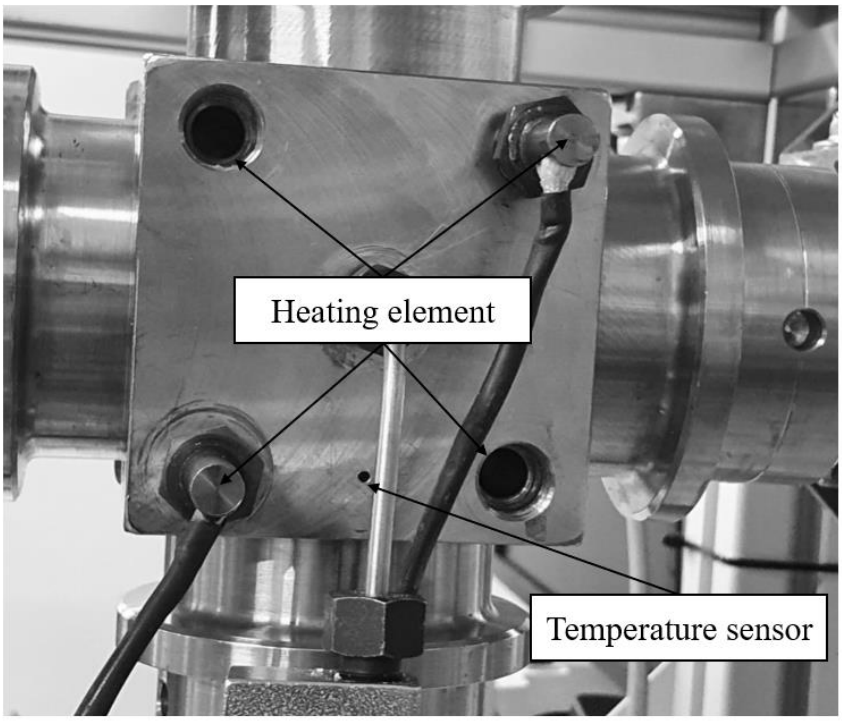


Figure 11: New location of the temperature sensor (side view)

11. Input CO2 temperature can be adjusted before entering the environment

The spiral pipe in Figure 12 is the most suitable solution for the current setup. Since this method does not need the modification of CO_2 tank, it does not interfere with other plants at Ruhr University Bochum's high-pressure lab. Moreover, the cost of the pipe adjustment is significantly lower than the second solution. Additionally, the beaker can be placed on a heating magnetic stirrer to increase the efficiency.

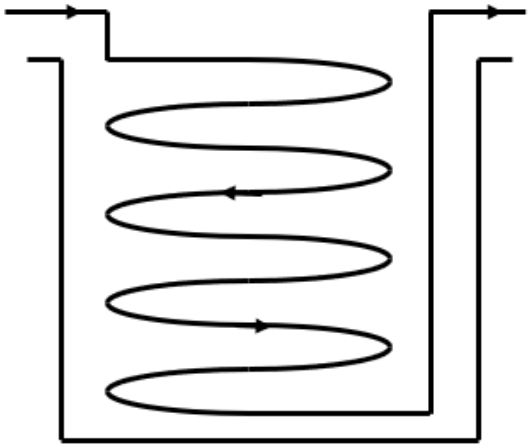


Figure 12: Heating the CO2 before entering the system

With this method, the operator can also control the temperature of the incoming CO_2. Moreover, the plant requires less time for heating and stabilize the new CO_2. Therefore, it is sufficient to have this change.

12. Inlet and Outlet of CO_2 must not interfere with levitation process

The sheet method will greatly reduce the possibility of requirement 20 and 29 solutions. Therefore, it is more reasonable to relocate the height of the pipe.

14. WG input at different concentration

For the first step, WG 7% is used because the gelation time at this concentration is longer than 8%. Therefore, the operator can be familiar with the transition from sol to gel.

16. Measure the probe temperature while levitating under high pressure

Since the location of the sensor is fixed in one location and the location of the pressure node depends on the frequency input from the transducer, the sensor might detect the environment temperature. Thus, the measured temperature is not correct so PID thermo camera is more suitable for this investigation.

17. Maintain constant pressure while increasing temperature during the process and vice versa

The electric valve is the better choice because the operator can adjust the pressure easily with a self-written code. Moreover, the change of pressure is not sudden, so the drop will not fall out from the pressure node. However, the code and suitable tool is needs in order to develop this electric valve.

18. Reflector must be stable during droplet injection and levitation

By repositioning the injector, two or more injectors can be implemented inside the systems. Therefore, the operator can put multiple liquids in the pressure node. The fix position of the injector can be suppressed by finding an optimal area around the pressure node. At this area, the injected drop is automatically pulled in the pressure node.

19. Indicate the distance between reflector and transducer

A scale is sufficient for the scope of the investigation because it does not require additional adjustment for the autoclave. Furthermore, the material of the scale needs to withstand the high pressure and temperature conditions.

20. Prevent/Minimize the falling of drop onto the surface of the reflector

The CO_2 inlet and outlet should be located at the reflector level because the automatic pressure adjustment while increasing the temperature can pull the droplet from the pressure node. Further optimizations can be applied such as using both inlet and outlet at pressure node and reflector positions.

21. Avoid gelation at input source before oscillating (levitation).

The pre-injection method at the PTFE tube is more reliable than the other solutions. Since the gelation only occurs within the PTFE tube, the stainless-steel input pipe can completely avoid the gelated WG. Then, the operator just needs to remove the PTFE tube with the new one.

22. Determine frequency and amplitude at different temperature and pressure

A data bank of the frequency and amplitude at different temperature and pressure will greatly reduce the duration of an experiment. Since the operator does not need to find the correct value of frequency and amplitude in order to levitate a probe.

23. Insert desire probe volume
High-performance liquid Chromatography (HPLC) pump (P4.1S, AZURA, Germany) is a suitable option because the operator can control the exact flow rate with 0.01 step. Moreover, the pump can operate up to 400 bar and deliver 10 ml per minute.

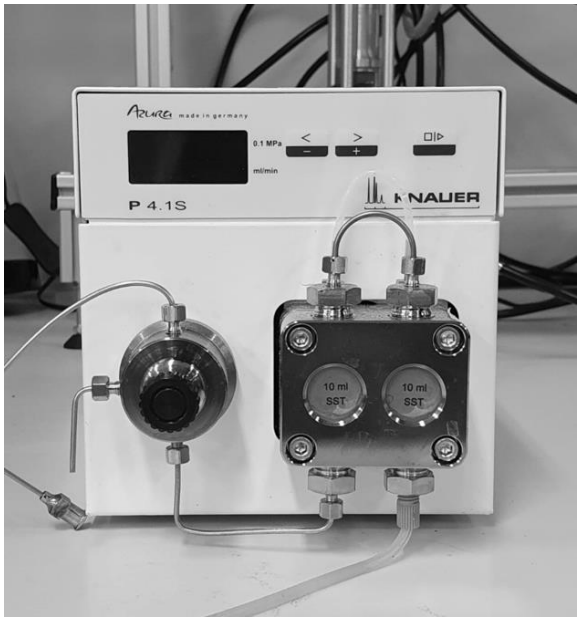


Figure 13: AZURA P4.1S electric pump

26. Clean WG input pipe

It is possible to combine two solutions because the pressure lap does have the air blower and the electric pump which can use to clean the pipe with distilled water at maximum flow rate.

27. Clean the reflector surface

Because WG is nearly 95 % distilled water, the cotton swab is more than enough. However, the operator must gently clean the surface to avoid damaging the reflector surface.

5 CONCLUSION AND OUTLOOK

This thesis aims to suggest a concept for the investigation of hydrogel's gelation time under pressurized CO_2 because the study of this field currently is not widely available and challenging. With the suggested concept solutions, the acoustic levitator might be able to conduct the study about the gelation time. The current setup of the plant still cannot perform the investigation because the plant is not able to maintain constant pressure while increasing the temperature, prevent the gelation at the injector, and determine the temperature of the unknown liquid while levitating. Moreover, the current studies of the gelation under ambient condition show that there are many factors such as catalyst, pH value of the solution, salinity, temperature, and the ratio of sodium silicate/water which directly affect the gelation time. Furthermore, these factors can potentially impact the gelation time under the pressurized CO_2 especially SCCD. Beside the effect of the stated factors, the CO_2 itself can also act as an attractive medium and accelerate the transition from sol to gel. Therefore, the investigation of gelation time under pressurized CO_2 with mentioned factors is critical for the future optimization of the aerogel synthesis. Since the current state of the plant cannot provide a stable testing environment for the study, a guideline is conducted to adjust and improve the plant setup. The guideline consists of eleven criteria in which three out eleven criteria have already been satisfied. The following is the most important criteria for the acoustic levitator:

- Maintain a constant pressure while changing the temperature,
- Insert the WG probe inside the testing environment,
- Indicate the WG probe' temperature during levitation,
- Perform the experiment consistently.

If the plant does not satisfy the criteria in the guideline, the drop might fall out from the pressure node due to the sudden pressure changes. Moreover, the operator cannot put the WG droplet inside the pressure node and measure the temperature of the droplet. Thus, the operator is not able to determine the gelation time. A requirement list is created based on the guideline in order to avoid the stated problems. Then, the suggested solutions concerning each requirement are generated and the most optimal solutions are chosen after a discussion of their advantages and disadvantages.

The present thesis does not cover the "Wish" requirements and solutions for the droplet's contour detection in the MATLAB code. Therefore, further adjustments can be made to support the indication of gelation point. After all of the adjustments and improvements, the acoustic levitator can perform the study in the determination of density, viscosity, and interfacial tension between WG and CO_2 and indicate the gelation point under high temperature and pressure. The next step of this work will implement and justify the new concepts in section 4.2 such as the new position of CO_2 inlet and outlet, pre-inject the WG and squalene in the PTPE tube, and the electric pressure valve from the solution suggestions. Then the investigation will measure the gelation time of WG 7 % and 8 % with different catalyst, salinity, temperature, and pH value in CO_2 environment.

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DECLARATION OF ORIGINALITY

I confirm, that the submitted thesis is original work and has been written by me without further assistance. Appropriate credit has been given where reference has been made to the work of others. Moreover, I confirm, that the thesis was not examined before, nor has been published.

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