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MASTER'S THESIS

INVESTIGATION OF THE ROLES OF WATER IN THE DECARBOXYLATION OF AROMATIC CARBOXYLIC ACIDS IN SUPERCRITICAL WATER

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Chapter 1   Introduction

1.1.   Research Background

Supercritical water is defined as water above its critical point (374 °C, 22.1 MPa). For the past decades, it has been studied extensively for different reasons and purposes. Some for organic synthesis, waste treatment, improving chromatography, extraction, and so on. But the reason this medium has attracted so much attention is because of its many advantages over other solvents – it is environmentally benign, abundant, and most of all its tunable physical and transport properties.[1,2]

When changing the conditions, various properties of SCW, such as density, dielectric constant, ion product (K_w), to name a few, vary over a wide range of temperature and pressure. The solubility of organics and inorganics also changes with the changing properties of water.[1] Because of this, careful control of the reaction conditions allows the control of these properties as well.

Researchers have taken advantage of this and performed many reactions in supercritical conditions. Some reactions that have been successfully performed in SCW include total oxidation, hydrolysis, dehydration, decomposition, water-gas shift reaction, disproportionation reactions, partial oxidations, rearrangements and coupling.[1]

As a consequence of this, researchers are led to study the roles of water in SCW as they also change depending on the conditions.[3–5] Some of the roles that have been identified are as a reactant or product, as a catalyst, as a medium and as a participant in intermolecular interactions. If as a reactant or product, water can participate in elementary reaction steps. As a catalyst, it can act as an acid or base catalyst via –self dissociation or as a molecule that modifies and stabilizes transition states. It can also affect the kinetics of reactions through the changes in its intermolecular molecular interactions with solutes at near critical to critical regions. As a medium, physical effects are observed even in the absence of intermolecular interactions due to the effects in the collision and diffusion processes in reactions.[4,5] By understanding these roles, controlling reactions in this medium becomes possible.

One reaction where the roles of water could be investigated is the decarboxylation reaction. Compared to other reactions, decarboxylation reactions are straightforward, involve only a few products which make analyses easier (as there are possibly fewer side products to deal with), and has almost no side reactions; therefore, it is easier to isolate the effect of water on the reaction and exclude other possible contributing factors. Moreover, the behavior of aromatic carboxylic acids in sub- and supercritical water is important in at least three different fields. One is in the plastic and fiber industries. Aromatic diacids are usually utilized as intermediates and their behavior during synthesis and purification are performed in high temperature of water is important to be understood. Another field is in fuel processing, specifically coal liquefaction. Coals contain several aromatic carboxylic acid groups, which influence their reactivity during liquefaction. The third field is waste treatment. Wastewater streams from chemical activities are abundant in carboxylic acids. A better understanding of carboxylic acid behavior in HTW can assist in improving methods, like wet air oxidation, to degrade them into safer compounds. [6]

It is therefore unsurprising that decarboxylation in aqueous conditions has been studied extensively. These include kinetic, mechanistic, and stability studies, among others. Studies revealed that benzoic acid is the most stable, and as various substituents are added, its reactivity is enhanced.[6,7] While most studies found that benzoic acid remains stable up until 350 °C in relatively long reaction times, a study found that by adding an inexpensive catalyst Cu_2O greatly improves the conversion.[8] However, the reactivity is not only affected by substituents and substrate structure, but also by the interaction of the COOH with water molecule, and consequently by solvent effects. Computational simulations of the mechanism of benzoic acid decarboxylation and its derivatives illustrated how water interacts with the carboxylic acid portion to form a transition state through which the activation energy of the reaction is lowered, and consequently facilitates -COOH removal.[3,9] Based on these calculations, it could be said that water acts as a catalyst. However, not enough data is present to confirm this. Additionally, other possible roles of water have not been explored yet. Thus, in light of the aforementioned research results, an explanation of how water interacts with the carboxylic portion still needs to be understood for researchers to be able to predict experimental results and make generalized conclusions.

Thus, in this research, the effect of changing water properties was used to deduce the roles of water in decarboxylation reactions. However, when pressure and temperature is changed, not only one property change but altogether. And therefore, it is difficult to attribute the effect of water to one property. However, by focusing on one property, it is easier to explain the observed effects and to manipulate the reaction.

Among the properties of water, density seem to have a greater effect in hydrothermal reactions than others. According to Fujii et al.[10], in oxidation in SCW, water density affects the decomposition rate of compounds like CO[11], methanol[12], and phenol[13]. Many reports have suggested that water density also influences other kinds of reactions, for example, hydrolysis, dehydration, and retro-aldol reactions[1]. There have also been literatures mentioning the effect of density on decarboxylation reaction. Dunn et al.[6] and Zheng et al.[8] have concluded that as pressure is increased, which consequently increases density, increases the conversion of benzoic acid. Although it has been mentioned, an extensive explanation is not yet available. Focusing on density to deduce the roles of water in decarboxylation reactions is only suitable.

1.2. Significance of the study

Despite the decades-long investigation of SCW, there is still not enough information for researchers to be able to make generalizations on what reactions is best conducted in SCW. Likewise, the roles of water are rarely discussed in research concerning hydrothermal reactions. Though there have been numerous studies in SCW, the understanding of the effect of water on reactions and the role it assumes is still not on par with the number of experiments that attempts to solve the problems with the technical difficulties in building the reactors. But to further advance this technology and apply it more and more to industry, there should be understanding in both areas, and therefore, it is very important that studies are conducted in unravelling the roles of water in reactions in SCW.

Although the focus of this research is on decarboxylation, the techniques and analyses applied in this reaction may also be employed to other reactions conducted in SCW. Moreover, the data obtained for this

experiment will hopefully substantiate or debunk experimental results and computer simulations that have already been performed for decarboxylation reactions.

1.3. Research Objectives

Thus, this research aims to investigate the roles of water in the decarboxylation of aromatic carboxylic acids in SCW by varying water density. The specific objectives are:

1. to measure the conversion and yield of phthalic acid decarboxylation at different densities by varying the pressure,
2. to calculate the rate constant and relate it with pressure and density,
3. to propose a numerical relationship between density and pressure and reaction rate, and
4. finally, to propose possible roles of water in the decarboxylation reaction based on the conclusions obtained from the experimental data.

Chapter 2   Review of Related Literature

2.1.   Properties of supercritical water

In this section, some of the changes that occur in the properties of water at the supercritical state are elaborated. The references were limited to those that are relevant to the discussions in this thesis

2.1.1. Density

The density of water increases with pressure but is inversely related with temperature. Above the critical temperature, it is feasible to vary the density with pressure by holding the temperature constant[1], which allows reactions to be investigated over a wide range of density values while eliminating the effects of temperature changes. As seen in Figure 1, the density is greatly reduced with an almost infinite slope at 25 MPa around 400 ℃. Density is usually experimentally controlled by changing the pressure.
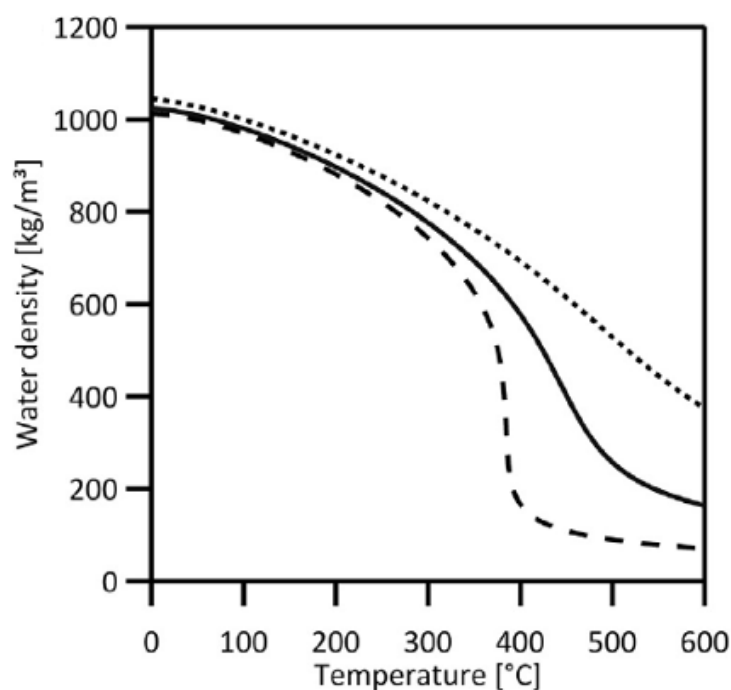

Figure 1. Density of water as a function of density. Dashed line: 25 MPa; solid line: 50 MPa; dotted line 100 MPa. (Reprinted from ref. 1 Copyright 2013 with permission from The Society for Biotechnology, Japan.)

Many other properties of water also change alongside density and consequently could affect a reaction in various ways depending on the conditions. Examples of such properties are the structure of HTW, hydrogen bonding, dielectric constant, diffusivity and ionic constant. While the focus of this research is on the effect of density, it is important to note that both the temperature and density could be used to control these properties.

According to Akiya and Savage[4] at subcritical temperatures and above, the structure of HTW becomes more similar to a simple gas as density is decreased. This could be associated with hydrogen bonding which is the foundation of several distinctive properties of liquid water. Generally, the hydrogen in water weakens and becomes less persistent as temperature is increased and density decreased. The hydrogen bond network is also

changed in HTW as it occurs in the form of small clusters of hydrogen-bonded water molecules – in contrast with the countless pervading network of hydrogen bonds existing in ambient liquid water. Studies reveal that although HTW is much less ordered than ambient liquid water, some liquid water-like structure is still kept intact on a microscopic level. It follows that these changes in the extent of hydrogen bonding result to corresponding variations in the static dielectric constant of water, as well. (discussed further in Section 2.1.2)

Finally, ion product (Kw) is another important property of water that varies considerably with changes in temperature and density. The value of K_w for liquid water near the critical temperature is about 3 orders of magnitude higher than that of ambient liquid water (further discussion at Section 2.1.3).

Considering the discussion earlier, a change in density means the concentration of water in the space around the molecule also increases – increasing water concentration, if it results to increase in conversion, could mean that water is acting as a reactant. Increase in density also means that the distance between individual water molecules is shorter, affecting hydrogen bonding. If the reactant in the reaction, to an extent forms hydrogen bonds with water molecules in any step in the course of the reaction, then the change in density would consequently affect the reaction in some way. For example, in forming transitions states in decarboxylation, water participates in forming the transition state through hydrogen bonding.[3,9] How the kinetics will be affected is not clear, however. As a medium, it has something to do with diffusion and mass transfer. If these are also affected by density, then an influence could also be anticipated.

2.1.2. Dielectric constant

As temperature is increased and density decreased, the static dielectric constant of water decreases.[4] In fact, the dielectric constant reaches to about 2 at 420 °C and 25 MPa which resembles hexane.[1] Subsequently, small organic compounds are very soluble in HTW and completely miscible in supercritical water (SCW), while ions mostly occur as contact pairs, resulting in decreased solubility for inorganic salts.[4] Thus, solvation behavior of various compounds in HTW is somehow affected.

This change in solvation due to the variation of the dielectric constant, in many cases, is also associated with changes in the reaction rates of chemical reactions. For example, in the progress of a reaction, the polarity of transition states may be higher or lower than the starting material. When the relative dielectric constant is high, the activation energy is reduced with a more polar transition state. Thus, by changing the dielectric constant through temperature and pressure variations, control of reaction rates is possible. This effect of the solvent, e.g. in organic solvents, in classical chemistry is expressed in terms of the relative dielectric constant ε of the solvent. Similarly, the same is applied in HCW in several occasions to illustrate the pressure dependence of chemical reactions.[5] Other ways by which reactions are affected by dielectric constant changes have been investigated but is not included in the scope of this study.

2.1.3. Ionic constant

Between 200 to 300 °C, the ionic constant of water increases marginally up to around 10-11 and reaches a maximum. At temperatures greater than the critical temperature, a drastic decrease occurs though it increases as pressure is increased. Compared to ambient water, sub- and supercritical water at high pressures has an ionic product of some orders of magnitude higher. In these conditions, water may act as an acid or base catalyst

precursor due to high amounts of H_3O^+ and OH^- ions. [4,5] This property of water is taken advantage of to push forward acid- and base-catalyzed reactions in water.

On the other hand, K_w for SCW at gaslike densities (<0.1 g/cm3) can be tens of orders of magnitude lower than for ambient liquid water. Consequently, free-radical chemistry governs at these high-temperature, low-density conditions. [4] Antal et al. suggested that ionic mechanisms are favored when K_w is below 10-14 and free-radical mechanisms are favored when Kw is 10-14. [4,14] This competition between radical and ionic mechanism changes as the water density changes have been investigated numerous times.

2.2. Roles of water in reactions

As mentioned in the introduction, as a consequence of the property changes in SCW, the roles of water in reactions also change. Akiya and Savage[4] provided in their review paper an intensive discussion of these roles in reactions, however, research papers following suit are still few. Thus, most of subsequent discussion were cited from their paper review. Moreover, discussion will only cover those that are related in this research.

2.2.1. Water as a reactant/product

As a reactant or product, water participates in elementary reaction steps. Some known reactions where this role of water has been observed are hydrolysis, hydration, hydrogen exchange, and free-radical oxidation chemistry. For decarboxylation, reactions performed in supercritical water are at times treated mistakenly as hydrolysis reactions. A more suitable term for the reaction of carboxylic acid in pure HTW would be hydrothermolysis or hydrous pyrolysis. [4] Decarboxylation is the removal of the whole -COOH portion and not solely the breaking down of a water molecule, although as suggested in previous literature, is involved in the mechanism. Thus, in this case, water is probably not acting as a reactant or product. Though to confirm this, investigating the effect of the concentration of water in the reaction it might be necessary.

2.2.2. Water as a catalyst

The two ways that water can act as a catalyst in hydrothermal reactions are as a donor of an acid or base catalyst, or as a modifier of the transition state to stabilize it. The high natural concentrations of the H^+ and OH^- ions coming from the high K_w of liquid HTW allow it to act as an acid or base catalyst donor making acid- and base- catalyzed reactions in water facile. [4]

As a participant in the transition state, water catalyzed the reaction by reducing its energy. This is significant for reactions with some form of intramolecular hydrogen transfer in the mechanism. Generally, water molecules allow geometries of the transition state to be less trained and more favorable for the reaction to progress. During the formation and cleavage of the bonds, water molecules relay protons, thus easing the process to product formation. [4] Water in the generally accepted mechanism for decarboxylation in aqueous conditions is suggested to participate in this way.

2.2.3. Solute-solvent interactions/Solvation effects

Solute-solvent interactions affect the rate constant for a reaction in as solvent by modifying the free energy of activation and the transmission coefficient. Effects caused by the solvent on the free energy of activation are typically termed as equilibrium solvation effects, while those which affect the transmission coefficient are termed nonequilibrium effects. Depending on the ability of the solvent molecules to adjust to the changes in the reacting system, one or other is the more dominant effect. When the molecules are capable of immediately adjusting, the equilibrium solvation effects are dominant. Through these effects, the pressure and density dependence of reaction rate constants can be understood. On the other hand, when the solvent molecules cannot adjust to the change, nonequilibrium solvation effects dominate. In this case, effects of pressure (density) on the transmission coefficient must also be considered.[4]

2.2.4. Roles of water as a medium

Even without the solute-solvent interactions, there are physical solvent effects at play. Coming from merely the presence of the solvent, effects of the solvent on the reaction can be observed. Nominally unimolecular reactions in gas-like environments are triggered by collisions with neighboring molecules, and the rate can be affected by collision frequencies. Hence, the rate is dependent on the concentrations of "third bodies" able to participate in transferring energy during collisions. In a liquid-like environment, the diffusion process that acts on the colliding of reactants and splitting of products, dominates the reaction kinetics. The rate of these reactions controlled by diffusion rely on solvent viscosity. As SCW can be gas-like or liquidlike depending on the temperature and pressure, both collision processes and diffusion process can be important for the kinetics of the reactions.[4]

2.3. Decarboxylation reactions in aqueous conditions

This section presents the related literature about decarboxylation reaction in aqueous conditions.

In the years 1990 to early 2000s, most research are focused on aqueous formic acid, acetic acid, and their derivatives, and other simple aromatic ones.[15–20] This is because researchers want to understand the basic mechanisms of the reaction and to give an explanation as to why doing it in water results to a lower activation energy. Mostly involved studying the kinetics and mechanisms of various representative carboxylic acids, hoping that the results could be used to concoct generalizations for decarboxylation reactions in aqueous conditions. Recent ones are mostly improvements of older research.

However, to date, these generalizations are still not made into reality yet, and little by little, research on decarboxylation is picking up the pace again. This is not because researchers need to know more about the nature decarboxylation itself, but to explore more the effects of water in organic reactions. There are numerous literatures but, in this section, the results of papers that were mostly referred to in this thesis are discussed.

2.3.1. Dunn et al., 2003[6]

Their research investigated the stability of different aromatic carboxylic acids in high temperature water. Specifically, they used benzoic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid, trimellitic anhydride, isophthalic acid, and o-phthalic acid. They investigated the stability of these acids in water up to temperatures of 350 °C using a batch reactor. In this temperature, they found out that benzoic acid remained stable. Thus, they increased the reaction temperature for this compound only up to 450 °C. They also compared their results with previous literature that seemed to have contradictory results. They clarified that the results are most likely not really contradictory, but that the conditions used are basically different, and attributed the differences in the density values used. To confirm their hypothesis, they also investigated the decarboxylation of benzoic acid at different densities. Their results lead them to conclude that the decarboxylation of benzoic acid is a function of density.

They also investigated the kinetics of trimellitic anhydride and terephthalic acid. They concluded that the kinetics is consistent with an autocatalysis model. This is because as CO_2 is produced, carbonic acid is formed and dissociates to form H^+ that catalyzes the reaction. Another result worth mentioning is the conversion of *o*-phthalic acid at 300 °C. They found that the yield is about 73% after 30 min. Results of this research will show later that only after 0.41 min at 400 °C at 40 MPa resulted to 100 % conversion.

2.3.2. Li and Brill, 2003[3]

They investigated the decarboxylation rates of aqueous benzoic acid and 12 mono-, di-, and trihydroxy derivatives of benzoic acid in water at 275 bar in the temperature range of 120 – 330 °C. Similar with Dunn, et al.[6], they also found that the unsubstituted benzoic acid is the most stable. They found out that the decarboxylation follows first-order (pseudo-first) rate kinetics, and consequently obtained the rate constants and the Arrhenius parameters for the decarboxylation of the acids. With regards to the speed of decarboxylation in terms of the position and number of substituents, the order is multiple ortho, para -OH substitution > ortho substitution > para substitution > meta substitution. Based on experimental results, they concluded that the rate differences are mainly governed by activation entropy. Finally, they performed calculations to obtain the transition states of the reactions using density functional theory. Results showed that for the gas phase reaction, the transition state is formed through a four-membered ring, while the addition of a water molecule through a six-membered ring, which greatly reduces the activation energy. Based on this, they described the mechanism as involving a water-catalyzed transition state that is formed by water forming two hydrogen bonds with the -COOH group and the leaving proton from the ring, facilitating bond cleavage.
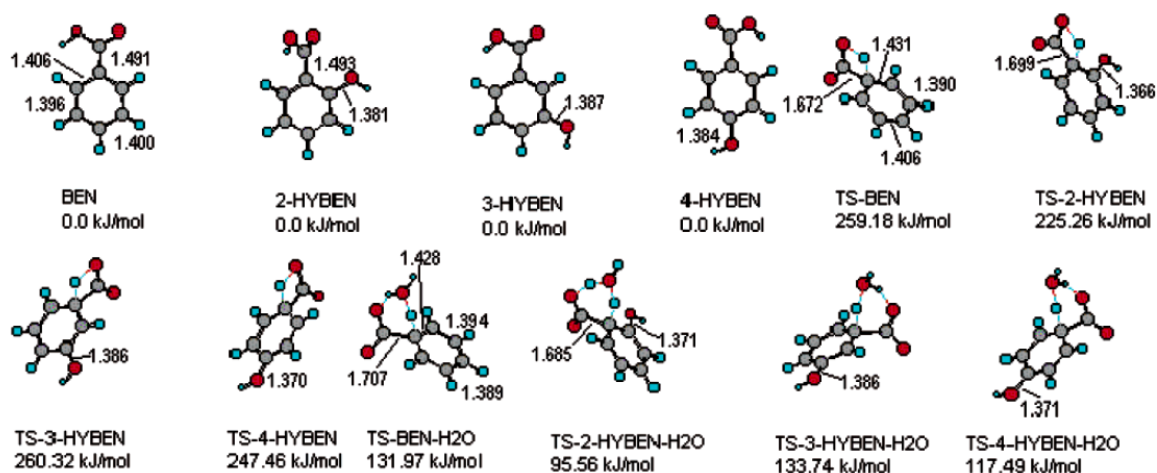
Figure 2. Transition state structures of benzoic acid and monohydroxybenzoic acids with and without one water molecule (B3LYP/6-31//B3LYP/6-31G). Bond distances are in angstroms. Reprinted with permission from Li, J. & Brill, T. B. Spectroscopy of hydrothermal reactions 23: The effect of OH substitution on the rates and mechanisms of decarboxylation of benzoic acid. *J. Phys. Chem. A* Vol. 107, 2667–2673 (2003). Copyright 2003, American Chemical Society.[3]

However, an apparently more important role in the experimental data is played by the activation entropy. It might be hypothesized therefore that differences in the solvation shell of the reactant and the transition state structures are responsible.

2.3.3. *Chuchev and Belbruno, 2007*[9]

They investigated in detail the mechanism of the decarboxylation of benzoic and or ortho-substituted benzoic acids (2-methylbenzoic acid, 2-chlorobenzoic acid, 2-fluorobenzoic acid, salicylic acid, 2-aminobenzoic acid). They also used density functional theory like Li and Brill[3], but they used a slightly different basis set. They also started the mechanism from the isomerization of the parent and substituted acids from the *syn*-conformer to the *anti*-conformer through a rotational transition state; in contrast, Li and Brill[3] started the calculations from the *anti*-conformer. Moreover, they found out that for salicylic acid, the -OH participates in the transition state formation, resulting to a slightly different mechanism when the *ortho* substituent do not participate. It could be said that this is possible when the substituent is capable of hydrogen bonding, but for 2-aminobenzoic acid, they found out that the mechanism follows that of the previously reported direct mechanism.

2.3.4. *Lindquist and Yang, 2011*[21]

They investigated the stability of benzoic acid and some of its derivatives in water (anthranilic, syringic acid, salicylic acid) in subcritical conditions. They conducted the reaction in a batch reactor in which the temperature is set to a range of 50-300 °C with heating times of 10-630 min. They found that degradation of the derivatives began beyond 150°C and became completely degraded at 300 °C after 10 minutes. Similar with previous studies, benzoic acid remained stable up to 300 °C. So, they increased the temperature to 350 °C and the heating time to 630 min, but still, 56% remained.

2.3.5. Synthesis

In all of these literatures, it was consistent that benzoic acid is very stable, and that as substituents are added, its stability decreased. These results were aptly supported by the mechanism obtained from calculations. However, the effect of water on the decarboxylation rate and kinetics is rarely discussed. Calculations and comparisons of the gas phase and with water indicate that water acts as a catalyst, but there are some discussions about the effect of solvation from Li and Brill.[3] However, as we will see later, their hypothesis that the high polarity of water would accelerate the reaction was not supported by this research's results. Clearly, there is not enough clarity on the effect of water on decarboxylation, and a more generalized explanation is necessary.

Chapter 3   Methodology

3.1.   Determination of the appropriate reaction conditions

3.1.1. Starting material

In choosing the starting material, the following factors were considered: reactivity, solubility in water, and detectability of the products. For reactivity, the starting material should have at least more than 20 % conversion but below 80 % to be able to get accurate results for kinetic studies. For the solubility, enough sample should be dissolved so that the product produced would be detectable in the HPLC. However, aromatic carboxylic acids usually have low solubility in water. Unfortunately, increasing the solubility by heating to increase the starting material concentration proved to be difficult because of the immediate cooling of the solution right after injection, causing plugging. Therefore, it was made sure that the sample dissolves completely in water before injection. Thus, several preliminary tests were conducted to make sure the suitability of the starting material for the decarboxylation experiments. Some of the acids that were considered were benzoic acid, phthalic acid, and anthranilic acid.

3.1.2. Flow reactor conditions

For the flow reactor conditions, the following factors were considered: the pressure range and temperature should represent the density changes well; the pump flow rate should allow residence times that would not allow 100 % conversions, but not slow enough that conversion is insignificant. In cases where the residence times cannot be adjusted using the pump flow rate, the reactor was cut or lengthened as necessary.

3.2.   Reagents and Reactor

3.2.1. Reagents used

This section describes the reagents and materials used in the study. The reagents used for the decarboxylation experiments are shown in Table 1, while those for analyses are shown in Table 2. The distilled water used for all experiments – in acid solution preparation, buffer preparation, and all other steps in the whole experiment – is purified using an Aquarius (manufactured by RFD240 HAADVANTEC) distillation apparatus.

3.2.2. Reactor Used

This section describes in detail the materials and equipment used in building the reactor. The use of flow reactor was because of the ease of control of the reaction conditions such as the pressure, temperature, and flow rate, in this apparatus. Table 3 describes the equipment specifications. The reactor is roughly divided into 3 parts: a raw material supply part, a preheating and reaction part, and a cooling / recovery part. For the reaction part, a 1/6 inch and 0.8 mm (outer and inner diameters, respectively) Hastelloy reactor was chosen because of its

good oxidation resistance, high-temperature strength and exceptional stress-corrosion resistance[22]. Shown in Figure 3 is the schematic diagram of the reactor used.

3.3. Experimental procedure

3.3.1. Basic procedure

3.1.1.1. Preparation of the acid solution and water

A certain amount of phthalic acid was weighed to prepare a solution of approximately 0.02 M. To facilitate dissolution, the solution was heated to about 60 to 80 °C. The sample acid solution and distilled water were put in a glass bottle. Both the sample aqueous solution and distilled water were degassed beforehand with N_2 gas for about 30 minutes to remove dissolved oxygen which could affect the reaction (via supercritical oxidation). A line of N_2 gas was placed in the glass bottles of sample aqueous solution and distilled water and sent while degassing (see Figure 3). The pressure of the N_2 gas at this time was 0.02 to 0.04 MPa.

3.1.1.2. Operating the reactor

The degassed acid solution and distilled water were sent through the pump with set flow rates. The ratio of the acid solution with water was kept constant throughout a certain run. To check whether the pumps are flowing properly, a graduated cylinder was used to check the volume at the outlet. Once the influent comes out of the outlet, the back pressure regulator is set to the desired pressure. The reactor was also checked for any possible leaks.

3.1.1.3. Collecting blank samples

To be able to measure the actual concentration of the acid solution being pumped into the reactor, a few milliliters of sample were collected after 1 hour of saturating the reactor. No heat was also applied to ascertain that no premature decarboxylation occurs. This sample is called as the blank. Any change in the density due to increase in pressure was deemed negligible at room temperature.

3.1.1.4. Setting the reactor temperature

Three heaters were used to preheat the water while one heater was used to maintain the reactor temperature. For the first three heaters, the temperature was set to about 30 to 100 degree Celsius higher than the desired to make sure that the target temperature was reached once it mixes with the acid solution (in room temperature). On the other hand, the oven for the reactor was set to about a few degrees lower, just enough to maintain the desired reactor temperature. Temperatures were carefully adjusted and monitored with the help of three thermocouples attached: 1) in the preheater line, 2) before the mixer part, and 3) through the mixer part. The temperature at the mixer was taken as the reaction temperature.

3.1.1.5. Decarboxylation reaction

Once the reaction temperature was reached after adjusting the oven temperatures, 3 times of the residence time was elapsed before collecting samples at the outlet. The temperature and pressure were periodically checked to make sure that they were constant. The temperature and pressure were kept within ± 1-2 °C and ± 0.5-1 MPa, respectively.

3.1.1.6. Quenching the reaction

To ascertain that the reaction proceeded only at the calculated residence time, cooling water was circulated in parallel with the reactor. This makes sure that the reaction is quenched by quickly bringing the solution to room temperature after passing through the reactor.

3.3.2. *Preliminary investigation of density dependence*

In this experiment, pressure was varied at 5 MPa intervals using the back pressure regulator. The pressure settings and the corresponding residence time and densities are shown in the appendix. Since every pressure change corresponds to a different density, temperature is also adjusted to make sure that it remains constant. For every 5 MPa change in pressure, 5 times of the residence time is passed to allow the system to stabilize and to ascertain that the reaction proceeded sufficiently.

3.3.3. *Kinetic studies*

In this experiment, residence time was varied by changing the flow rate of the pumps at 0.5 ml/min intervals. The flow rate settings and the corresponding residence time are shown in the appendix. The ratio of the phthalic acid solution and water were kept at a 1:9 ratio. For every 0.5 ml/min change in the flow rate, 5 times of the residence time was passed to allow the system to stabilize and to ascertain that the reaction proceeded sufficiently. Temperature of the ovens were also adjusted when the flow rate was too fast to achieve the target temperature (400°C) at the mixing point.

Table 1. Reagents used for the decarboxylation experiments.

Reagent Name	Purity	Manufacturer
Phthalic acid	min.99.5%	Kanto Chemical Co., Inc.
Benzoic acid	min.99.5%	Wako

Table 2. Reagents used for the HPLC analysis.

Reagent Name	Purity	Manufacturer
Phosphoric acid	min. 85 % (mass/mass)	Wako
Potassium dihydrogen phosphate	min. 99.5 %	Wako
Acetonitrile	HPLC Grade ≥99.9%	Sigma-Aldrich

Table 3. Specifications of the equipment and apparatus used for operating the flow reactor.

| Name of apparatus	Usage	Product name	Manufacturer
High-pressure pump	Pumping acid solution and distilled water	PU-2080 Plus	JASCO
Back pressure regulator	Controlling the pressure	SCF-Bpg	JASCO
Heaters	Preheating	SH-OMT	Nikko Science
	Preheating	ARF-50KC with AMF-CB temperature controller	Asahi Rika Seisakusho
	Preheating	IM-2-200	Sakaguchi Electric Heat
	Heating the mixer part and reactor	GC-4000	GL Sciences
Thermocouples	Temperature measurement	T-35 type sheath thermocouple	Sakaguchi thermocouple
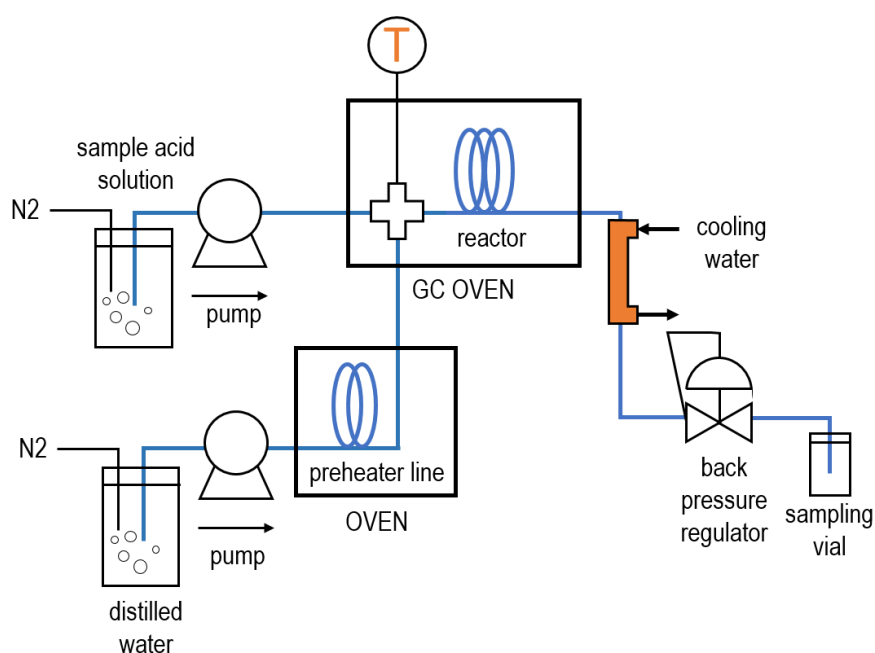
Figure 3. Schematic diagram of the flow reactor.

3.4. Methods of Analysis

In this section, the methods used to analyze the samples will be described in detail.

3.4.1. Quantitative Analysis

To analyze the concentration of the reactant and products in the sample, High-Performance Liquid Chromatography with photodiode array detector was mainly used. Table 4 shows the instrument specifications while Table 5 shows the details of the method of analysis. Standard plots for phthalic acid and benzoic acid were prepared for measuring the concentration of the unreacted reactant and products. Standard plots are shown in the appendix.

3.4.2. Qualitative Analysis

To confirm the identity of the reactant and the products in the sample, a Gas Chromatograph equipped with a mass spectrometer was used. The GC-MS used was from the Kashiwa Branch of the Environmental Science Center Main Building of the University of Tokyo. Table 6 and 7 describe the equipment specifications and settings, respectively. Note that no pre-analysis steps were conducted. The identities of the phthalic acid and benzoic acid were confirmed by comparing the MS spectrum with those that are saved in the GC-MS library.

3.5. Definition of terms

This section defines the technical terms that will be used in this thesis.

3.5.1. Conversion

The conversion (expressed in percentage) indicates the amount of the reactants that are transformed into products before and after the reaction. It is obtained by calculating the concentration of the amount of reactant present before and after the reaction as shown in Equation 1. In this study, phthalic acid is the reactant, assuming that the volume of the solution does not change before and after the reaction.

$$\textbf{Equation 1: } X_A(\%) = \frac{C_{A0} - C_A}{C_{A0}} \times 100$$

(C_{A0}: initial concentration of phthalic acid、 C_A: concentration of phthalic after the reaction)

The initial concentration of phthalic acid concentration was obtained from the blank samples.

3.5.2. Yield

The yield indicates the ratio of the amount of the product actually obtained to the theoretical amount of product if all reactants are converted completely. It is obtained by dividing the concentration of the product, benzoic acid, by the concentration of the reactant, phthalic acid, before any of it is converted as shown in Equation

2. This is only valid if the reaction stoichiometry is 1:1. In this study, the yield (Y) is defined as follows, assuming that the volume of the solution does not change before and after the reaction.

$$\textbf{Equation 2}: Y_R(\%) = \frac{C_R}{C_{R100}} \times 100$$

(C_R: concentration of benzoic acid after the reaction、 C_{R100}: concentration of benzoic when phthalic acid is completely converted to benzoic acid)

Similarly, the initial concentration of phthalic acid concentration was obtained from the blank samples.

3.5.3. Residence time

In a flowing type reaction experiment, it is the time it takes for the fluid to pass through the reaction part of the equipment. Shown below is the equation used to calculate the residence time.

$$\textbf{Equation 3: } \tau = \frac{v}{v_o}$$

(τ: residence time in min, v: volume of the reactor; v_o: volumetric flow rate)

The flow rate is corrected for density changes upon temperature and pressure increase.

Table 4. HPLC instrument specifications.

Name of the equipment	Product name	Manufacturer
Control software	ChromNav	JASCO
System controller	LC-NetII/ADC	JASCO
Pumps	PU-980	Nikko Science
Degasser	DG-2080-53	Asahi Rika Seisakusho
PDA detector		Sakaguchi Electric Heat
Autosampler	AS-950	Shimadzu
Column oven	CO-965	Sakaguchi thermocouple

Table 5. HPLC settings for analysis.

Parameters	Description
Column	Finepak SIL C18S (manufactured by Jasco), inner diameter 4.6 mm, length 150 mm
Mobile phase	Pump A: pH 2.8 Phosphate buffer (5.94 g KH2PO4 + 1.02 mL 14.7 M H3PO4) / 1 L water Pump B: HPLC-grade acetonitrile
UV wavelength	254 nm
Oven temperature	40.0 °C
Flow rate	Pump A: 0.80 ml/min Pump B: 0.20 ml/min
Injection volume	20.0 μL
Retention time (approximate)	Phthalic acid: 4 min Benzoic acid: 12 min
Analysis time	60.0 min

Table 6. GC-MS instrument specifications.

Name of the equipment	Product name	Manufacturer
GC-MS unit	GCMS-QP2010	Shimadzu
Control program	GC solution	Shimadzu

Table 7. GC-MS settings for analysis.

Parameters	Description
Column	TC-1701 (manufactured by GL Sciences)
Carrier gas	Helium
Vaporization chamber temperature	200 ℃
Interface temperature	200 ℃
Ion source temperature	200 ℃
Detector voltage	Set appropriately with -0.2 to 0.1 kV
Retention time	Phthalic acid: 4 min Benzoic acid: 12 min Benzene:
Column temperature	40.0 ℃ for 2.00 min 40.0 – 200 ℃ with 10℃ increase per minute, then 1.00 min holding time at 200 ℃
Injection mode	Split
Injection volume	1.0 μL
Analysis time	min
m/z range	29-180

Chapter 4   **Results and Discussion**

4.1.   **Determination of appropriate conditions and preliminary investigation of the reaction**

4.1.1. Choosing the starting material

The first aromatic carboxylic acid that was considered was benzoic acid. According to several reports, among the aromatic carboxylic acids to which decarboxylation was conducted, benzoic acid is the least reactive.[3,6,21] Because of its stability, reports about the effect of water in its decarboxylation are few. With this as motivation, benzoic acid was first used to study the roles of water in the decarboxylation of aromatic carboxylic acids in SCW. Results showed that there is a decreasing trend in the area of the benzoic acid (analyzed using GC-FID) versus pressure.
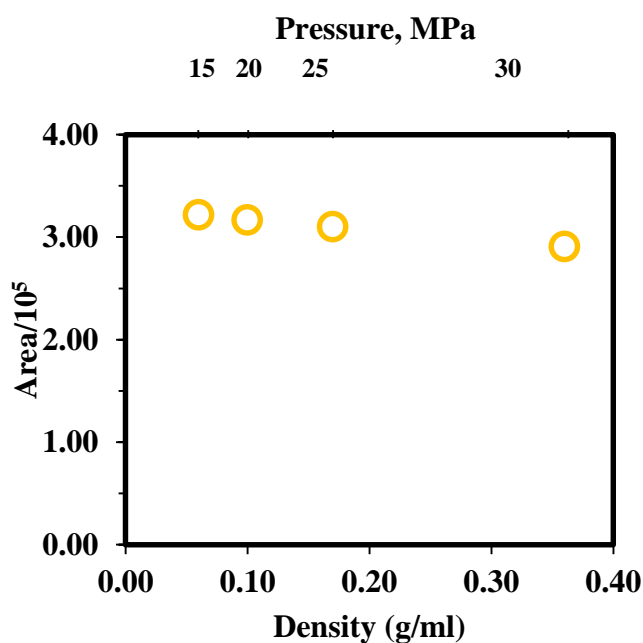
Figure 4. Peak areas of benzoic acid plotted against water density and reactor pressure (400 ℃).

Though, there is a decreasing trend, the data is not conclusive since the residence time also changes with density. Nevertheless, the data suggested that there might be a relationship with the conversion of benzoic acid decarboxylation and density. Other than that, the data also supported results from previous studies researchers that benzoic acid was very stable. As a consequence, however, it became difficult to obtain a significant conversion using a flow reactor. Many experiments and adjustments were conducted to increase the conversion and yield such as lengthening the reactor (up to 38 m), adding a polar solvent prior to analysis, etc., but only up to 7-8 % conversion was obtained. Other major problems encountered also included the difficulty detecting benzene, the decarboxylation product, due to the small amounts produced, and its weak response to HPLC-UV detector, and the inconsistent concentration values obtained for the blank samples which resulted to negative values for conversion during calculations. The solubility of benzoic acid was also relatively low which limited the amount of acid that can be dissolved to give a higher detectable benzene yield. There is still a possibility to increase the conversion and yield of this reaction by using higher pressures, but for the whole process of the

experiment (including kinetic studies), the use of benzoic acid might be impractical. Thus, it was agreed to use a different starting material.

Considering the problems encountered with benzoic acid, the next starting material that was considered was phthalic acid. Figure 5 shows the decarboxylation of phthalic acid.
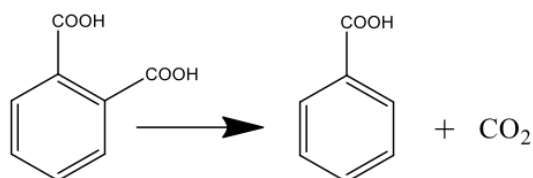

Figure 5. Decarboxylation of phthalic acid to benzoic acid and carbon dioxide.

There are numerous reports revealing that a second functional group enhances the ring's reactivity presumably because of the ring effects of the substituent. Moreover, according to Chuchev and Belbruno[9], salicylic acid, another carboxylic acid with a notable reactivity in HTW, seems to pass through a transition state absent from the decarboxylation mechanism of other difunctional carboxylic acids. This is because the -OH group of salicylic acid is also participating in the transition state. Based from this assumption, it was hypothesized that the same occurs with phthalic acid. This could mean that it decarboxylates faster and thus, makes it more practical to use in the experiment. Results from the experiment could possibly reveal more about the nature of the decarboxylation in water. In addition, the solubility of phthalic acid is higher, which makes the acid solution preparation easier. The decarboxylation product, benzoic acid, is also easy to detect in HPLC (data such as standards are also already available). As a preliminary investigation, the reactivity of phthalic acid at varying pressures was examined. The result is shown in Figure 6.

Comparing with the reaction with benzoic acid, however, there is a decreasing trend from 20 to 25 MPa, then started to slowly increase again from 25 to 40 MPa. This is despite the increasing residence time as density is increased (included in the corrections for the flow rate – see Appendix). The trend was unusual if the known mechanism based from previous literature is considered. [3,9] Kinetics studies were conducted to further investigate the effect of density on the reaction.

On the other hand, as seen in Figure 5, there is also carbon dioxide formed for every mole of benzoic acid. However, in this study, the amount of carbon dioxide was not measured since there was almost 100 % ring balance obtained from the results, confirming that only benzoic acid and CO_2 were produced.

4.1.2. Choosing the reactor conditions

For the pressure, initially, the range that was considered was from 15 MPa to 30 MPa. This is because at these pressures, there is a substantial change in the characteristics of water, from gaseous state, to liquid state, then to critical state. However, controlling the flow rate and temperature is also markedly difficult at lower pressures because of the low density of the gaseous state. The pressure range was then adjusted to 20 MPa to 40

MPa. This pressure range is better for two reasons: the control of temperature is relatively easier due to higher values of density, and secondly, the density values in this range is also highly varied (Figure 7). Thus, for this research, this pressure range was used.

For the temperature, two temperatures were considered: 380 °C and 400 °C. In choosing between the two, the density values were considered. The density values at the pressure range of 20 – 40 MPa for the two temperatures are plotted in Figure 7.

As seen from the figure, the density changes at 400 °C is more spread out at a longer range. Hence, for most of the experiments conducted in this study, the temperature was maintained at 400 °C.

For the residence time, the reactor length was modified to achieve suitable conversion values for kinetic studies (between 20 %-80 %). The initial reactor used for the decarboxylation of benzoic acid was too long (about 38 m) for phthalic acid decarboxylation as seen in Figure 8.

It is assumed that at longer residence times, the benzoic acid degraded further, probably to benzene. Though this has not been confirmed, no other degradation products were described in literature. Hence, the length was accordingly shortened from about 38 m to only about 1.5 m. The results are shown below. At 40 MPa, conversion and yield reached a maximum at around 0.41 min residence time (about 24 seconds) as shown in Figure 9.

For the flow rate, it is recommended for kinetic studies to only have a conversion of less than 80%. The flow rate range was adjusted accordingly from 1.0 – 3.0 ml/min to 2 – 4 ml/min. The ratio of the phthalic acid solution to water was also adjusted from 1:4 to 1:9. The results are shown in the graphs that are used in the next parts of the discussion.

4.2. Kinetic studies of phthalic acid decarboxylation

The results in Figure 6 showed that there is a possible effect of water at play in the decarboxylation of phthalic acid in SCW. To give more information about the reaction, kinetic studies were conducted. The results are shown Figure 10.

As expected, conversion and yield increased with time (conversion and yield were obtained 35 MPa but showed unusual trends probably due to instrumental errors). The values of the conversion and yield converge indicating that phthalic acid was converted only to benzoic acid and carbon dioxide (1:1 stoichiometry). These time profiles were also used to determine the rate law for phthalic acid decarboxylation. The conversion values were first expressed as $-\ln(1-x)$ to test if it follows first order kinetics. The result of the graph for 40 MPa is shown in Figure 11. Graphs for other pressures are shown in the appendix. The figure showed great linear dependence, and thus indicate first-order rate kinetics.

The rate constants for the reaction were taken from the slope. Figure 12 presents the rate constants for the decarboxylation of phthalic acid at different pressures. From the figure, it can be seen that there is a steep decrease from 20 to 25 MPa, meaning that as pressure is increased, the rate decreases, and the reaction occurs

faster at lower pressures. The rate constant continued to decrease at higher pressures. (The value for 35 MPa was obtained, however, it did not fit the plot even after measuring twice. Unfortunately, not enough data was obtained to explain those results. Most likely, however, instrumental errors were the reason since in the preliminary investigation for the effect of density (Figure 6), the point for 35 MPa fit the graph) The trend revealed from the graph cannot be explained by the reaction mechanism described from previous literature. From Li and Brill[3] and Chuchev and Belbruno[9], using computer simulations, they described that the mechanism as passing through a transition state interacting with water. The reaction mechanism for salicylic acid in a gaseous atmosphere and with one water molecule is shown in Figure 13. From this mechanism, water could be thought of as a catalyst that participates in the formation of the transition state and lowering its energy. Thus, initially, it was hypothesized that upon increasing density, where water molecules are more intact, the rate would increase. However, this was not the case. It was supposed that there must be a different factor at play affecting the rate, and thus another approach was considered in accounting the plausible effects of water on the observed pressure dependence.

4.3. Study of solvation effects

The trend observed in Figure 12 could be attributed to many water properties, but a previous study by Fujii et al.[10] had seen a similar trend with formic acid decarboxylation. Similarly, the rate of the decomposition of formic acid decreased as pressure is increased (Figure 14).

In their discussion, they have considered solvation effects to explain the trend. To evaluate the solvation effects from pressure changes, they considered the activation volume. According to them, the partial molar volume of the solute is affected by interactions between the solute and the solvent, so the relationships between the states of the reaction species, i.e., the reactants and transition state, and the solvent properties are important in determining the pressure dependence of rate constants. Moreover, they mentioned that theoretically, the partial molar volume of a polar species is smaller than that of a non-polar species in a polar solvent since the polar species attracts solvent molecules. When the polarity of the transition state is weaker than those of the reactants, the activation volume is positive and the rate constant exhibits negative pressure dependence, according to Le Chatelier's Principle. Then they correlated the isothermal compressibility of water with the trends from the partial molar volume and pressure. They concluded that pressure has a negative effect on the decomposition of formic acid.[10]

The process could possibly be applied in the decarboxylation of phthalic acid as well. However, it involves deriving an equation relating pressure and rate since there is no equation directly relating the two, it could be considered a more tedious approach. Another way to relate the rate with the pressure while considering the solvent properties is by considering the dielectric constant of the solvent. The polarities of phthalic acid, the transition state, and benzoic acid are presumably varying, and therefore, their solvation in a solvent would be different. A higher polarity means higher solvation in a polar solvent. According to Connors[23], if two neutral reactant molecules produce a polar product, then most likely the transition state will be intermediate in polarity, and an increase in rate is expected as the solvent polarity is increased. This is because the stabilization of a more polar species is greater in a polar solvent than a less polar species. Based from the results earlier, as the polarity of water is increased as density is increased, it can be assumed that the during decarboxylation, the polarity of transition from the reactant to the transition state during decarboxylation decreases, resulting to a decrease in rate.

This could be supported by examining the dielectric properties of the reactants, transition states, and products by performing molecular simulations and calculation. For the time being, it remains a topic in the future. It is also recommended to compare modelling results to the known mechanism to determine whether it agrees well with the results of this experiment.

It might be difficult to visualize the effect of structure polarity without the modelling, and, hence a numerical expression such as the Kirkwood's expression was used as a quantitative description to further support the apparent solvation effect of water on the rate of decarboxylation. It expresses the free energy of transfer of a dipole moment of μ from a medium having $\varepsilon = 1$ to a medium of dielectric constant, ε,

$$\textbf{Equation 4: } \Delta G_{tr}^0 = -\frac{\mu^2}{r^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)$$

where r is the molecular radius. This equation accounts only for the electrostatic component, and it treats the solvent as a continuous isotropic medium. Considering the dipole moment of the reactant, μ_A and the forming transition state M‡ with dipole moment, μ_M, the equation can be derived to form linear equation shown in Equation 5:

$$\textbf{Equation 5: } lnk_s = lnk_0 + \frac{N}{RT}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\left(\frac{\mu_M^2}{r_M^3} - \frac{\mu_A^2}{r_A^3}\right)$$

where k_0 is the rate constant in a hypothetical medium of $\varepsilon = 1$ and N is Avogadro's number.[23] Plotting the log k and $(\varepsilon - 1)(2\varepsilon + 1)$ using the rate constants from different pressures and the dielectric constants of SCW at different pressures at 400 °C (Figure 15), an inverse linear relationship was observed. A good correlation between the rate constant and the dielectric constant supports the earlier hypothesis.

Finally, since there is good agreement between the reaction rate and dielectric constant, it could be said that the role of water is mostly as a participant in the intermolecular interactions through solvation effects. Furthermore, the catalytic effect of water, as proposed by previous researchers, was not confirmed in this work.
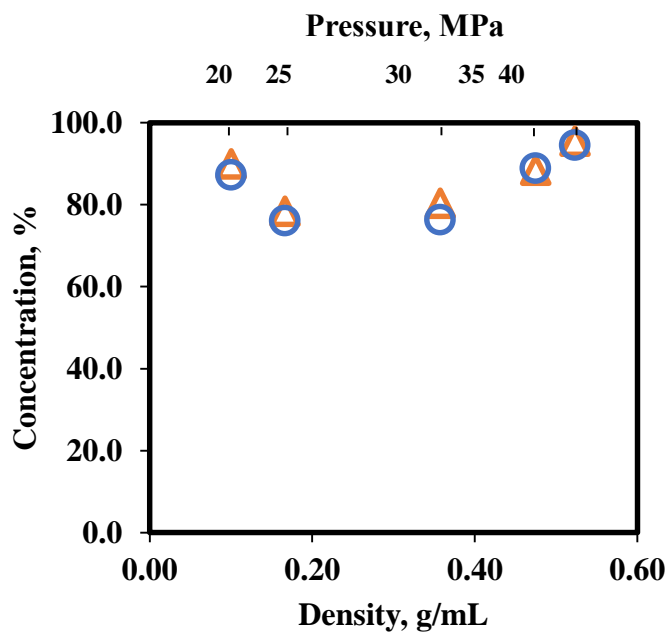
Figure 6. Conversion of phthalic acid (circle) and yield of benzoic acid (triangle) at 400 ℃ versus density and pressure.
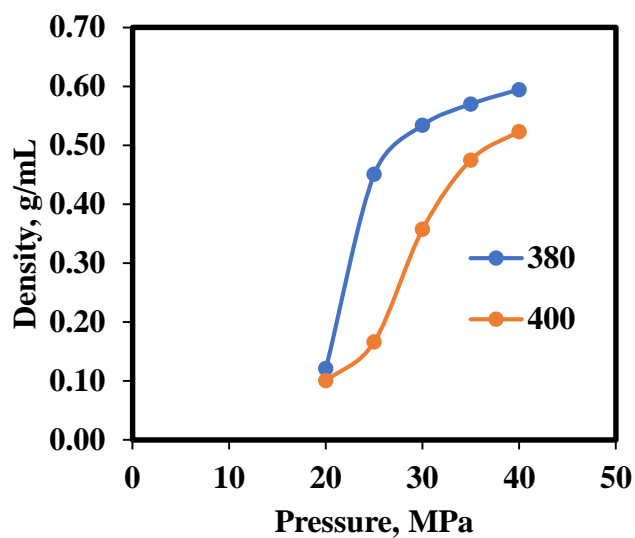

Figure 7. Density of supercritical water at different pressures at 380 °C and 400 °C. (Values obtained from W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data, 31 (2002) 387-535. Calculated by Physical Properties for Water ver 5.1 (Prof. Richard L. Smith, Tohoku University).
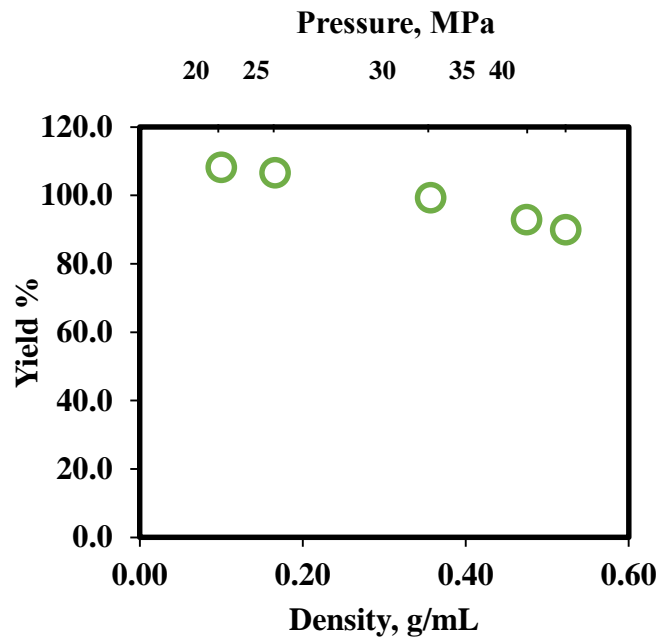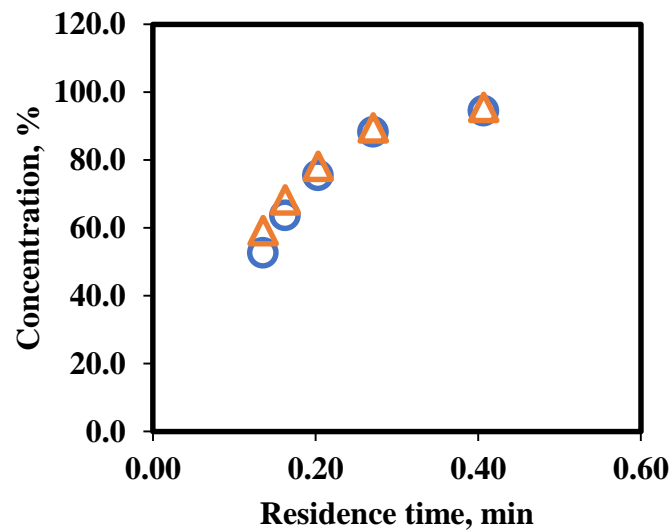
Figure 8. Yield of benzoic acid for the decarboxylation of phthalic acid at 40 MPa and 400 ºC with a 38 m reactor (volume about 21 mL).

Figure 9. Conversion of phthalic acid (circle) and yield of benzoic acid (triangle) at 400 ºC and 40 MPa versus density and pressure with a 1.5 m reactor (volume about 0.7 mL).
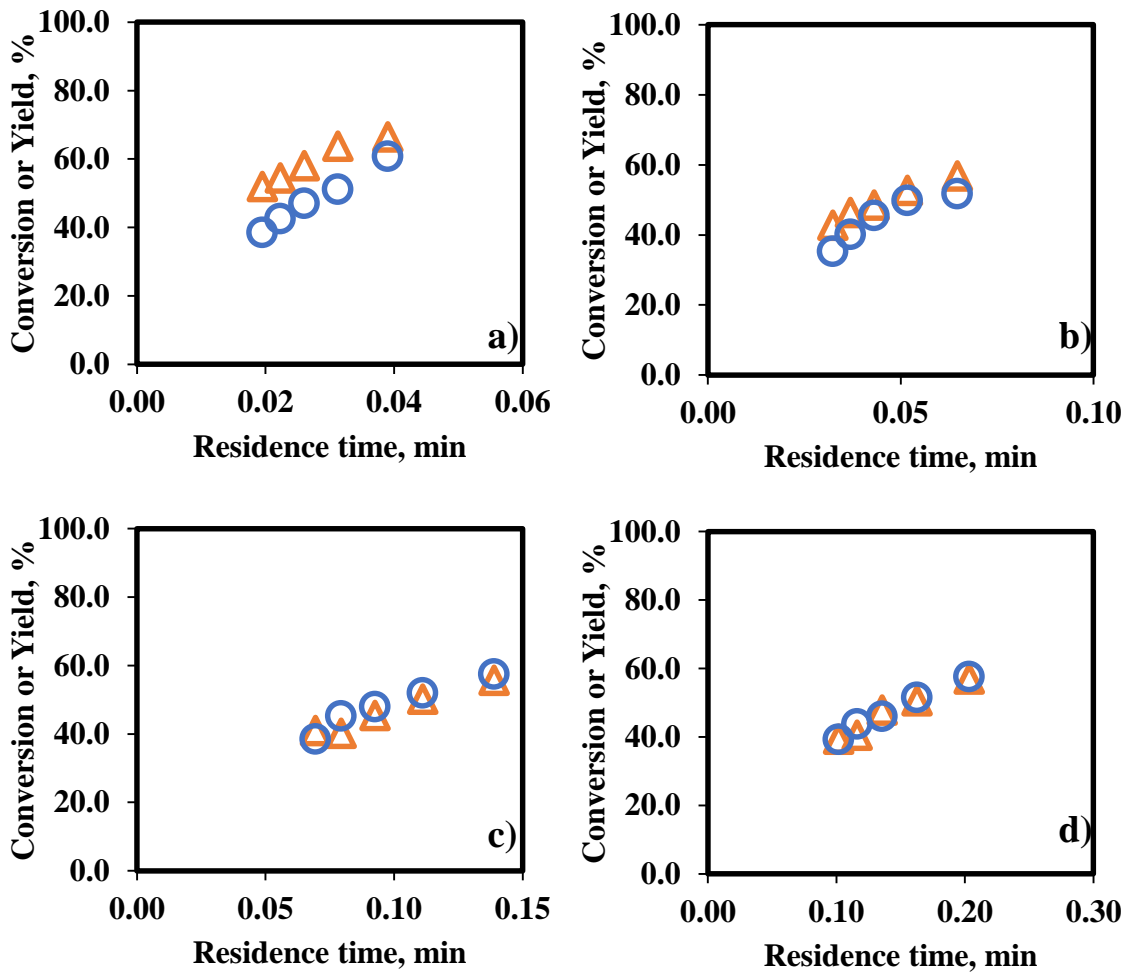
Figure 10. First order plots for the rate of phthalic acid decarboxylation at 400 ℃ at a) 20 MPa, b) 25 MPa, c) 30 MPa, and d) 40 MPa
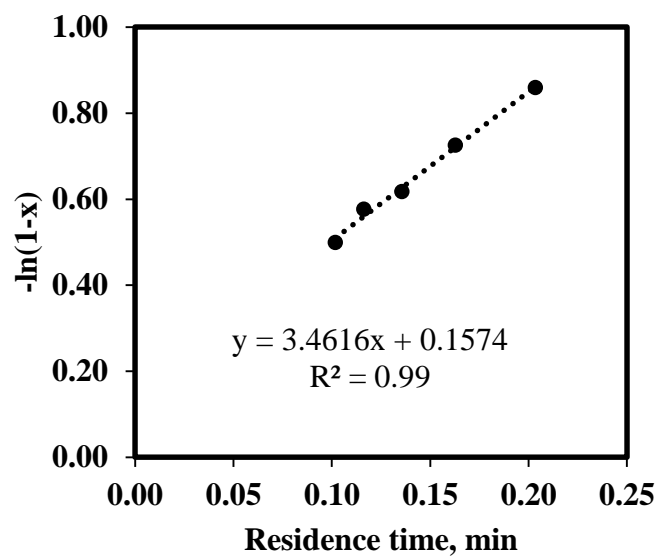
Figure 11. First order plots for rate of phthalic acid decarboxylation at 400 °C and 40 MPa.
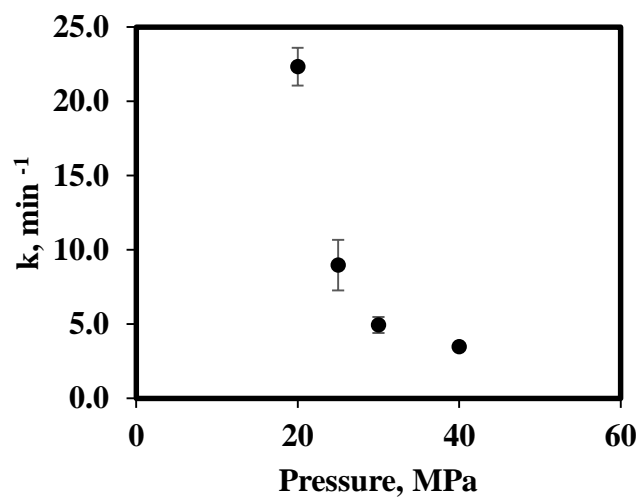

Figure 12. First order rate constants for phthalic acid decarboxylation as a function of pressure at 400 °C. Error bars were estimated by considering the deviations of temperatures, pressures and flow rates of the reaction systems.
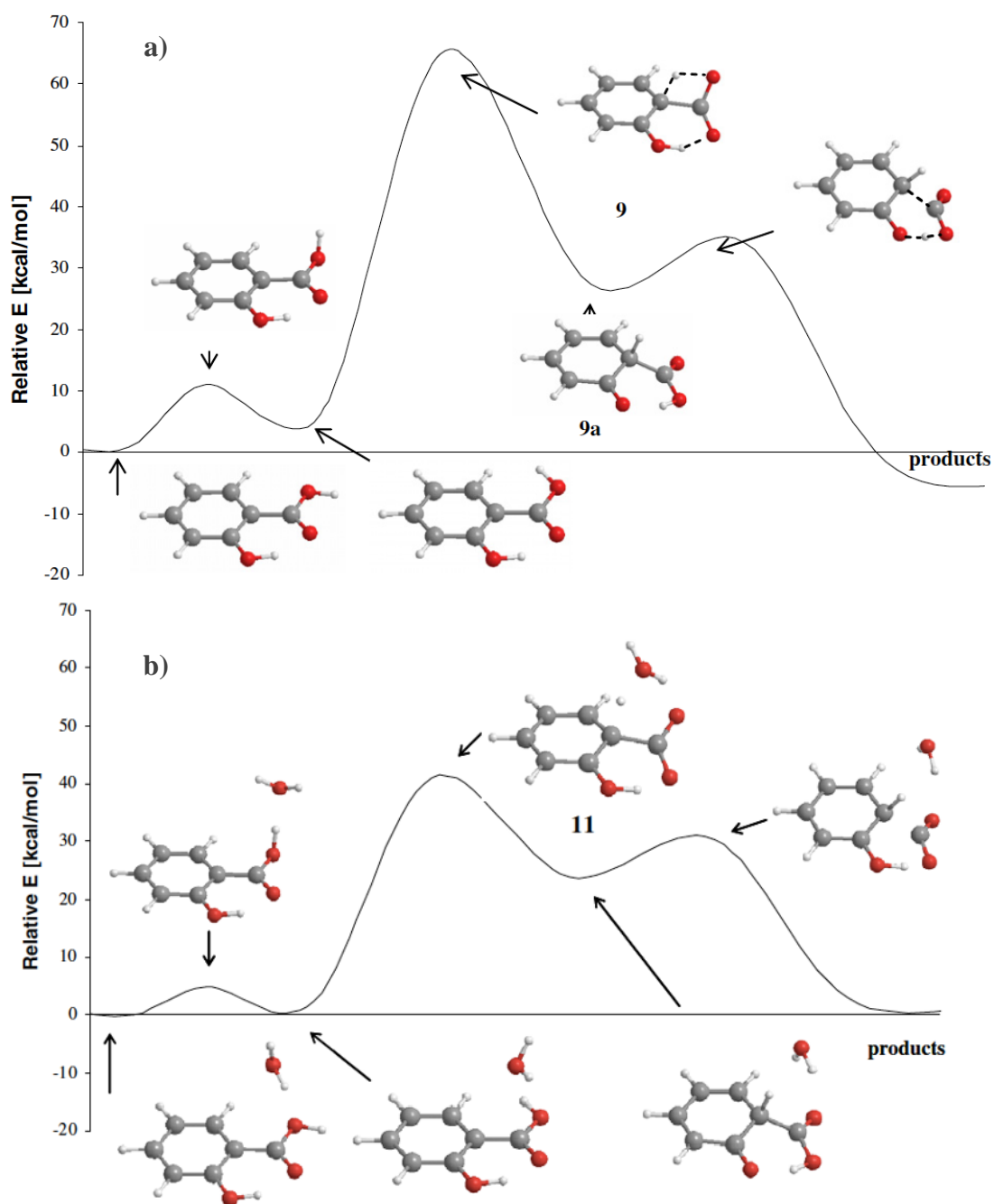
Figure 13. Gas phase (a) and water-assisted (b) reaction pathways of the decarboxylation of salicylic acid beginning with the lowest energy conformer. Reprinted from Journal of Molecular Structure: THEOCHEM Vol. 807, Chuchev, K. & BelBruno, J. J. Mechanisms of decarboxylation of ortho-substituted benzoic acids., Copyright (2006), with permission from Elsevier [9]
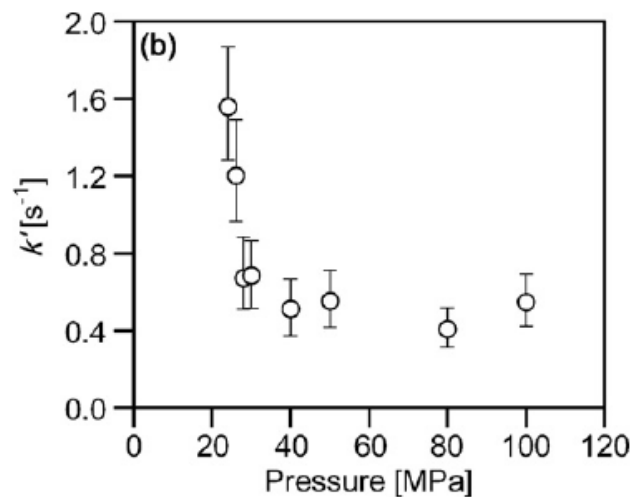
Figure 14. Pseudo-first order rate constants for formic acid decomposition as a function of pressure at 400 °C. Reprinted from the Journal of Supercritical Fluids Vol. 71, Fujii et al. Effects of pressure on decomposition of formic acid in sub- and supercritical water, Copyright (2012), with permission from Elsevier.[10]
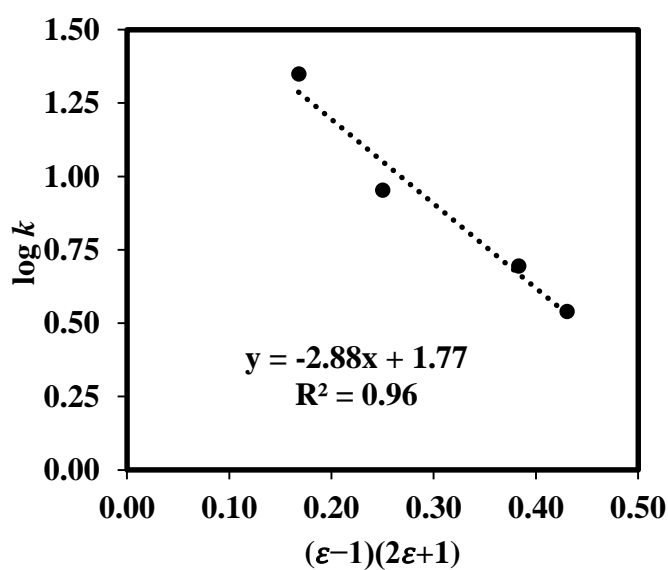

Figure 15. Plot of log of the rate constant of the decarboxylation of phthalic acid at varying pressures at 400 °C versus the Kirkwood dielectric constant.

Chapter 5   Summary, Conclusions, and Recommendations

5.1. Summary

This study was conducted at the Environmental Process Engineering Lab at the University of Tokyo, Kashiwa Campus, Kashiwanoha, Kashiwa, Chiba, Japan. The study aimed to investigate the roles of water in the decarboxylation of aromatic carboxylic acids in SCW by varying water density. Specifically, it was the goal of this research: 1) to measure the conversion and yield of phthalic acid decarboxylation at different densities by controlling the pressure, 2) to calculate the rate constant and determine its relationship with pressure and density, 3) to propose a numerical relationship between density/pressure and reaction rate, and 4) to propose possible roles of water in the decarboxylation reaction based on the conclusions obtained from the experimental data.

Decarboxylation was conducted using a flow reactor made up of Hastelloy with internal diameters of 0.80 mm and outer diameter of 1/16 in. with a total reactor volume of about 0.7 ml. A GC oven was used to maintain the reactor temperature at 400 °C. Two HPLC pumps were used to inject the acid solution and the distilled water at a fixed flow rate. A pre-heater made of stainless steel was connected to the distilled water line to ascertain that the target temperature was achieved at the mixing point. Pressure was regulated using a back-pressure regulator. Cooling water was circulated in parallel with the reactor after the reactor part to quickly quench the reaction. The cooled sample was then collected in a vial. For analysis, HPLC-PDA was used for quantitative measurements while GC-MS for the confirmation of the identity of the contents of collected samples.

In choosing the proper starting material for the decarboxylation reaction, factors including reactivity, solubility in water, and detectability of the product were considered. Phthalic acid satisfied all the conditions. For the parameters of the reactor, the pressure, temperature, flow rate, residence time, and acid : water ratio were carefully selected by several tests and analyses. The pressure range chosen was from 20 MPa to 40 MPa, while the temperature was 400 °C for the reason that density is highly varied in these conditions. The flow rate (and corresponding residence time) was chosen based on the sufficient conversion and yield suitable for accurate kinetic analysis (20 – 80%). The flow rate range was from 2 ml/min to 4 ml/min. The reactor length was also accordingly altered when flow rate adjustments was not possible to shorten/lengthen the residence time.

Preliminary investigation of the effect of density on the decarboxylation of phthalic acid was conducted by varying the pressure of the system at 5 MPa intervals. The conversion and yield were obtained, analyzed, and plotted against density and pressure values.

Kinetic studies were conducted by varying the flow rate of the system at 0.5 ml/min intervals. The conversion was obtained and plotted as $-\ln(1-x)$ against residence time to determine if the reaction follows first order kinetics.

Results from the preliminary investigation of the effect of density on the decarboxylation of phthalic acid showed a drop in conversion and yield from 20 MPa to 25 MPa. Then from 25 MPa, the conversion and yield started to increase again. This result was used as a guide in investigating the effect of density on the rate of the reaction.

Kinetic studies supported the preliminary results when the calculated rate constants from the first-order plots plotted against pressure showed an inverse relationship. In other words, in the decarboxylation of phthalic acid in SCW, pressure has a negative effect on the rate.

To explain this trend, solvation effects of water was considered. With regards to solvation, the higher the polarity of a species, the higher its solvation in a polar solvent, and a more polar transition state results an increase in rate of the reaction as the solvent polarity is increased. Data from the experiments indicated that the transition from the reactant to the transition results to a decrease in polarity, since the rate decreased when the solvent polarity increased when the density was increased. To support this numerically, Kirkwood expression was used which relates the rate of the reaction with the dielectric constant of a solvent. Plotting log k versus the Kirkwood dielectric constant resulted to an inverse linear relationship, properly representing the trend from the results of kinetic studies. Thus, it was concluded that solvation effects of water were the dominant factor contributing to the rate changes in the decarboxylation of phthalic acid in SCW.

5.2. Conclusions

The study succeeded in investigating the roles of water in the decarboxylation of aromatic carboxylic acids in SCW by varying water density. The conversion and yield of phthalic acid decarboxylation at different densities were calculated and analyzed. The rate constants for each pressure were obtained and plotted against pressure. The relationship obtained was that as pressure and density is increased, the rate constant, and consequently, the rate, decreased. The relationship was interpreted using Kirkwood's expression. An inverse relationship was found, indicating that water affected the reaction rate through its solvation effects.

5.3. Recommendations

In a study by Fujii, et al.[10], the ionic effects in the decomposition of formic acid in sub- and supercritical water revealed that water positively affects the reaction at higher pressures. Thus, as a recommendation, ionic effects could also be investigated for phthalic acid decarboxylation to explore the effect of water as an acid- and base-catalyst varying the pH of the system.

It is also worth exploring the effects of other water properties in SCW. As a starting point, the effects of those properties in phthalic acid decarboxylation could also be investigated. Some worth mentioning are the effect of water concentration and isomer effects. There have been many mentions of water acting as a catalyst[3,9,18,24] which were often based on computer simulations and comparisons of gas phase and water-assisted decarboxylation. The investigation of other properties could be a more empirical approach to clarify such claims.

A greater goal of this research is to push the progress of SCW in the industry as an alternative medium for many reactions and industrial processes such as large-scale waste treatments. Thus, it is also recommended that research on how to apply the results of this research to other reactions conducted in SCW should be pushed forward. Computer simulations to produce generalizations of the results of this research may be used to achieve this goal, and hence, suggested as a future topic for research.

Chapter 6   Appendix

6.1. Supplementary data for the experimental section

6.1.1. Preliminary investigation of density dependence

Table 8. Experimental conditions for the preliminary investigation of density dependence of phthalic acid decarboxylation.

Temperature, ºC	400
Flow rate (total), ml/min	1.00
Water, ml/min	0.80
Phthalic acid, ml/min	0.20
Initial acid solution concentration, M	0.20
Reactor volume, mL	0.7

Table 9. Density of water with corresponding residence time values with a 0.7 mL reactor at different pressures at 400 ºC.

Pressure, MPa	Density, g/ml	Residence time, min
20	0.10	0.08
25	0.17	0.13
30	0.36	0.28
35	0.47	0.37
40	0.52	0.41

Table 10. Experimental conditions for the kinetic studies of phthalic acid decarboxylation.

Temperature, ºC	400
Flow rate (total), ml/min	2.00-4.00 ml/min
Acid solution-water ratio	0.1
Initial acid solution concentration, M	0.02
Reactor volume, mL	0.7

Table 11. Residence time of phthalic acid decarboxylation using a 0.7-mL reactor at different pressures.

Total Flow rate (ml/min)	Residence time, min				
	20 MPa	25 MPa	30 MPa	35 MPa	40 MPa
2.0	0.04	0.06	0.14	0.18	0.20
2.5	0.03	0.05	0.11	0.15	0.16
3.0	0.03	0.04	0.09	0.12	0.14
3.5	0.02	0.04	0.08	0.11	0.12
4.0	0.02	0.03	0.07	0.09	0.10

6.2. Standard curves
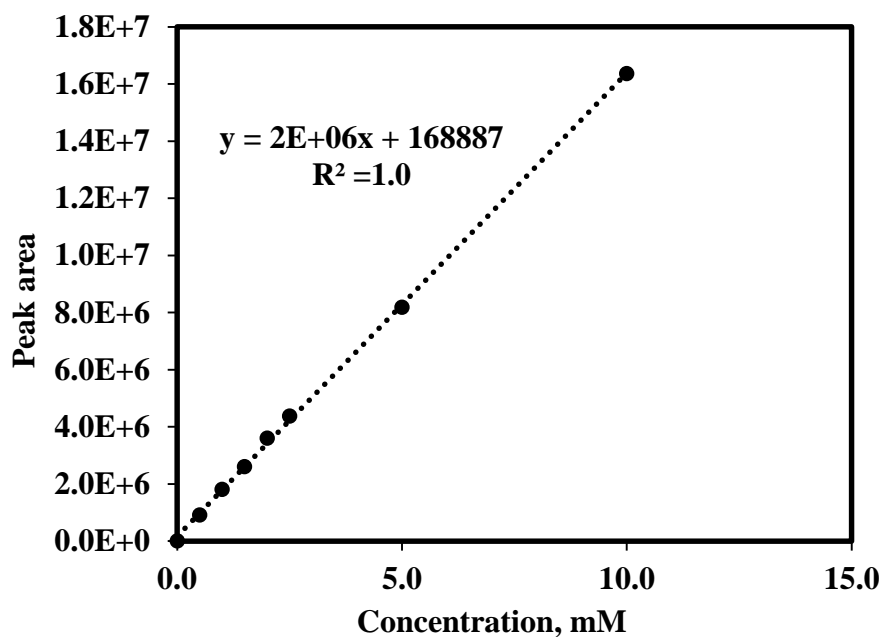
Figure 16. Standard curve for phthalic acid.

y = 2E+06x + 168887
R² =1.0
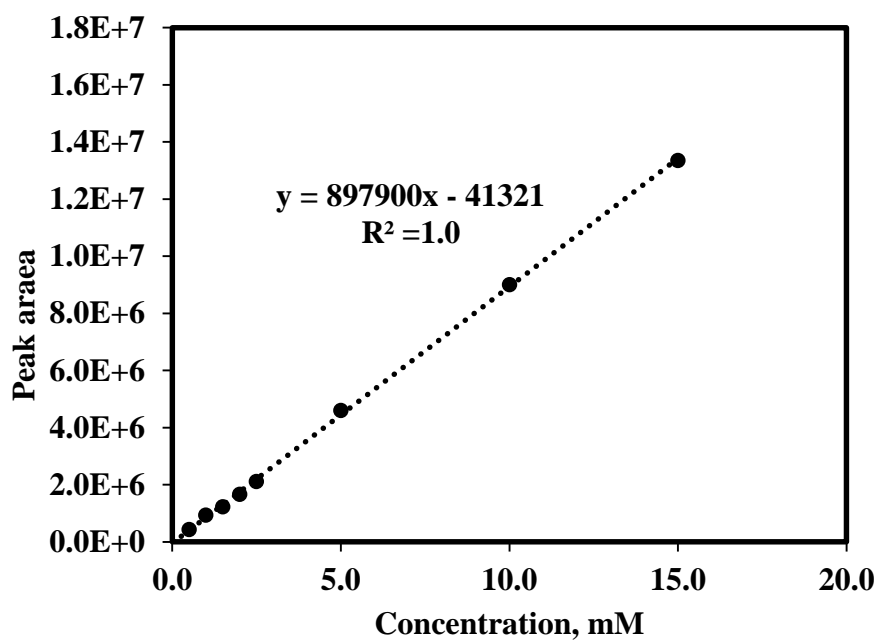
Figure 17. Standard curve for benzoic acid.

y = 897900x - 41321
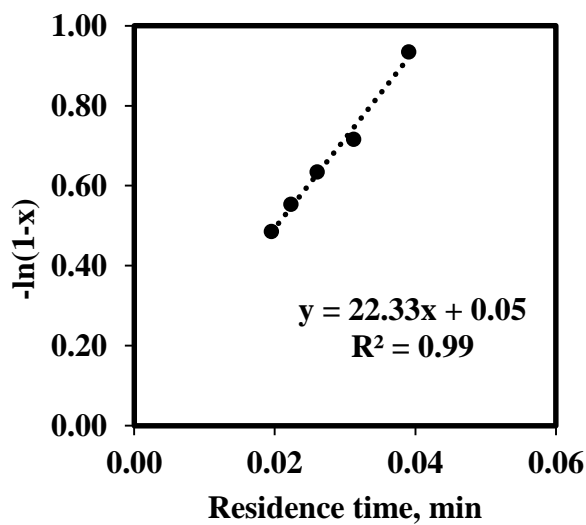R² =1.0

6.3. First order plots

Figure 18. First order plots for rate of phthalic acid decarboxylation at 400 °C and 20 MPa.
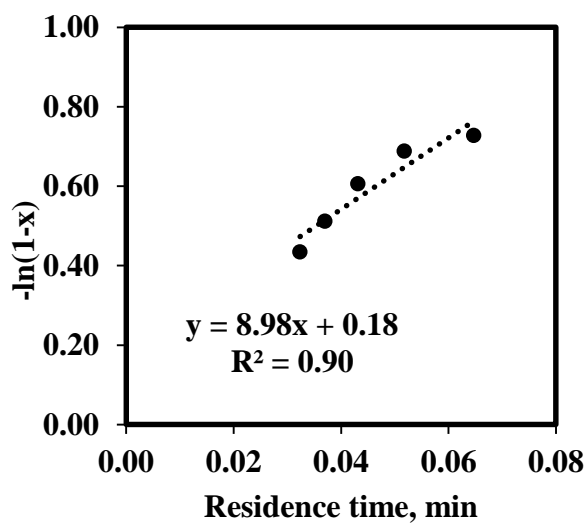

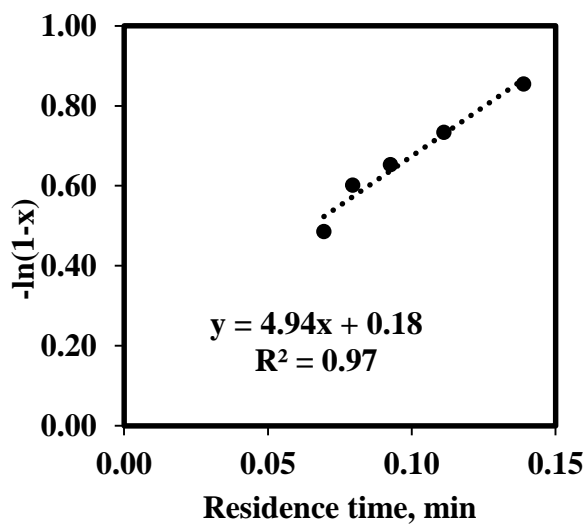**Figure 19.** First order plots for rate of phthalic acid decarboxylation at 400 °C and 25 MPa.

Figure 20. First order plots for rate of phthalic acid decarboxylation at 400 °C and 30 MPa.

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6.4. Supplementary data for plotting Kirkwood expression

Table 12. Values of the rate constants of phthalic acid decarboxylation and the dielectric constant of water at different pressures.

Pressure, MPa	k, min^{-1}	ε^{*}	log k	$\dfrac{(\varepsilon - 1)}{(2\varepsilon + 1)}$
20	22.3	1.75	1.34	0.17
25	8.97	2.50	0.95	0.25
30	4.94	5.92	0.69	0.38
40	3.46	10.3	0.54	0.43

* Values obtained from W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data, 31 (2002) 387-535. Calculated by Physical Properties for Water ver 5.1 (Prof. Richard L. Smith, Tohoku University)

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