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RSC Advances PAPER Effect of subcritical water on homogeneous Cite this: RSC Adv., 2016, 6, 64977 catalysis of used cooking oil hydrolysis† Ong Lu Ki,a Tran Nguyen Phuong Lan,b Soetaredjo

1 **Felycia Edi,c** Ismadji **Suryadi*c** and Ju **Yi-Hsu*a**

2 **The effect of temperature and pressure on the batch hydrolysis of used cooking oil in fatty acids- (autocatalytic system), dilute acid- (pH 5.0), and dilute Cu-catalyzed systems (500 mg CuSO₄ per kg solution) was studied. The reaction was carried out using a fixed water/acylglycerides molar ratio of 30 : 1 under various temperatures (200–250 C) and initial pressures (1.96–4.90 MPa) for 2 h. Experimental data were processed statistically using ANOVA and the Spearman correlation method aside of conventional**

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2data interpretation. The Cu-catalyzed system was superior to the other systems. Temperature had greater

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2effect on oil hydrolysis than initial pressure. The use of CO₂ as the pressurizing gas altered fatty acid production and Cu soap formation particularly by oil dilution that also accompanied by a slight

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2acidification of the aqueous phase. The water ionization constant was the most influencing property for

www.rsc.org/advances fatty acid production and Cu soap formation. 1. Introduction Fatty acids (FAs) are the constituent of lipoidal matters in nature. These substances have been used for centuries to make various useful goods from soap and detergents to renewable biodiesel fuel. Hydrolysis of vegetable oils and animal fats is the common way to produce these platform chemicals. In hydro- lysis of oils and fats, a molecule of triacylglyceride is reacted with three molecules of water to yield three molecules of fatty acid. This reaction in addition to requiring a large excessive amount of water, compressed hot water at elevated temperature known as superheated water or subcritical water (SCW) is absolutely required for excellent conversion of oil.1,2 In subcritical state, water possesses higher ionic product, which allows production of more H₃O⁺ and OH⁻ for catalyzing hydrolysis reaction.3 Lower dielectric constant of SCW than water at ambient condition makes it an excellent medium for fast, homogeneous and efficient reactions with non-polar species, such as oil.1,3 Lower viscosity and density may also improve mixing of SCW with the other liquids. By controlling pressure and temperature of the reaction, those properties can be easily aDepartment of

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c6ra14807g manipulated. High temperature of SCW also bene?ts oil hydro- lysis, which was identi?ed as an endothermic reaction.4,5 In industrial scale, oil hydrolysis is carried out with or without a presence of catalyst. The non-catalytic approach, such as in Colgate–Emery process, utilizes SCW properties to induce

1 self- catalysis mechanism of available FAs

beside improving oil–water miscibility.1,6 Industrial catalysis process for

1 oil hydrolysis reaction may employ acid, base, transition metal, or enzyme.

2,7 Among all catalyst, only inorganic type can be involved in subcritical water state due to thermal degradation of enzyme in very hot water. Since the

1 use of base as catalyst generates sludge, soap by-product, and hard wastewater in the down-stream of the process,

Bronsted or Lewis acid catalyst such as mineral acid or transition metal is commonly used as industrial catalyst for oil hydrolysis.8 Global scarcity of water, especially in the arid and semi-arid area is one of the top issues that the world faces now and is expected to get worse in the future. This issue promotes waste- water reuse and recycling to satisfy water demand for domestics, industrials, recreational, and agricultural purposes. Among of wastewater types, heavy metal laden wastewaters take a special position due to its toxicity to human and environment.9 Heavy metals in wastewater need to be separated before wastewater can be recycled for reuse. Many techniques are known today to treat heavy metals in wastewater,

1 such as membrane ?ltration, chemical precipitation, ion exchange, adsorption, and electro- chemical deposition.

10 However,

1 all these methods are generally expensive in terms of capital cost, material fabrication, and material regeneration,

which overall hinder its application for treating large volume of industrial wastewater.10,11 Heavy metals in wastewater come from numerous sources, such as metal plating facilities, battery manufacturing industries, electronic industries, mining, and metallurgical industries.10,12,13 Copper (Cu) is a heavy metal that o?en appears in wastewater, particularly in printed circuit board wastewater.14 With a fast growth in the production of communication devices lately, generation of large amount of Cu-containing wastewater is concomitantly increasing with printed circuit board demands. A recent study revealed that Cu-containing waste- water can be used to hydrolyze waste cooking oil, which may solve this issue from the wastewater reuse viewpoint.15 From the same study, water at subcritical state was mentioned to affect catalysis mechanism of acidi?ed and non-catalytic system. However, the effect of SCW was only hypothesized from the FA production rate at elevated temperature without any statistical assessment. Moreover, deeper and holistic discussions on the relationship between operating parameters, SCW properties, and the catalysis

mechanism involved are not found in published studies on the same subject.^{16,17} In this study, the effect of temperature and initial pressure towards the formation of FA and copper removal was analyzed statistically in this study to further understand the role of operating parameters in the SCW properties adjustment in the oil hydrolysis reaction. Correlation between water properties including negative logarithmic value of ionic product ($\log K_w$), static dielectric constant (ϵ), dynamic viscosity (μ), and density (ρ) at respective temperature and actual pressure to FA yield and copper removal percentage were evaluated. The use of CO₂ was also compared as the substitute of N₂ for pressurizing the reaction system. Thorough discussion of the effect of SCW properties towards the reaction catalysis was also incorporated. acetate (99.9%) were obtained from Merck (USA) and Echo Chemical (Taiwan), respectively. Industrial grade hexane was obtained from a local chemical supplier. A mixture of 37 fatty acid methyl esters (FAMES) obtained from Supelco (Bellefonte, PA, USA) was used to identify fatty acid profile of used cooking oil.

2.2. Used cooking oil hydrolysis
Used cooking oil and CuSO₄ solution

1 **with a concentration of 500 mg CuSO₄ per kg solution was** introduced into a custom-made **batch reactor**. A constant **molar ratio of triacylglycerides to water** at **1 : 30** was always used. **The reactor** apparatus comprised **a 200 mL glass chamber, 316 -grade stainless steel autoclave body, a K-type thermocouple, a PID temperature controller, a pressure gauge, a magnetic stirrer, and an external electric heater (Fig. S1†)**. **Afer** closed **the reactor tightly**, nitrogen **was**

introduced to purge out oxygen. For the evaluation of pressure effect, nitrogen pressure in the reactor headspace was kept at 1.96–4.90 MPa. The

1 **reactor was then heated to the desired temperature**

(200 C, 225 C or 250 C) for 2 h. Final pressure at the corresponding temperature was recorded to determine the values of SCW properties according to Alexandrov, et al.¹⁸ The reaction system was then cooled down to 50–60 C. Glycerol was removed by washing the oil twice with warm water

1 **in a separation funnel. The top layer (oil product) was** weighed **and analyzed** for its **acid value (AV)**

and Cu content. The FA yield percentage was

1 **calculated by using the following equations:**

AVoil

1 **product 0mg KOH per g oil** m **oil product 0g** AVOil **feed 0mg KOH per g oil**
oil feed 0g

m FA yield 0% ¼ 0SV AVoil

1 **feed 0mg KOH per g oil** m oil **feed 0g 100% (1)**

12. Experimental 2.1. Chemicals Used **cooking oil was** collected **from a local**
 restaurant **in Taipei, Taiwan. The oil was stored in** an amber glass **bottle and**
used without further **pretreatment.**

Reagent grade chemicals were used:

1 **KOH (85%, Across Organics, USA), anhydrous**

CuSO₄ (97%, Shimakyu, Japan), anhydrous MgSO₄ (99.5%, Showa Denko, Japan),

1 **HCl (37% purity, Across Organics, USA), H₂SO₄ (95– 97%, Scharlau Chemical,**

Spain), NaCl (99.5%, Showa Denko, Japan),

1 **ethanol (95%, Echo Chemical, Taiwan), and oxalic acid**

dihydrate (99%, Koku- san Chemical Co. Ltd., Japan). Phenolphthalein (Sigma Aldrich, USA) in ethanol
 was used as titration indicator. CuSO₄ stock solution was made from its anhydrous salt

1 **with a concentration of 25 000 mg kg 1.**

Analytical reagent grade HNO₃ (90%, May and Baker, UK) was used for copper ion extraction of fatty acids
 products. A mixed standard solution

1 **(solution IV, 1000 mg L 1, Merck Chemicals, USA)**

was used to obtain Cu calibration curve in the inductively coupled plasma (ICP) measurement. HPLC grade
 methanol (99.5%) and ethyl Acid catalytic and FA autocatalytic systems were evaluated also by changing

the copper solution with H₂SO₄-acidified water (pH 5.0) and deionized water, respectively. In the other type of experiments, CO₂ was used as the pressurizing gas. Experiments involving different catalyst systems and gas types were done at the studied temperature and pressure range with the same acylglycerides/water molar ratio (1 : 30). 2.3. Oil analysis AV was analyzed titrimetrically according to ASTM D1980-87 method and calculated from the amount of KOH used. VKOH ðmLÞ CKOH ðNÞ 56:1 AV ðmg KOH per g oilÞ ¼ wt: of sample ðgÞ (2)

1SV was determined by titration method (ASTM D5558-95)

as the basis of maximum obtainable fatty acid in the used cooking oil. SV was calculated by using eqn (3). SV ðmg KOH per g oilÞ ¼ VHCl of blank sample ðmLÞ NHCl ðNÞ 56:1 (3) wt: of sample ðgÞ Ester value (EV) and average molecular weight of the used cooking oil (MW_{av}) as pure triacylglycerides can be calculated from eqn (4) and (5), respectively. EV

1(mg KOH per g oil) ¼ SV (mg KOH per g oil) AV (mg KOH per g oil)

(4) was determined by extraction using a previously studied method with slight modification.²⁵ Oil sample (5 g) was mixed with 10% (v/v) HNO₃ (20 mL) and held at 60 C for 4 h under magnetic stirring (500 rpm). After extraction, the

1mixture was let to separate into oil and water layers and cooled

in a refriger- erator

1to solidify the oil layer. Aqueous part was

taken after filtration

1using a 5 mm filter paper (Advantec Grade No. 2) and

analyzed using ICP. Copper removal percentage was

1expressed as the number of Cu²⁺ transferred into the oil phase to the total Cu²⁺ introduced into the reaction system as shown in

eqn (6). Cu removal ð%Þ ¼ Cuoil product ðmg kg⁻¹Þ moil product ðkgÞ Cuoil feed ðmg kg⁻¹Þ moil feed ðkgÞ CCuSO₄ solution ðmg kg⁻¹Þ mCuSO₄ solution ðkgÞ MMWWCuCSuO₄ 100% (6) MW_{av} ¼ 1000 56:1 3 (5) EVoil feed ðmg KOH per g oilÞ Reaction behavior of oil feedstock is often dictated by its fatty acids composition that determines its oxidation stability, solubility, and acidity (FA dissociation) according to the

unsaturated part and alkyl chain length.¹⁹ Fatty acids composition of used cooking oil was determined in the form of methyl esters by using gas chromatography (GC-2010, Shi-madzu, Japan) equipped with a Rtx-2330 column (10% cyanopropylphenyl–90% biscyanopropyl polysiloxane; 30 m 0.25 mm I.D. 0.2 mm). The detail of GC operation condition was described elsewhere.²⁰ Prior to the GC analysis, 200 mg oil sample was saponified and transesterified using 5 mL of 0.5 N KOH in methanol at 65 °C for 15 min and then underwent acidification and esterification by reaction with 15 mL of methanolic 5 wt% H₂SO₄ at 65 °C for 1 h. After that, the esters were separated and purified from the methanolic phase by means of hexane dilution (50 mL) and washing with 5 wt% NaCl solution (3–25 mL). Hexane was evaporated under vacuum and esters were further dried by N₂ purging. Prior to injection, esters were dissolved in 10 mL of ethyl acetate and dried by passing the solution over anhydrous MgSO₄ in a syringe coupled with a PVDF membrane (0.22 µm). The result (Table S1†) showed that used cooking oil mainly comprised linoleic acid, palmitic acid, and oleic acid, and a small amount of palmitoleic acid and linolenic acid. This could indicate that the used cooking oil was soybean oil, which mainly composed of linoleic acid, oleic acid, palmitic acid, and stearic acid.^{21,22} A high spike of palmitic acid and lower stearic acid in the used cooking oil in contrast with refined soybean oil might come from the fatty acid interchange during deep-frying of chicken meat and other foods.²³ Other remarkable point is its lower content of unsaturated fatty acids than the original soybean oil, which was the result of oxidation during frying process.²⁴ In Cu-catalyzed reaction system, Cu was extracted out from the water to the oil phase. The amount of Cu inside the oil phase

2.4. Statistical analysis

Statistical analysis of all data obtained in this study was carried out using Minitab 17 software. The significance of the effect of employing different catalyst systems, gas types, temperature level, and additional pressure on FA yield was compared using analysis of variance (ANOVA) with interaction term up to second order. The ANOVA test on the influence of gas type, temperature, and initial pressure towards Cu removal percentage in Cu-catalyzed system was also performed. Spearman correlation analysis was used to evaluate the impact of SCW properties on each pressurized catalyzed system. Categorical variables of catalyst systems and gas types were encoded to ordinal variable for correlation test purpose. N₂ and CO₂ were labeled as gas 1 and 2, while the code for autocatalytic, Cu-catalytic, and acid-catalytic systems were system 1, 2, and 3, respectively. Insignificance effect of a term was stated by null hypothesis, which was failed to be rejected if the p-value of corresponding term is larger than

4. significance level (a) of 0.05. 3. Results and discussion 3.1. Effects of

experimental parameters on hydrolysis of used cooking oil

Operating parameters of a process determine the product yield, thus the efficacy of the process. In this study, ANOVA test was employed to evaluate the effect of operating parameters collectively besides conventionally plotting experimental data in certain groups. The collective effect of catalyst system, type of pressurizing gas, temperature, and initial pressure on FA yield is illustrated in Fig. 1, where all experimental data were drawn according to the catalyst system and gas type in Fig. S2.† It is clear that catalyst system had more impact on FA yield than the other parameters. The selection of catalyst can only be explained as a unique criterion in process optimization. In Fig. S2,† this uniqueness is shown as different trend of FA yield with respect to the manipulation of temperature and pressure in each system. Higher FA yield of Cu-catalyzed system than that in the other systems at the same pH underlines that Cu in Fig. 1 Main effects plot of catalytic system, gas type, temperature and added pressure with respect to FA yield. wastewater might be a potential catalyst in oil hydrolysis reaction. Following catalyst system, temperature took the second place in increasing FA yield, whereas the influence of initial pressure and gas type were relatively minor. Detailed results of ANOVA test (Table S2†) also shows similar rank of effect on all parameters, which can be seen by the order of magnitude of sum of square error

(SS) or mean of square error (MS) term on the mean value of FA yield for each parameter. Higher significance of the effect of temperature than initial pressure using subcritical or supercritical water was observed too in several publications.^{26–28} Although the extent of effective pressure for increasing FA yield differed from one to another, it can be clearly understood that the role of pressure was mainly to retain water in liquid phase, while temperature has abilities to accelerate reaction kinetics in addition to affecting vapor–liquid equilibrium (VLE). Based on that logic, the lesser effect of pressure in this study may be explained by the excessive water/acylglycerides molar ratio used (30 : 1). This result was in agreement with the data depicted in Fig. S2,† which showed relatively flatter slope of FA yield improvement for the increase of additional pressure in comparison with the ones that describe the raise of temperature. Substitution of N₂ by CO₂ has relatively low effect since the solubility of CO₂ in water, which was expected to induce H₂CO₃ catalyst, is low at the studied temperature.²⁹ On the contrary, CO₂ is more likely to dissolve in oil than in water that caused a slight decrease of FA yield regardless of catalyst system by means of limiting reactant concentration dilution.³⁰ This was also observed by the absence of bubbles in the aqueous phase and foam of bubbles on the oil layer when the ester-reaction products were carefully transferred into separation funnel as shown in Fig. S3.† It is also worth to note that the dilution effect of CO₂ was different in each catalyst system (Fig. S2†). While CO₂ only lowered down FA yield without changing the trend of enhancement in acid- and Cu- catalyzed systems, CO₂ dramatically altered the shape of surface plot of autocatalytic system. Severe consequence of oil dilution in relatively weak catalysis system is depicted in Fig. S2(B),† where FA yield was suppressed with the increase of CO₂ pressure. ANOVA test on interactions between parameters indicates that combination of catalyst system and temperature is the most effective combination in affecting FA yield (Fig. 2 and Table S2†). This is generally true since catalyst and thermal energy input are critical for activation of any reactions. In all catalyst systems, interaction effect of gas type and additional pressure is meaningful particularly related to oil dilution effect by CO₂. This problem is also inseparable in the explanation of the significance of catalyst system-added pressure interaction term besides the influence of pressure on SCW properties. The remaining interaction terms generated small variance with respect to the overall mean of FA yield, but their significance is legitimate since the characteristics of main effects were involved in the interaction term too. The insignificance of temperature and pressure interaction is reflected by the parallel lines of mean FA yield in Fig. 2 that increased with increasing temperature, but remained relatively constant under various additional pressures. This again verifies greater effect of temperature to enhance reaction kinetic and the liquid water amount was sufficient in all temperature and pressure ranges studied. Although the interaction between catalyst system and gas type appeared to be quite weak, further evaluation on this interaction can give deeper insight on the utilization of CO₂ with respect to each catalyst system. Fig. S2† indicates that the effect of CO₂ depends on catalyst system. Systems with relatively strong catalysis power, such as the acid- and Cu-catalyzed system, were affected slightly by the increase in temperature and additional CO₂ pressure (ca. 5% reduction of FA yield at 250 C and 4.90 MPa CO₂). Autocatalysis by FA was too weak to counteract the effect of CO₂ dilution since less catalyst was produced from partial FA deprotonation in water. At lower temperature (200 C) and high added pressure (4.90 MPa), where CO₂ solubility in water was considerably high (Fig. S4;† calculated using the Fig. 2 Plot of interaction between catalyst system, gas type, temperature and added pressure towards of FA yield. model from Duan and Zhang³¹), dilution in the oil phase and inhibition of Cu soap formation by acidic H₂CO₃ in aqueous phase became more prominent. This caused a marked decrease in FA yield with more added CO₂ compared with the N₂-pressured catalyst system under the same conditions.

3.2. Effects of experimental parameters on Cu removal percentage

Cu removal is determined by equilibrium ion exchange reaction between free Cu²⁺ and formed fatty acid that produced hydrophobic Cu soap.¹⁵ Therefore, the extent of experimental parameters should be also evaluated in the same way as for FA yield. The main and interactional effects of temperature, additional pressure, and gas type on Cu removal percentage in Cu-

catalyzed system are shown in Fig. 3 and 4, respectively. ANOVA test results for Cu removal affecting parameters are given in Table S3.† Fig. 3 indicates that temperature and additional pressure enhanced Cu soap formation, while substitution of N₂ by CO₂ lowered it. From ANOVA test results, those three parameters Fig. 3 Main effects plot of gas type, temperature, and added pressure towards Cu removal percentage. Fig. 4 Interaction effects plot of gas type, temperature, and added pressure towards Cu removal percentage. demonstrated significant effects on Cu removal with additional pressure as the most influencing term. These facts suggest that SCW properties strongly affect the formation of Cu soap. In addition to SCW properties, Cu soap formation was also controlled by the amount of water in the liquid form that specified good mixing profile between oil and water phase.¹⁵ In this case, pressure controls the amounts of liquid water by restraining water evaporation under high temperature, explaining its slightly stronger effect than temperature. This control on evaporation may be inadequate under certain operating condition if the additional pressure could not produce total pressure higher than saturation steam pressure as shown at additional pressure of 1.96 MPa in Fig. 3. A thorough observation on the 3D plot of Cu removal percentage (Fig. S5†) revealed that substitution of gas type had also altered the effect of added pressure with respect to Cu removal. The reduction of Cu removal in the case of gas type substitution can be explained by the presence of H₂CO₃ from CO₂ solubilization in water. Carbonic acid itself may deprotonate to produce free proton that finally caused inhibition of Cu soap formation in the aqueous phase.¹⁵ This also explains the significance of gas type and added pressure interaction in ANOVA test (Table S3†). Nevertheless, FAs dilution by supercritical CO₂ that limited diffusion of FAs into the water phase was still the main reason for the inhibition of Cu soap formation since CO₂ solubility in the water phase was considerably low. Parallel arrangement of the lines of responses for interaction of gas type-temperature and temperature-added pressure (Fig. 4) resulted in insignificant interpretation of those terms in Table S2.† Insignificant interaction between gas type and temperature underlines that gas type did not mainly influence the reaction behavior of Cu soap formation in the aqueous phase. As depicted in Fig. 4, gas type did not significantly change the trend of increasing Cu removal with increasing temperature regardless of the gas type used, which can be translated as the supremacy of SCW properties over the negative effect of carbonic acid deprotonation as the main controlling factor in Cu soap formation. This insignificance was not related to the gas solubility since even a small amount of dissolved CO₂ can decrease the amount of Cu removed. Approximately similar Cu concentration in similar excessive water environment can theoretically explain the insignificant interaction between temperature and added pressure in influencing Cu soap formation.

3.3. Correlation between SCW properties, FA yield, and Cu removal percentage

SCW properties have been acknowledged as the reasons for utilization of SCW in various organic reactions and processes.^{3,32} Although deemed as physical terms, those properties may affect chemical reaction, especially on the generation of acid–base catalyst and miscibility of aqueous-organic phases. In this study, the effect of SCW properties were measured statistically by correlation constant to observe fluctuation of measurable production parameters (i.e., FA yield and Cu removal) with respect to SCW properties. Non-linear Spearman correlation was employed to anticipate non-linear fluctuations of SCW properties by the changes of temperature and added pressure. Correlation coefficients of SCW properties towards FA Table 1 Spearman correlation index and its bracketed p-value between subcritical water properties and FA yield in each catalytic system and gas type

System	Gas	log(K _w)	r	m	FA autocatalytic	Cu-catalyzed	Acid-catalyzed	FA autocatalytic	Cu-catalyzed	Acid-catalyzed
N ₂	0.531	(0.075)	0.622	(0.031)	0.604	(0.038)	0.790	(0.002)	0.671	(0.017)
	0.865	(0.000)	0.930	(0.000)	0.531	(0.075)	0.986	(0.000)	0.622	(0.031)
CO ₂	0.947	(0.000)	0.604	(0.038)	0.979	(0.000)	0.790	(0.000)	0.986	(0.000)
	0.671	(0.017)	0.897	(0.000)	0.865	(0.000)	(0.000)	0.531	(0.075)	0.622
N ₂	0.604	(0.038)	0.790	(0.002)	0.671	(0.017)	0.865	(0.000)	0.947	(0.000)
	0.930	(0.000)	0.531	(0.075)	0.986	(0.000)	0.622	(0.031)	0.979	(0.000)
CO ₂	0.790	(0.002)	0.671	(0.017)	0.865	(0.000)	(0.000)	0.531	(0.075)	0.622
	0.604	(0.038)	0.947	(0.000)	0.604	(0.038)	0.979	(0.000)	0.790	(0.002)

Table 2 Spearman correlation factor of subcritical water properties- Cu removal percentage with p-value in parentheses Gas log(K_w) r m N₂ CO₂ 0.238 (0.457) (0.001) 0.301 (0.342) (0.067) 0.238 (0.457) (0.457) 0.301 (0.342) (0.342) yield

and Cu removal percentage are presented in Tables 1 and 2, respectively. In each system, log Kw demonstrated significant correlation with FA yield regardless of the gas used to pressurize the system. Negative sign of correlation factor between log Kw and FA yield indicated that FA yield increased with decreasing log Kw. In other words, FA yield increased with increasing water ionization constant (Kw). This signifies the important role of water as the medium for generation and transfer of free proton (H_3O^+) in the catalyst system. With sufficient capacity of proton generation, autocatalytic as well as acid catalytic mechanisms were enhanced dramatically. In Cu-catalyzed system, increasing ionization constant facilitated production of FA, which promoted Cu soap formation. That relationship was also observed specifically in Table 1. Meanwhile, negative signs of the other correlation factors of remaining SCW properties denoted better reaction performance by means of better miscibility and mixing properties between water and oil with lower β , m , and r . From this strong correlation and the dynamic portrait of SCW properties change in Fig. S6,† the main and interaction effect of temperature and additional pressure towards FA yield and Cu removal become much clearer. A surge in the mean value of FA yield and Cu removal (Fig. 1) can be explained by a large decreasing of log Kw from 200 to 225 C. Since log Kw reduction was also caused by the rising of added pressure, the significance of added pressure in affecting Cu removal is also reasonable. Although the correlation values for β , m , and r were not as significant as the log(Kw), it is still important to realize that without good mixing and miscibility of water and oil, the catalysis mechanism might fail to take strong effect on the oil hydrolysis reaction. Substitution of N_2 by CO_2 showed alteration of correlation factors, especially for the autocatalytic system, where β , r , and m became significant in effect. Although $\log(Kw)$ remained significant, the same phenomena also occurred in the acid-catalyzed and Cu-catalyzed systems. This can be described as the effect of oil dilution by CO_2 that eventually revealed the role of mixing properties of SCW in FA production, which explained why mean FA yield was only slightly lowered despite of dilution (Fig. 1). Under N_2 pressure or no dilution effect, SCW properties were approximately similar (Fig. S6†) since the temperatures and actual pressures were very close to those using CO_2 , but the effect of those properties became less appreciated since no hindrance existed for the excess liquid SCW to reach oil molecules. Cu removal percentage was influenced by water ionization constant (Table 2) that implies water activity to form more FA during Cu soap formation. In the presence of CO_2 , the influence of water ionization constant became insignificant (p -value > 0.05), but statistically made some difference (p -value < 0.1). One plausible reason for this change is enhanced dilution of FA by CO_2 that inhibited Cu formation. The other properties associated with mixing and miscibility of oil and aqueous phase (i.e., β , m , and r) did not correlate significantly with Cu removal. This can be described as the weakness using the correlation analysis. Since the data majority indicated sufficiently low polarity that allowed remarkable amount of FA to dissolve easily in the water without certain degree of mixing, the effect of β , m , and r were showed to be insignificant. When the data analysis was reduced to contain only the data with remarkable change of SCW properties, especially on the β , m , and r , the correlation analysis resulted into very high correlation between SCW properties and FA yield (all correlation factors are 1.000 with p -values < 0.000). This also occurred for the correlation between SCW properties and Cu removal.

3.4. Relation between operating parameters, SCW properties, and catalysis mechanism

Reaction medium affects catalysis mechanism. The role of water as reaction medium and reactant is greatly influenced by its dielectric constant (β) and ionic product ($\log Kw$), while water density (r) and viscosity (m) only affect the mixing behavior. In this study, Cu soap formation and oil hydrolysis reaction were found to be significantly influenced by the decrease of log Kw along with three explicit catalysis mechanisms: strong Bronsted acid catalysis of H_2SO_4 , Lewis acid catalysis of Cu soap, and weak Bronsted acid catalysis of FFA. Comprehension on the interrelationship between temperature as the most significant operating parameter that drastically affected log Kw and β with SCW properties and the mechanism of the hydrolysis reaction with the involving catalysis mechanism may contribute better insight on the reaction in SCW. The effect of log Kw can be well explained from its in?

uence on the acid deprotonation with respective proton balance mathematical relationships for strong and weak Bronsted acid as follows: $33 \frac{1}{2} H_3O^+ \rightleftharpoons \frac{1}{4} CA \rightleftharpoons CA \rightleftharpoons 4 Kw \frac{1}{2} H_3O^+ \rightleftharpoons \frac{1}{4} KA \rightleftharpoons KA \rightleftharpoons 4$ where $[H_3O^+]$ is the concentration of the liberated proton, while CA and KA are the acid concentration and weak acid dissociation constant, respectively. From these equations, it is clear that $\log Kw$ only affects the strong Bronsted acid catalysis mechanism, where the ionized water molecules exponentially increases the concentration of proton in the system in addition to the protons from strong acid ionization. The existence of OH from water dissociation indeed counterbalances the amount of H_3O^+ from water, but OH also can trigger more complete deprotonation of polyprotic acids, which produces another water molecule by acid–base reaction. Although described in a different way, the effect of OH from water ionization is quite similar with the ability of water to receive more proton in addition to the uniformly distribute around the structure of polyprotic acid (i.e., H_2SO_4 in this studied system) to construct stable molecular conformation of completely deprotonated structure.³⁴ On the other hand, $\log Kw$ surprisingly does not govern FA deprotonation that influences weak Bronsted acid catalysis and Cu soap formation as explicitly described in the relationship between water and weak acid ionization ($Kw \frac{1}{4} KA KB$). Based on this, the autocatalysis by FFA in the SCW–oil hydrolysis reaction should be re-assessed. Regarding FFA autocatalytic ability, it is possible that FA dissociation was enhanced by the manipulation of reaction conditions. However, according to previous studies, FA dissociation decreased with increasing temperature and the drop in dielectric constant of the medium.^{35,36} Thus, the behavior of FA in the reaction condition applied in this study can be predicted to be less prone to dissociation, resulting in less production of free proton as catalyst. Consequently, autocatalysis is not the dominating mechanism in this system though autocatalysis of FA is still quite valid since the dissociation is not nullified. In line with the correlation analysis, the active catalysis in the auto-catalyzed system is more likely to be the auto-generation of proton from water molecules, while the OH produced might randomly react with FAs to produce another water molecule without interrupting the positive net balance of proton generation. This indication also proves the difference made by dielectric constant (ϵ) in FA production (Table 1; $0.05 < p\text{-value} < 0.1$) that improved water penetration into oil phase to catalyze the reaction. Moreover, this minute net generation of the protons from FAs and water molecules may explain why FA yield of auto-catalyzed system was remarkably small compared to catalyzed systems. The involvement of SCW in Cu-catalyzed system is more complicated since Cu soap formation was included. By considering the decrease in FAs deprotonation occurred in the applied conditions, it can be deduced that more formation and solubility of FAs promoted Cu soap formation by means of ion exchange reaction. This can be done with the help of proton from water ionization on the hydrolysis of acylglycerides as reflected in the significance of $\log(Kw)$ and low polarity (low ϵ) environment that can enhance FAs solubility in the water phase, which took place at high water temperature.³⁷ Complexation between Cu^{2+} and FAs was very unlikely to occur since the stability complex of Cu-FAs is declining at higher temperature.³⁶ The other possible mechanism is the alkalization of Cu^{2+} by OH generated from water dissociation, which rendered to more reaction with the FAs with more self-ionization of water.³⁸ The alkalization of Cu^{2+} is also known as the result of Cu^{2+} hydrolysis. Coincidentally, the Cu^{2+} hydrolysis exhibited endothermic nature ($\Delta H_0 \frac{1}{4} 17.5 \text{ 2 kcal mol}^{-1}$) with positive entropy ($\Delta S_0 \frac{1}{4} 11.4 \text{ 7 cal mol}^{-1} \text{ K}^{-1}$), which also supports the proposed mechanism of Cu^{2+} alkalization with the ionized water at elevated temperature.³⁹ As Cu soap formed entered into oil phase, further reaction with water as electron donor proceeded. In this step, the role of Cu soap as Lewis acid that produced free proton from water was strengthened with higher water ionization constant. In addition, water ionization might be involved in acid catalysis of H_2SO_4 formed as the by-product of Cu soap formation by means of cation exchange between $CuSO_4$ and FAs. With both mechanisms worked simultaneously, Cu-catalyzed system could produce more FAs than H_2SO_4 -catalyzed system as illustrated in Fig. 1. Based on the elucidated effect of SCW properties on reactions and the

relationships of operating parameters and SCW properties in Fig. S6,† the enhancement of log Kw was proven to successfully increase the formation rate of FA and Cu soap, respectively. The ionization behavior of water with the increase of temperature verified the activity of SCW as the combination of reactant and active catalyst in the oil hydrolysis reaction. Low dielectric constant of SCW also improved the solubility of FAs in water, which increased FAs concentration in water.³⁷ Low polarity also promoted the formation of non-charged and hydrophobic Cu soap from Cu²⁺ and FAs anion in synergy with increasing FAs concentration.³³ This behavior may explain the negative effect of water at certain amount in transesterification and esterification reactions either in acid-catalyzed system or supercritical methanol system by means of ester hydrolysis.^{40,41} As described by van't Hoff equation, water ionization is more endothermic than that of methanol (DH₀ at 25 C: 390.8 kcal mol⁻¹ vs. 381.4 kcal mol⁻¹) leads to more ionization that results in a higher rate of hydrolysis than ester formation.⁴²

4. Conclusion

The effect of operating parameters and SCW properties on oil hydrolysis using three different catalyst systems was evaluated. Temperature has more influence on FA production than initial pressure due to its role in enhancing reaction rate in addition to controlling vapor–liquid equilibrium. Substitution of pressurizing gas did not show significant effect on FA yield, but CO₂ inhibited Cu soap formation by primarily diluting the oil and contributing small amount of H⁺ from its deprotonation in water. SCW properties affected catalyst formation through enhancement of catalysis mechanism and mixing properties between oil and water. Low polarity and high ion product of SCW influenced the catalysis by increasing the concentration of water-soluble FAs, Cu soap formation, or better miscibility of proton into oil phase. Water in subcritical state is very active as reactant, medium, and catalysis promoter for oil hydrolysis reaction.

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