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## paper text:

RSC Advances PAPER Direct reuse of Cu-laden wastewater for non-edible oil hydrolysis: basic mechanism of metal extraction Cite this: RSC Adv., 2016, 6, 25359 and fatty acid production† Lu Ki Ong,a Phuong Lan Tran Nguyen,b Felycia Edi Soetaredjo,c Suryadi Ismadji*c and Yi-Hsu Ju*a Fatty acids are platform chemicals to produce various useful chemicals and fuels. Hydrolysis of waste cooking oil using synthetic copper wastewater as the water and catalyst source to produce fatty acids was studied by carrying out reactions at 200–250 C, water/acylglyceride molar ratio of 30 : 1–90 : 1, and CuSO4 concentration of 250–1500 mg kg 1. Comparison between catalytic and non-catalytic systems was also evaluated. Increasing temperature influenced fatty acid yield, acylglycerides conversion, and copper removal by enhancing fatty acid deprotonation. Minimum loss of fatty acids by micellar solubilization mechanism was achieved by using CuSO4 in the concentration range of 250–750 mg kg 1. Received 4th November 2015 Copper was transferred into the fatty acid product during the process by ion exchange mechanism. Accepted 28th February 2016 Considerable copper removal from the aqueous phase (98.87%) was achieved by 5 times recycling of the aqueous phase product into the hydrolysis process of pristine waste cooking oil. Direct utilization of DOI: 10.1039/c5ra23153a copper-containing wastewater for industrial processes such as oil hydrolysis offers a potential symbiotic www.rsc.org/advances approach in industrial wastewater management and production of valuable chemicals. 1. Introduction Fatty acids (FAs) are an important raw material for producing products such as soap, detergents, lubricants, and biodiesel. FAs can be seen as green chemicals due to their renewability and the fact that they possess various economic and ecological advantages. FAs are derived from the hydrolysis of triglycerides, which are the major component in oils. In hydrolysis reaction, excessive water is o?en introduced to force the equilibrium towards FA formation. Formation of FAs is more favored, for instance, in two-step biodiesel production due to its lowering effect on the esteri?cation reaction temperature and time, by improving its miscibility with the alcohol precursor.1 Industrial oil splitting is carried out in either catalytic or non-catalytic hydrolysis process. The non-catalytic approach utilizes high pressure steam or water at high temperature. Water at those conditions possesses low dielectric constant and high self-dissociation constant so that high water-in-oil solu- bility can be attained,2 self-catalysis mechanism of available FAs aDepartment

2**of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung** Rd., **Sec. 4, Taipei** 10607, **Taiwan. E-mail:** yhju **@mail. ntust.edu.tw; Fax: +886 2 2737 6644; Tel: +886 2 2737**

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra23153a can be induced,3 and reaction can be accelerated.4 An example of this approach is the continuous countercurrent fat splitting process called Colgate-Emery process (260 C, 50 bar), which is used most extensively for triglyceride hydrolysis.5 Catalyst may lower down oil hydrolysis temperature by reducing activation energy and promoting easier water diffusion into oil phase.6,7 Catalyst employed in oil hydrolysis reaction may be acid, base, transition metal, or enzyme.5,8 Compared to catalytic approach, non-catalytic approach has shortcomings such as excessive energy requirement, expensive thick and corrosion-resistant reactor, and greater risk of side reactions to be occurred, such as isomerization, oxidation, dehydration, polymerization and interesteri?cation.4,9 However, there are yet inherent problems associated with catalytic process such as the frequent make-up for unrecoverable catalyst and regeneration of catalyst activity.10 Long reaction time and the need of surfactant and/or organic solvent are particular problems related to enzymatic process.9 These problems increase produc- tion cost and impede the implementation of catalytic hydrolysis process in industry. Straightforward strategy to overcome this cost issue is to use an abundant and cheap catalyst. Acid or base seems to be an appropriate option. However, the use of acid/base as catalyst generates sludge, soap by-product, and hard waste- water in the down-stream of oil splitting process. The employment of low-quality and inexpensive feedstock to replace expensive re?ned oils has been found to be crucial in order to minimize biodiesel production cost, where the cost of feedstock comprises more than 70–95% of the total expenditure.11 The use of non-edible fatty waste material that two to three times cheaper than re?ned vegetable oil, such as waste cooking oil, is attractive for minimizing the total cost. Moreover,

utilization of waste cooking oil as an oil feedstock for petroleum diesel alternative accommodates its disposal issue that increase proportionally with the continued growth of the human pop- ulation in a more sustainable and environmental-friendly way.12 Meanwhile, rapid development and expansion of industries together with increasing global population raise a concern on the available fresh water reserves to meet all current and future demands. In response to this issue, wastewater reuse has the potential to satisfy urban, non-food agricultural, and industrial needs with less energy and cost compared to conventional waste- water treatment. Among various types of wastewater, heavy metal containing wastewaters have more limited scope for direct reuse than organic wastewater due to their toxicity, bio-accumulating, and non-biodegradable nature.13,14 Heavy metal containing waste- waters are generated from various industries such as metal plating industry,15,16 printed circuit board manufacturing,17 and semi- conductor industry.18 Among heavy metals, copper o?en appears in wastewater as the major metal ion. Some conventional physico- chemical technologies exist for the removal of such metals such as ?ltration, chemical precipitation, ion exchange, adsorption, elec- trochemical deposition and membrane process.13 Although viewed as necessary, all these methods are generally expensive in terms of capital cost and material regeneration.19,20 On the other hand, copper is classi?ed as one of transition metals, which are known as catalyst in oleochemical processing.21,22 Therefore, direct reuse of wastewater laden with copper to hydrolyze non-edible oil feed- stock, such as waste cooking oil may offer a more bene?cial and greener solution in waste management and supply the large amount of water required in oil splitting process. In this study, synthetic wastewater containing copper sulfate was used as a prototype model to investigate the potency and the basic reaction mechanism of industrial copper containing wastewater as the catalyst and water source for waste cooking oil hydrolysis. The effects of temperature, time, and concentration of copper in synthetic wastewater on FA yield were systemati- cally studied in reference with the proposed reaction mecha- nism of copper soap formation and its catalytic mechanism on the oil hydrolysis reaction. The metal content of the hydrolyzed oil was determined and discussed. (FFA) content analysis and quanti?cation of acylglycerides. Detailed analysis procedure can be found elsewhere.23 All chemicals used were reagent grade, including KOH (85% purity, Across Organics, USA), anhydrous CuSO4 (97% purity, Shimakyu, Japan), concentrated HCl (37% purity, Across Organics, USA), ethanol (95%, Echo Chemical, Taiwan). Anhy- drous oxalic acid ($99% purity, Kokusan Chemical Co. Ltd., Japan) was used to standardize KOH solution. Indicator for titration analysis was phenolphthalein (Sigma Aldrich, USA). CuSO4 stock

4**solution with a concentration of** 25 000 **mg** kg **1 was**

made and stored in a dark bottle at room temperature for later use. Analytical reagent grade HNO3 (90%, May and Baker, UK) was diluted to 10% (v/v) with deionized water for trace metal analysis. A standard solution containing Cu, Fe, Mg, Ca, Na, and K (solution IV, 1000 mg L 1, Merck Chemicals, USA) as well as one containing Pb and As (solution IX, 100 mg L 1, Merck Chemicals, USA) were used for the preparation of cali- bration curves. 2.2. Hydrolysis of WCO A certain amount of oil and synthetic wastewater containing CuSO4 with a concentration of 500 mg CuSO4 kg 1 solution was put into a batch reactor. The molar ratio of oil to water was 1 : 30. The reactor consists of a 190 mL glass chamber, a 316-grade stainless steel autoclave, a K-type thermocouple, a PID temperature controller, a pressure gauge, a magnetic stirrer, and an external electric heater (Fig. S1†). A?er closing the reactor tightly, oxygen was purged by nitrogen. The reactor was then heated to the desired temperature and held for a predetermined time under stirring. At the end of reac- tion time, the reactor was rapidly cooled to room temperature and the collected product was washed with warm water to remove glycerol. The washing ?ltrate was separated gravita- tionally in a separation funnel and the top layer was weigh- ed and analyzed to obtain acid value (AV), saponi?cation value (SV), ester value (EV) and metal content. All experi- ments were conducted in duplicate. The FA yield and acyl- glycerides conversion were calculated by using the following equations: FA yieldð%Þ ¼ AVoil product ðmg KOH=g oilÞ m oil product ðgÞ AVoil feed ðmg KOH=g oilÞ oil feedðgÞ m ðSV AVÞoil feedðmg KOH=g oilÞ moil feedðgÞ 100% (1) 2. Experimental 2.1. Chemicals Waste cooking oil (WCO) was obtained from a local restau- rant in Taipei, Taiwan. The collected oil was stored in a dark bottle and used without any pretreatment. Gas chromatog- raphy (Shimadzu GC-2014) equipped with a ZB-5HT column (15 m 0.32 mm 0.1 mm) was employed for free fatty acid Acylglycerides conversionð%Þ ¼ 100% EVoil product ðmg KOH=g oilÞ moil productðgÞ EVoil feedðmg KOH=g oilÞ oil feedðgÞ m (2) Control experiments were performed by replacing CuSO4 solution with a very dilute H2SO4 solution in the water with the same pH as that of the copper solution (pH 5.0).

3**Water to** acylglyceride **molar ratio** was varied **from** 30 : **1 to** 90 : **1** by changing **the amount of**

copper

4**solution with a concentration of** 500 **mg** CuSO4 kg **1** solution. **The**

effect of copper concentration was evaluated by varying copper concentration (250–1500 mg CuSO4 kg 1 solution), while keeping the molar ratio of water to acylglyceride at 30 : 1. Reactions were performed at 225 C for 8 h and the oil product was then processed in the same manner as described previously. Non-catalytic hydrolysis of WCO was carried out by replacing copper solution with deionized water. All other parameters used were the same as the catalytic process. magnetic stirring. The mixture was le? to separate into oil and water layers and cooled to solidify the oil layer. Solid fat was ?ltered out by using a 5 mm ?lter paper (Advantec Grade no. 2) and the acid solution was collected for inductively coupled plasma (ICP) analysis. Removal of copper (%) can be expressed as the number of Cu2+ transferred into oil phase per total Cu2+ introduced into the reaction system as shown in the following equation: Cu removalð%Þ ¼ Cuoil productðmg kg 1Þ moil product ðkgÞ Cuoil feedðmg kg 1Þ oil feedðkgÞ m 100%: (6) CCuSO4 solutionðmg kg 1Þ mCuSO4 solutionðkgÞ MWCuSO4 MWCu 2.3. Oil analysis where Cuoil product, Cuoil feed, moil product, and moil feed are FA content in WCO and hydrolyzed oil was determined as acid copper concentration in oil product, copper concentration in value (AV) by using the titration method described in ASTM oil feed, mass of oil hydrolysis product and mass of oil feed D1980-87. Each sample was titrated with standardized KOH (0.5 (WCO), respectively. CCuSO4 is the concentration of copper N). The amount of KOH used in titration was translated into AV solution used, while mCuSO4 solution is the mass of copper using eqn (3). solution feed. Conversion of CuSO4 concentration into VKOHðmLÞ NKOH 56:1 atomic Cu was done by using the ratio of molecular weight AVðmg KOH=g oilÞ ¼ wt of sampleðgÞ ; (3) (MW) of Cu and CuSO4. where VKOH and NKOH are the volume and normality of KOH solution used to titrate the samples, respectively. 3. Results and discussion Saponi?cation value (SV) was acquired by the titration 3.1. Effects of temperature and time on hydrolysis of WCO method according to ASTM D5558-95. Sample and blank were WCO used in this study comprised of 84.03% triglycerides, titrated against standardized HCl solution (0.5 N) in the pres- 9.28% diglycerides, 0.29% monoglycerides, and 6.30% FFAs. ence of phenolphthalein indicator until the pink color dis- appeared. SV was calculated according to eqn (4). Initial FFA content of WCO obtained from acid value titration technique was relatively similar from the GC result (i.e., 12.35 SVðmg KOH=g oilÞ ¼ 0.69 mg KOH/g oil equivalent to 6.21 0.35% as oleic acid). This similarity was observed also in the previous study.25 VHCl of blank sampleðmLÞ NHClðNÞ 56:1 ; (4) Therefore, titration method was used in this study due to its wt of sampleðgÞ accuracy and absence of damage risk to GC column by metal where VHCl and NHCl are the volume and normality of HCl deposition. solution used to titrate the samples, respectively. Temperature played an important role in the endothermic Total acylglyceride was estimated in terms of ester value (EV), hydrolysis of WCO. Increasing temperature drove FA yield and which is the difference between SV and AV. Average molecular glycerides conversion faster towards equilibrium and increased weight (MWav) of acylglyceride in WCO was obtained using eqn Cu removal (Fig. 1). Above 225 C, temperature had negligible (5). effects on FA yield, acylglycerides conversion and Cu removal. Hence, 225 C was selected as the temperature for evaluating MWav ¼ 1000 56:1 3 EVoil feedðmg KOH=g oilÞ ; (5) the effect of the amount and concentration of synthetic wastewater. where EVoil feed is the ester value of WCO that used as reaction All reactions reached equilibrium in about 8 h, judging from feed of this study. unchanging FFA yield, acylglycerides conversion, and AV (Fig. 1 and S2†). From Fig. 1A and B, hydrolysis reaction resulted in the 2.4. Analysis of metal content in oil same values for FA yield and acylglycerides conversion at equilibrium (also equilibrium AV in Fig. S2†) regardless of Metal in the oil phase was extracted using the slightly reaction temperature due to the same amount of water used, modi? ed method of Leonardis, et al.24 Typically, 20 mL of which was also con?rmed by Sturzenegger and Sturm.26 The 10% (v/v) HNO3 was added to 5 g of oil sample and the same water to acylglyceride molar ratio (30 : 1) used in the mixture was placed in a water bath at 60 C for 4 h under reactions implies that free glycerol was distributed between oil and aqueous phases to the same extent, which resulted in the Fig. 1 Percentage of (A) FA yield, (B) acylglycerides conversion, and (C) copper removal of hydrolysis reaction at (-) 200 C, (C) 225 C, and (:) 250 C with control experiment points in open symbols (water to acylglycerides molar ratio of 30 : 1 and CuSO4 concentration of 500 mg kg 1). same incomplete degree of hydrolysis (around 80%) in all reaction temperatures.2 It is worthwhile to notice that no induction period was observed in this study. Previous studies reported that by using high reaction temperature of 260–280 C (ref. 2 and 27) and initial FFA content of 10–20 wt%,3,8 sufficient water can be supplied into oil phase by means of better water–oil miscibility to diminish induction period in oil hydrolysis. Since the temperature and initial FFA content of WCO used in this study are lower than the minimum required values stated above, it seems that a small amount of hydrophobic copper soap in the oil phase increased the solubility of water into the oil by the formation of unstable water-in-oil emulsion.28 Although recog- nized as unstable emulsion, agitation during the process may help the emulsion to be re-stabilized. In control experiments, catalysis of H+ from added H2SO4 accelerated FA formation that caused induction period to be reduced to about 30 min at 200 C and 15 min at 225 C (Fig. 1). The mechanism shown in Fig. S3† explains how the reaction was facilitated in the presence of copper. Copper acted domi- nantly as Lewis acid, which was veri?ed by comparably high FA yield in the copper catalyzed system and the control experi- ments. Direct copper soap catalysis mechanism provided small augmentation to Cu catalytic performance in the oil phase. Liberation of proton in the cation exchange between Cu2+ and fatty acids gave acidic ?nal aqueous solution with pH of 2.2–3.0. No copper soap was formed in the control experiments, thus Cu removal percentages in the control experiments were zero. Catalytic activity of metallic soaps, particularly copper soap in the oil hydrolysis process was highlighted also in the some patents.29,30 It is worth to noting that the amount of fatty acid produced during the reaction increased signi?cantly with the increase of copper removal as shown in Fig. 1A and C. This again proves that the role of copper soap as catalyst in the fatty acid production. The effect of temperature on copper removal can be easily understood from the proposed reaction between Cu2+ and deprotonated FA to produce hydrophobic metallic soap (Fig. S3†). As temperature increases, water possesses relatively low dielectric constant (3) and larger self-ionization constant (Kw), which facilitates oil–water miscibility and FA dissociation. Fig. S4† shows 3 and log(Kw) of water as function of temper- ature and pressure. The increasing FA deprotonation and enhanced oil–water miscibility promotes more reaction between Cu2+ and

FAs. Fig. 1C depicts that accelerating effect of temperature towards Cu–FA equilibrium, which intensi?ed at higher temperature. As shown in Fig. S4,† Kw approaches constant with nearly the same low 3 at 225 C, which explains why this is the optimum temperature in affecting FA yield, conversion, and Cu removal. The indication of control system to catch up the catalytic performance of copper catalyzed system at 225 C and higher can be explained by the same reason. Table 1 Effect of copper solution amount on FA yield, acylglycerides conversion, Cu in the oil and Cu removal (CuSO4 concentration: 500 mg kg 1, T ¼ 225 C, t ¼ 8 h) Water/acylglycerides FA yield Acylglycerides conversion Cu in the oil Cu removal molar ratio (%) (%) (mg kg 1 oil) (%) 30 : 1 77.61 60 : 1 82.04 90 : 1 77.99 83.02 72.23 93.65 209.67 94.25 260.73 0.72 51.82 1.14 78.63 3.52 65.66 3.2. Effects of amount and concentration of copper solution on hydrolysis of WCO As suggested by the reaction mechanism of copper soap formation in Fig. S3,† copper ion quantity affects the amount of FAs in the product. Hence, appropriate amount of wastewater with a certain copper concentration should be carefully selected. In this study, CuSO4 concentrations from 250 to 1500 ppm were evaluated as the model of real industrial Cu-laden wastewater.16,17 Table 1 and Fig. 2 show the effect of amount of copper solution and copper concentration, respectively, on hydrolysis of WCO. As water to acylglyceride molar ratio was Fig. 2 Effect of copper solution concentration on (A) FA yield and acyl- glycerides conversion; (B) Cu removal and concentration of Cu in oil (water to acylglycerides molar ratio ¼ 30 : 1, T ¼ 225 C, t ¼ 8 h) with fitting result of Cu removalð%Þ ¼ ð3067:8:49255 þCCuuSOSO44coconncecenntrtartaiotionnÞ (R2 ¼ 0.966). increased from 30 : 1 to 60 : 1, acylglycerides conversion increased from 83.02% to 93.65% (Table 1). This was caused by the diffusion of glycerol out from the oil phase by excessive water, which shi?ed equilibrium towards product forma- tion.26,27,31 Although there was an improvement in acylglycerides conversion (10.63%) as water to acylglyceride molar was increased from 30 : 1 to 60 : 1, FA yield only increased 4.43%. In fact, as water to acylglyceride molar ratio was increased to 90 : 1, FA yield decreased to approximately the same value as that obtained at 30 : 1. The decrease in FA yield at increasing water feed was due to more Cu2+ involved in the reaction system, which consumed more FAs to generate copper soap as shown in the increase of copper amount in the oil phase (Table 1). A sudden drop in copper removal at a water to acylglyceride molar ratio of 90 : 1 (Table 1) may be explained by the mixing behavior. To certain extent, adding water can improve mixing by creating less viscous oil–water mixture. However, more water tends to make low-density oil ?oating on the surface during mixing. The non-uniform mixture of oil and aqueous phase may result in less metal extraction by the proposed mechanism and may explain the diffusion limitation in glycerol extraction. Reactor loading affects mixing pro?le, hence reactor performance. Table S1† shows that oil loading had little effects on FA yield and conversion. Nevertheless, mixing worsened at higher oil loading, as indicated by lower Cu content in oil and Cu removal, particularly at a water to acylglyceride molar ratio of 60 : 1. This was evident from an observation of oil ?oating away from the stirring bar at large oil loading while keeping ?xed total reactants mass. At a water to acylglyceride molar ratio of 90 : 1, the effect of oil loading was less pronounced since water was in large excess for both oil loading studied (27.49 g and 48.12 g). Increasing CuSO4 concentration had insigni?cant effect on the increase of acylglycerides conversion as expected, since catalyst can only accelerate the reaction without affecting equilibrium yield. The slight increase in acylglycerides conver- sion at high CuSO4 concentration (1250 and 1500 mg kg 1) in Fig. 2A may be due to the additional Cu2+ that reacted with FAs that shi?ed the equilibrium to acylglycerides conversion. Formation of more copper soap that yielded more driving force for copper diffusion into oil phase is evident from the rise of Cu content in oil and Cu removal in Fig. 2B. While Cu concentration in the oil product increased linearly with the linear increase of CuSO4 concentration, Cu removal increases in hyperbolic trend similar to that of Michaelis– Menten kinetic pro?le. That similarity can be traced through the analogy between the formation of copper soap and Michaelis–Menten assumption of limited substrate and exces- sive enzyme. Removal of copper began in aqueous phase, where a limited portion of FAs was dissolved in subcritical water.8 Reaction then proceeded between Cu2+ and water-soluble FAs as described in Fig. S3.† Copper soap was then transferred from aqueous phase into oil phase because of its hydrophobicity. Increasing copper concentration triggered competition between Cu2+ ions to react with ?nite amount of FAs in aqueous phase. At certain point, addition of copper only slightly increased the removal percentage due to Cu–FA reaction equilibrium. A sudden drop in FA yield at 1000 mg kg 1 suggests micellar solubilization of FAs by copper soap that remained in aqueous phase. Although copper soap is insoluble in water, its existence in aqueous phase a?er reaction was probably stabilized by the extracted glycerol and small amounts of emulsi?er (mono- glycerides and diglycerides) existed in the aqueous phase. A series of slightly turbid solution that become more yellowish (Fig. S5†) shows micellar solubilization enhancement of FAs with increasing CuSO4 concentration. 3.3. Comparison of catalytic and non-catalytic hydrolysis of WCO Autocatalysis by FFAs in oil feedstock is known to accelerate oil hydrolysis in sub- or supercritical water by utilizing H+ from the dissociation of FAs. Despite the fact of acid catalysis mecha- nism, autocatalysis system is o?en named as non-catalytic because of the absence of externally added catalyst, which is CuSO4 in this study. As shown in Table S2,† FA yield and acyl- glycerides conversion of non-catalytic system are lower than that of the catalytic system at temperatures below 250 C. The presence of copper resulted in higher reaction rate and water-in- oil solubility than those without copper. Lower water solubility in the absence of copper soap was characterized by the induc- tion period in the non-catalytic system (Fig. 3). From the same Fig. 3 Acid value–time profile of Cu-catalyzed and non-catalyzed waste cooking oil hydrolysis reactions with respect to control system (dilute H2SO4, pH 5.0) at 225 C (water to acylglycerides molar ratio ¼ 30 : 1). graph, the control system showed a very small induction period (#15 min) due to the catalytic role of H+ from a small amount of added H2SO4, which was enhanced in subcritical water condition. Equal FA yield and acylglycerides conversion between cata- lytic and non-catalytic systems at 250 C indicates the remark- able effect of autocatalysis mechanism. Application of high temperature (250 C and higher) to induce autocatalysis of FFA was also observed in previous studies.3,32,33 Since both systems worked at the same temperature and pressure, there is likeli- hood that autocatalysis scheme also occurred in the catalytic system. At 250 C and reacted for 6 h, about the same FA yield and acylglycerides conversion was obtained in both catalytic and non-catalytic systems, which reveals that non-catalytic system has slower reaction rate at lower temperature. A close look at Table S2† reveals that there are discrepancies between FA yield and acylglycerides conversion in either cata- lytic or non-catalytic system. The difference between FA yield and conversion may be caused by the loss of FAs either from being extracted into aqueous phase during reaction and/or from washing of oil product. An almost constant difference between FA yield and acylglycerides conversion (5–7%) for catalytic, non- catalytic, and control systems denotes minimum FA loss in the catalytic system and leads to stronger conviction that diglycer- ides and monoglycerides are responsible for the loss. Holliday et al. (1997) also reported FA loss in the form of emulsion in their study on the subcritical water hydrolysis of vegetable oils. Based on the current data, mass balance of fatty acid can be built and analyzed to evaluate speci?c FA loss as the result of copper soap formation in this study. Evaluation by the mass balance of copper ion with the aqueous phase as the boundary system was not performed since the amount of each copper species (i.e., free copper ion and copper soap in aqueous phase) cannot be speci?ed. FA mass balance with oil phase as the boundary system can be written as follows: dFA dt ¼ FAinput FAoutput þ FAgeneration FAdegeneration (7) dFA dt ¼ FAinitial FAfinal þ FAloss to aqueous phase þ FAfrom acylglycerides FAreacted with Cu (8) when the reaction achieved equilibrium, the equation can be simpli?ed to: 0 ¼ FAinitial (FAfinal + FAloss to aqueous phase) + FAfrom acylglycerides FAreacted with Cu (9) By introducing measured parameter for each term, the ?nal mass balance becomes: 0 ¼ AVinitial AVfinal FAloss to aqueous phase + (EVinitial EVfinal) FAreacted with Cu (10) FA reacted with Cu term can be neglected in the control system, thus FA loss to the aqueous phase as water soluble acylglycerides can be calculated using the data in the control experiment at equilibrium state. Table 2 Mass balance of fatty acids in equilibrium state of control and copper-catalyzed systems (CuSO4 concentration: 500 mg kg 1 and water/acylglycerides molar ratio ¼ 30 : 1) Temperature time AVcontrol ?nal AV?nal EVcontrol ?nal EV?nal Mass yield FAreacted with Cu Cu soap ( C) (h) (mg KOH/g oil) (mg KOH/g oil) (mg KOH/g oil) (mg KOH/g oil) (%) (mg KOH/g oil) formeda (%) 225 8 170.26 170.46 34.54 34.22 92.09 0.12 52.54 250 6 170.34 170.31 34.34 34.24 92.10 0.13 56.92 FAreacted with Cuðmg KOH=g oilÞ MWCu a As Cu removal ð%Þ : 2 MWKOH moil productðgÞ 500 mg CuSO4=kg solution 0:0288 kg solution MWCu 100%. MWCuSO4 Control: 0 ¼ AVinitial AVcontrol final FAloss to aqueous phase + (EVinitial EVcontrol final) (11) FAloss to aqueous phase ¼ AVinitial AVcontrol final + (EVinitial EVcontrol final) (12) FA reacted with Cu then can be calculated by substituting the value of FA loss from the control experiment into eqn (10). FAreacted with Cu ¼ AVcontrol final AVfinal + EVcontrol final EVfinal, (13) where lower indices of “control ?nal” and “?nal” refer to the equilibrium state of oil in control and copper catalyzed system (reactions at 225 C for 8 h and 250 C for 6 h), respectively. The value of each measured property and the predicted amount of copper soap formed as Cu removal percentage are presented in Table 2. The predicted copper soap formed from this balance shows comparable values to the copper removal percentage presented in Fig. 1C. Slight difference between the predicted and measured values (0.72% and 3.46% for reaction at 225 C and 250 C, respectively) indicates that some copper soap formed might be dissolved in the aqueous phase. At higher temperature (250 C), it was possible that more glycerol was extracted more into the aqueous phase, thus enhancing the stability of copper soap in the aqueous phase. Since the amount of Cu introduced into the system was considerably small, the amount of FA lost due to reaction with Cu was also small (ca. 0.06–0.07% as oleic acid). This can be viewed as positive point in using copper in wastewater as the catalyst for oil hydrolysis. 3.4. Metal content in product Metal concentrations in the hydrolyzed oil product are summarized in Table 3. Copper content in the hydrolyzed oil increased drastically due to Cu2+ uptake during the reaction. A slight increase in iron content may be due to leaching of reactor surface during reaction. Concentrations of other metals drop as the result of being absorbed into water phase in the course of reaction. Metal contamination in WCO and hydrolyzed oil has de?- nitely disquali?ed its utilization in food as recommended in the Codex Alimentarius standards.34,35 Biodiesel produced from hydrolyzed product of WCO catalyzed by copper containing wastewater may pass ASTM D6751 since excessive copper and other metal contaminants may be removed in the washing step during biodiesel production. To be merit for food and phar- maceutical application, oil product may need to be puri?ed by acid extraction of metal or fatty acid extraction by means of distillation or supercritical CO2 extraction to separate fatty acids from metal soap.5,36 High metal contamination on the FAs product signi?es the capability of this studied process for reducing heavy metal toxicity in wastewater. Several published studies had referred the potency of vegetable oil to extract heavy metal such as Hg2+,37 Cu2+,38–40 Cr6+,41 and Cd2+.42 The critical role of carrier Table 3 Concentration of metals in waste cooking oil and product of copper-catalyzed hydrolysis (CuSO4 concentration: 500 mg kg 1, water/ acylglycerides molar ratio ¼ 30 : 1, T ¼ 225 C, t ¼ 8 h)a Concentration (mg kg 1) Element Waste cooking oil Hydrolyzed oil Max. (mg kg 1 oil) Reference Cu Fe Pb As Ca & Mg Na & K Total ash (%) 4.56 5.11 0.36 0.02 8.32 13.01 0.0045 72.23 7.18 ND ND 4.94 4.14 0.0096 0.1–0.4 1.5–7.0 0.1 0.1 5.0 5.0 0.02 Codex Stan. 210-1999 Codex Stan. 210-1999 Codex Stan. 19-1981 Codex Stan. 19-1981 ASTM D6751 ASTM D6751 ASTM D6751 a ND: not detected. Table 4 Sequential recycle of aqueous product for batch hydrolysis of pristine WCO (Initial CuSO4 concentration: 500 mg kg 1, water/acyl- glycerides molar ratio ¼ 30 : 1, T ¼ 225 C, t ¼ 8 h) Batch Cumulative mass of Acid value FA yield Acylglycerides Cu in oil Cumulative Cu Cu2+ in water no. (i) make-up water (g) (mg KOH g 1) (%) conversion (%) (mg kg 1 oil) removala (%) phaseb (mg kg 1) 1 0 170.46 0.25 77.61 83.03 72.23 0.72 51.82 95.92 2 0.8 158.61 0.21 72.23 77.56 45.13 0.35 85.23 29.40 3 1.2 148.04 0.15 67.38 72.96 22.12 0.09 97.73 4.51 4 1.6 127.69 0.31 57.86 64.34 12.12 0.06 98.84 2.30 5 2.0 103.20 0.36 46.15 53.31 7.36 0.05 98.87 2.26 h i h i a Calculated by : X Cuoil product-i mg kg 1 moil product-i ðkgÞ Cuoil feed-i mg kg 1 moil feed-iðkgÞ 1 100%; i ¼ 1; 2; .; 5. i 500 mg CuSO4 kg 0:0288 kg MWCu b Calculated by : 500 mg kg ð100 Cumulative Cu removalÞ% MWCu MWCuSO4 1 . MWCuSO4 agent existence in vegetable oil to achieve high metal removal percentage was demonstrated by 50–100% copper removal a?er 24–28 h of extraction in the presence of di-2-ethylhexyl phos- phoric acid as carrier agent38 and only 10% removal by extrac- tion using various vegetable oil (i.e., corn oil, canola oil, sun?ower oil, and soybean oil) alone.39 Compared to previous studies, the process studied here shows that at least 5 times Cu removal can be achieved in shorter time without additional carrier agent. Furthermore, production of marketable FAs ampli? es the advantage of this studied process than the costly conventional wastewater treatment. Enhancement of metal capture to higher level is still possible by wastewater alkaliza- tion prior to the hydrolysis process43 or applying multistage reactor–extractor design to break metal saturation limit.44 Recycle of aqueous product up to 5 hydrolysis reaction batches of pristine WCO can increase copper removal up to 98.87% with a cost of decreasing FA yield and acylglycerides conversion in each cycle due to glycerol accumulation (Table 4). With such a low copper concentration le? in the aqueous phase, remain- ing glycerol and fatty components in wastewater can be further treated by biological treatment or reused as nutrient in the biobased process.45 4. Conclusion Hydrolysis of WCO by copper containing synthetic wastewater was performed. In situ formed copper soap catalyst worked particularly as Lewis acid in the reaction and as the vehicle for water to move into oil phase at low temperature. Higher temperature provides more deprotonated FA, which promotes copper soap formation. Inappropriate amount and concentra- tion of CuSO4 may reduce net FA yield in the product. Autoca- talysis by FFA may involve in the overall mechanism. Although the oil product requires further puri?cation for direct applica- tion, this study shows a possible process for direct reuse of heavy metal containing wastewater

3**to produce** FAs **from low quality oil.**

Studied process could remove about 51.82% and 98.87% of copper from wastewater in a batch process and 5 stepwise batch processes, respectively. References 1 R. D. Micic, M. D. Tomić, F. E. Kiss, E. B. Nikolić-Djorić and M. Đ. Simikić, J. Supercrit. Fluids, 2015, 103, 90–100. 2 V. Mills and H. K. McClain, Ind. Eng. Chem., 1949, 41, 1982– 1985. 3 E. Minami and S. Saka, Fuel, 2006, 85, 2479–2483. 4 R. L. Holliday, J. W. King and G. R. List, Ind. Eng. Chem. Res., 1997, 36, 932–935. 5 G. C. Gervajio, in Kirk-Othmer Chemical Technology of Cosmetics, ed. A. Seidel, John Wiley & Sons, New Jersey, 2013, pp. 450–451. 6 K. Ngaosuwan, E. Lotero, K. Suwannakarn, J. James, G. Goodwin and P. Praserthdam, Ind. Eng. Chem. Res., 2009, 48, 4757–4767. 7 L. Lascaray, Ind. Eng. Chem. Res., 1949, 41, 786–790. 8 L. Lascaray, J. Am. Oil Chem. Soc., 1952, 29, 362–366. 9 V. R. Murty, J. Bhat and P. K. A. Muniswaran, Biotechnol. Bioprocess Eng., 2002, 7, 57–66. 10 J. K. Satyarthi, D. Srinivas and P. Ratnasamy, Appl. Catal., A, 2011, 391, 427–435. 11 Y. Zhang, M. A. Dubé, D. D. McLean and M. Kates, Bioresour. Technol., 2003, 90, 229–240. 12 M. Pugazhvadivu and K. Jeyachandran, Renewable Energy, 2005, 30, 2189–2202. 13 M. A. Barakat, Arabian J. Chem., 2011, 4, 361–377. 14 E. Farahat and H. W. Linderholm, Sci. Total Environ., 2015, 512–513, 1–7. 15 M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M. R. Qtaishat and M. Alkasrawi, Chem. Eng. J., 2015, 260, 749–756. 16 M. Kul and K. O. Oskay, Hydrometallurgy, 2015, 155, 153– 160. 17 J.-C. Lou, Y.-J. Huang and J.-Y. Han, J. Hazard. Mater., 2009, 170, 620–626. 18 S. Bang, J.-W. Choi, K. Cho, C. Chung, H. Kang and S. W. Hong, Chem. Eng. J., 2016, 288, 525–531. 19 I. Petrinic, J. Korenak, D. Povodnik and C. Hélix-Nielsen, J. Cleaner Prod., 2015, 101, 292–300. 20 K. S. Low, C. K. Lee and S. C. Liew, Process Biochem., 2000, 36, 59–64. 21 H. J. Beckmann, World Conference on Oleochemicals Into the 21st Century, Kuala Lumpur, 1990. 22 A. Casas, M. J. Ramos, J. F. Rodriguez and A. Perez, Fuel Process. Technol., 2013, 106, 321–325. 23 L. H. Huynh, P. L. T. Nguyen, Q. P. Ho and Y.-H. Ju, Bioresour. Technol., 2012, 123, 112–116.

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