Turnitin Originality Report

BITE-15. by Suryadi Ismadji

From journal (Hippo-hippo)

Processed on 15-Feb-2018 21:51 WIB
ID: 916440077
Word Count: 5745

Similarity Index	Similarity by Source	
14%	Internet Sources:	9%
	Publications:	14%
	Student Papers:	5%

sources:

1 2% match (publications)
Go, Alchris Woo, Sylviana Sutanto, Suryadi Ismadji, and Yi-Hsu Ju. "Catalyst free production of partial glycerides: acetone as solvent", RSC Advances, 2015.

2 1% match (Internet from 13-Jan-2017)
https://www.mysciencework.com/publication/show/catalyst-free-fatty-acid-methyl-ester-production-from-wet-activated-sludge-under-subcritical-water-and-methanol-condition

3 1% match (publications)
Tsigie, Y.A.. "Maximizing biodiesel production from Yarrowia lipolytica Po1g biomass using subcritical water pretreatment", Bioresource Technology, 201205

4 1% match (publications)
Qi, Juanjuan, Fenfen Zhu, Xiang Wei, Luyao Zhao, Yiqun Xiong, Xuemin Wu, and Fawei Yan. "Comparison of biodiesel production from sewage sludge obtained from the A2/O and MBR processes by in situ transesterification", Waste Management, 2016.

5 1% match (Internet from 11-Nov-2011)
http://hub.hku.hk/bitstream/10722/41413/5/FullText.pdf?accept=1

6 1% match (publications)
Wang, Yi, Sha Feng, Xiaojuan Bai, Jingchan Zhao, and Siqing Xia. "Scum sludge as a potential feedstock for biodiesel production from wastewater treatment plants", Waste Management, 2016.

7 1% match (publications)
Adewale, Peter, Marie-Josée Dumont, and Michael Ngadi. "Recent trends of biodiesel production from animal fat wastes and associated production techniques", Renewable and Sustainable Energy Reviews, 2015.

8 1% match (student papers from 28-Nov-2016)
Submitted to University of Technology, Sydney on 2016-11-28

9 1% match (publications)
Yuliana, Maria, Bich Thuyen Nguyen-Thi, Sitti Faika, Lien Huong Huynh, Felycia Edi Soetaredjo, and Yi-Hsu Ju. "Separation and purification of cardol, cardanol and anacardic acid from cashew (Anacardium occidentale L.) nut-shell liquid using a simple two-step column

chromatography", Journal of the Taiwan Institute of Chemical Engineers, 2014.

10 < 1% match (publications)
Sangaletti-Gerhard, Naiane, Mara Cea, Vicky Risco, and Rodrigo Navia. "In situ biodiesel production from greasy sewage sludge using acid and enzymatic catalysts", Bioresource Technology, 2015.

11 < 1% match (Internet from 05-Apr-2017)
http://nportal0.urv.cat:18080/fourrepo/rest/audit/digitalobjects/DS?datastreamId=DocumentPrincipal&label=Repositori+URV&lang=es&mime=application%2Fpdf&objectId=PC%3A1

12 < 1% match (student papers from 25-Feb-2010)
Submitted to Universiti Putra Malaysia on 2010-02-25

13 < 1% match (Internet from 23-Jun-2014)
http://onlinelibrary.wiley.com/doi/10.1002/er.3165/full

14 < 1% match (publications)
Narayan, Ram C., and Giridhar Madras. "Alkylation of fatty acids in supercritical alcohols", Energy & Fuels, 2016.

15 < 1% match (publications)
Emmanuel Revellame. "Biodiesel from activated sludge through in situ transesterification", Journal of Chemical Technology & Biotechnology, 2009

16 < 1% match (Internet from 18-Sep-2017)
https://helda.helsinki.fi/bitstream/handle/10138/37101/varnai_dissertation.pdf?sequence=1

17 < 1% match (publications)
Seung Tae Hong. "Transesterification of palm oil using supercritical methanol with co-solvent HCFC-141b", Research on Chemical Intermediates, 02/2009

18 < 1% match (publications)
Moser, Bryan R.. "Biodiesel Properties and Alternative Feedstocks", Bioprocessing Technologies in Biorefinery for Sustainable Production of Fuels Chemicals and Polymers, 2013.

19 < 1% match (student papers from 17-Jun-2015)
Submitted to University Der Es Salaam on 2015-06-17

20 < 1% match (Internet from 20-Oct-2014)
http://www.fda.gov.tw/en/publishJFDAListContent.aspx?id=2150&chk=583a5b20-f9fc-482c-ba57-99af999c66cf¶m=pn%3d1%26cid%3d%26subcid%3d

21 < 1% match (publications)
Ong, Lu Ki, Phuong Lan Tran Nguyen, Felycia Edi Soetaredjo, Suryadi Ismadji, and Yi-Hsu Ju. "Direct reuse of Cu-laden wastewater for non-edible oil hydrolysis: basic mechanism of

metal extraction and fatty acid production", RSC Advances, 2016.

22 < 1% match (publications)
Handbook of Ultrasonics and Sonochemistry, 2016.

23 < 1% match (publications)
Nitin S. Kolhe, Anilkumar R. Gupta, Virendra K. Rathod. "Production and purification of biodiesel produced from used frying oil using hydrodynamic cavitation", Resource-Efficient Technologies, 2017

paper text:

Bioresource Technology 197 (2015) 30–36

16**Contents lists available at ScienceDirect Bioresource Technology journal homepage: www.elsevier.com/locate/biortech** Transesterification **of** activated sludge **in** subcritical solvent **mixture**

Phuong Lan Tran-Nguyen a, Alchris Woo Go b,

21**Suryadi Ismadji c, Yi-Hsu Ju a,⇑**

9**a Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10607, Taiwan** b **Department of Chemical Engineering, University of**

San Carlos – Talamban Campus, Nasipit, Talamban, Cebu City 6000, Philippines

20**c Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

highlights Produce biodiesel from activated sludge in subcritical methanol with acetic acid. Require much shorter time and much less methanol than acid catalyzed method. Less severe operation condition than that of supercritical methanol method.

11**article info Article history: Received** 22 **May 2015 Received in revised form** 2 **August 2015 Accepted** 3 **August 2015 Available online** 20 **August 2015 Keywords:** Acetic acid Activated **sludge Biodiesel**

In situ transesterification Subcritical solvents graphical abstract Transesterification Methanol Methanol AA Filtration + AA T (oC) = 250 Sludge Time (min) = 30 Methanol + AA+ FAME Methanol + Glycerol Biodiesel Separation abstract Most previous studies reported in literature

7on biodiesel production from sludge were performed by acid catalyzed transesterification that

required long reaction time (about 24 h) and high methanol loading. The objective of this study was to investigate the in situ transesterification of sludge in subcritical mixture of methanol and acetic acid. At 250 °C and a solvent (85% methanol and 15% acetic acid)

2to sludge ratio of 5 (mL g 1), a FAME yield of

30.11% can be achieved in 30 min, compared to

4the yield of 35% obtained by the acid-catalyzed (4% H2SO4) transesterification

which required 24 h

15at 55 °C and a methanol to sludge ratio of 25

(mL g 1). The method developed in this study avoided using mineral acid, significantly reduced reaction time and methanol loading to achieve comparable FAME yield. Ó 2015 Elsevier Ltd. All rights reserved. 1. Introduction Due to global warming caused by excessive emission of green- house gases, particularly carbon dioxide and the increasing energy demand, there is an urgent need to find alternative fuels to replace the traditional fossil-based fuels. Biodiesel is one of the candidates to solve the environmental pollution, reduce dependence on Abbreviations: AA, acetic acid; FAME, fatty acid methyl ester; FFA, free fatty acid; HTGC, high temperature gas chromatography; SCW, subcritical water. ⇑

8Corresponding author. Tel.: +886 2 27376612; fax: +886 2 27376644. E-mail address: yhju@mail.ntust .edu.tw (Y.-H. Ju). http://dx.doi.org/10.1016/j.biortech. 2015.08.033 0960-8524/Ó 2015 Elsevier Ltd. All

rights reserved. limited resources and increase the use of renewable resources. Biodiesel seems a very interesting alternative fuel for reasons such as it is renewable, less global warming than petroleum fuel, biodegradable and less toxic (Ahmad et al., 2012).

5Biodiesel is mainly produced from transesterification reaction of vegetable oils or animal fats with alcohol, usually methanol in the presence of an acidic/basic catalyst, with glycerol as a

co-product (Fan and Burton, 2009). Vegetable oil is the selected candidate of first generation biofuels in the past centuries (Mythili et al., 2014). Edible oils like soybean oil, sunflower oil, palm oil, rapeseed oil and

peanut oil are considered as the biodiesel raw materials. Atabani et al. (2012) claimed that more than 95% of

19**the world biodiesel is** produced from **rapeseed oil** (84%), **sunflower oil** and **palm oil** (13% **and** 1%, respectively), and **soybean oil and others (2%).**

However, those vegetable oils are also used for human consumptions. It can result in an increase of food price, causing high biodiesel cost, fuel crisis, and environmental problems (Atabani et al., 2012; Mata et al., 2010). Moreover, depending on feedstock, biodiesel was sold at a price 1.5–3.0 times higher than that of petroleum diesel (Fan and Burton, 2009). In order not to compete with edible vegetable oils and reduce biodiesel price, low cost feedstock such as non-edible oils, used cooking oils, animal fats, soap-stocks, and greases should be considered as feedstock to produce biodiesel (Mata et al., 2010). Some recent

6**studies have** reported **the potential of** municipal **sludge**

as biodiesel feedstock.

6**Mondala et al. (2009)** obtained a **maximum** FAME yield **of** 2 **.5%**

from secondary sludge and estimated that using

4**in situ transesterification the** price of **biodiesel from sludge**

($3.23/gallon) could be lower than that of petroleum diesel ($4.80/gallon) and soybean biodiesel ($4.50/gallon).

4**Dufreche et al. (2007)** estimated **that** the price of **biodiesel could be**

$2.50/gallon at an overall sludge biodiesel yield of 10%, which is competitive with soybean biodiesel in the market. Revellame et al. (2011) reported a sludge biodiesel yield of 3.93% under the following conditions: reaction temperature 75 °C, ratio of methanol to sludge 30 mL g 1, sulfuric acid concentration 10 wt.%, reaction time 24 h. In another study, they obtained a biodiesel yield of 4.79% in 24 h

15**at 55 °C,** a **methanol to sludge ratio of 25**

mL g 1 using 4 vol.% sulfuric acid as the catalyst (Revellame et al., 2010).

4**Production of biodiesel from wet activated sludge**

under subcritical condition at 175 °C was performed by Huynh et al. (2012). They reported a biodiesel yield of 45.58% in 8 h. To date, reports on biodiesel production from activated sludge are limited in literature. Most studies on biodiesel production from activated sludge employed conventional acid catalyzed transester- ification which required long reaction time (24 h) and high ratio of methanol to dried sludge. There is no report on biodiesel produc- tion from activated sludge with the aim to reduce reaction time using subcritical mixture of methanol and AA. In this study, sub- critical methanol was used to shorten the reaction time. The effect of methanol loading was also investigated to minimize the amount of methanol required. The effect of adding AA on reducing reaction time and increasing FAME yield was studied. 2. Methods 2.1. Materials Chemicals including methanol (99.9% purity), AA (99% purity), hexane (95% purity) were obtained from commercial sources and were of analytical reagent grade. Standards of FFAs, acylglycerides and FAMEs were purchased from Supelco (Bellfonte, PA). The activated sludge sample used in this study was collected from Hsin-Tung-Yang LTD Da-Yuan Factory which is a food processing plant. Water content of the wet sludge sample was 89.01% (Tran-Nguyen et al., 2013). The wet sludge was dried under sunlight. It was then ground and sieved. Powders that pass through standard mesh 24 (0.71 mm) but retained in mesh 60 (0.25 mm) were collected. The sludge powder was heated to 105 °C for 8 h to remove its residue moisture before use. The dried sludge was then stored at 20 °C before use. The moisture content of the dried sludge is 4.88%. Before biodiesel production, activated sludge was dried in an oven overnight and its moisture content was determined. Water content (MS) of a sludge sample was determined from the difference between weight of the sludge sample before and after drying at 105 °C, as shown in the following equation: MS ¼ ðWWS WDSÞ 100 ð1Þ W WS where MS is water content (%), WWS and WDS are the sludge weight before and after drying, respectively. 2.2. In situ transesterification reaction In situ transesterification reaction was performed based on the procedure of Huynh et al. (2012). Dried sludge and methanol either with AA or without AA, were loaded

1**into a glass chamber** (190 mL) **and** then **placed in a high pressure reactor**

(290 mL). Experimental set up for in situ transesterification of activated sludge is depicted in Fig. 1.

1**The reactor is** equipped **with an external electric heater.**

Stirring was provided by an external

1**magnetic stirrer. Temperature in the reactor was controlled to within ±2 °C.**

After sample was put in the reaction chamber, the reactor was sealed and carefully insulated.

21**The reactor was heated to the desired temperature**

in about 60 min at a heating rate of about 4 °C per

1**min. The** time **the reactor** temperature **reached the desired temperature**

was set

1as time zero. After the reaction, the reactor was cooled to ambient temperature, the product was collected

and solid was sep- arated by filtration. The solid was washed twice each with 50 mL methanol. The washed solution was pooled with the liquid phase from filtration. Solvent in the combined solution (methanol and AA) was removed by a vacuum evaporation

1(BUCHI Labortechnik AG in Flawil, Switzerland) operated at 40 °C and 13.3 kPa to obtain the crude product. Hexane (100 mL) and

salt solution (5% sodium chloride) (20 mL) were added into the separatory funnel to separate crude FAME from the aqueous phase and remove glycerol and resi- due acetic acid. The upper phase containing FAME was withdrawn and hexane was then removed by using a rotary evaporator. Crude FAME was weighed and its composition was analyzed by HTGC. At least two experiments were carried out for each reaction. The flow- chart of the in situ reaction is presented in Fig. 2. FAME yield is defined as the mass of FAME

1produced per mass of dried activated sludge used in the reaction and is calculated using

Eq. (2) Yield ð%Þ ¼ Mass of FAME in the product ðgÞ 100 ð2Þ Mass of dry activated sludge ðgÞ 2.3. Determination of FAME yield by HTGC Before analyzing, 20 mg sludge FAME sample was dissolved in 1 mL ethyl acetate and filtered using magnesium sulfate to remove moisture. A 1 IL aliquot of ethyl acetate solution was injected in a Shimadzu GC-2010. External standard calibration curves were pre- pared by using 0.2–20 mg pure standards dissolved in ethyl acet- ate. A 37 components FAME mix

3standard was used to identify individual FAME in the product. Chromatographic analysis was performed using a GC-2010 gas chromatograph (Shimadzu, Japan) equipped with a flame ioniza- tion detector. Separation was run on a

1ZB-5HT (5% phenyl) – methylpolysiloxane nonpolar column (15 m 0.32 mm i.d., 0.1 lm film thickness, Zebron, Phenomenex, Torrence, CA,

USA). The carrier gas was nitrogen

1with a linear velocity of 30 cm s 1 at 80 °C. The operating conditions were

as follows. Both injector and detector temperatures

14**were set at** 370 **°C. The** initial **oven temperature** began **at** 80 **°C,** increased **to** 365 **°C at** 15 **°C min 1 and** held **for** 8 **min. The**

total analysis time was 29 min. The hydro- gen

3**flow, air flow and make up flow were set at 50.** 0 mL **min**

1, 500.0 mL min 1 and 30 mL min 1,

3**respectively while the linear velocity and purge flow were 8.** 0 cm s 1 **and 3.** 0 mL **min**

1, respec- tively.

1**Data analyses were carried out by the** software **"GC Solution version 2.3", Shimadzu.**

7 2 6 V-8 8 3 4 1 5 Fig. 1. Layout of equipments for in situ transesterification of activated sludge. [1] Nitrogen cylinder, [2] needle valve, [3] reactor, [4] heater, [5] magnetic stirrer, [6] pressure gauge, [7] thermo couple, [8] controller. Solid Hexane + salt solution (5% NaCl) Aqueous phase 3. Results and discussion 3.1. Characteristics of activated sludge Dry sludge Methanol + acetic acid Reaction Filtration Filtrate Vacuum evaporation Methanol Crude product Separation Crude FAME GC analysis Fig. 2. Flowchart of biodiesel production from dried sludge. Table 1 Characteristics of lipid in dry activated sludge before and after SCW treatment (Tran- Nguyen et al., 2013). Lipid mass fraction dry activated sludge (%) Table 1 shows the crude lipid content of AS before and after SCW treatment. Before treatment, the extractable lipid content Composition Before SCW pretreatment After SCW pretreatmenta was 17.99%, which was increased 2.54 times to 45.42% after SCW Unsaponifiable 0.50 5.75 treatment. In addition to increase of

3**crude lipid, neutral lipid** con- **Wax and** gums **1.** 21 **1.**

71 tent also increased 2.33 times after SCW treatment. This increase Neutral lipid 16.28 37.96 of extractable lipid after SCW treatment was the result of SCW a Pretreatment condition: 175 °C, 4 MPa, 15 min. hydrolysis of phospholipids which are microbial by-products resulting from microbial activity such as death and lysis in 3.2. FAME production from activated sludge wastewater treatment (Olkiewicz et al., 2015). SCW pretreatment can release lipids from other macromolecules which may not be Reaction temperature is the major parameter influencing trans- extractable. FFA content and fatty acids profiles of the activated esterification process. Therefore, in the preliminary investigation of sludge oil were reported by Tran-Nguyen et al. (2013). this

5**study, the effect of temperature on** FAME **yield was**

investi- gated from 200 °C to 250 °C for 30 min with 30 mL methanol per gram dried sludge (data not shown). It was found that FAME yield was 7.32% at 200 °C and increased rapidly to 23.47% at 250 °C, an increase of about 3.2 times. It may be due to the increase of miscibility between methanol and oil thus an increase of reaction rate (Amit, 2012). Miscibility of methanol and oil are poor at room temperature. Reaction rate increased with increasing temperature owing to increase in solubility of methanol in the oil-rich phase. Higher reaction temperature results in shorter reaction time in mass transfer controlled reaction because esterification reaction is more preferred at higher temperature (Noureddini and Zhu, 1997). In addition, increasing temperature results in decreasing polarity of methanol and this leads to enhancing the solubility of fatty acids in methanol. Kusdiana and Saka (2004) also reported that in supercritical state, methanol acts as an acid catalyst in (trans)esterification reaction. A reaction temperature of 250 °C was chosen for all experiments in this study, which is a little higher than the critical temperature of methanol (239.6 °C); how- ever, the reaction was still happened under subcritical condition because of the presence of lipids which have much higher critical temperatures. 3.2.1. Effect of reaction time on FAME yield Most of the studies

> 7**on biodiesel production from** sludge **by acid catalyzed transesterification**

were carried out at 50 to 75 °C for 24 h

> 6**(Dufreche et al., 2007; Mondala et al., 2009; Revellame et al., 2010,** 2011). Choi **et al.**

(2014) produced

> 10**biodiesel from wet** sludge **with hexane** as **the**

co-solvent at 55 °C with

> 2**a methanol to sludge ratio of** 10 **mL g** 1 **and** reported **a** FAME yield **of**

9.68% in 8 h.

> 4**Acid-catalyzed in situ transesterification of** greasy sewage **sludge**

> 7**with methanol** using **hexane as** the co **-solvent was reported by** Gerhard **et al.**

(2015). A maximum methyl esters yield of 61% was achieved in 7 h at 55 °C and

> 10**a methanol to sludge ratio of 20** mL g **1. The** effect **of**

reaction time on FAME yield was investigated by carrying out reactions at 250

13**°C with** a **methanol to** dry **sludge** ratio **of 30 mL g 1**

for up to 240 min. It was found that FAME yield

5**increased with reaction time** and **reached a maximum** of 28.98% **at**

120 min (Fig. 3), then decreased slightly to 25.70% as the reac- tion time was prolonged to 240 min. It was possibly the results of reverse transesterification and formation of fatty acids (Encinar et al., 2012; Eevera et al., 2009). Compared to conventional acid/base catalyzed reaction, in situ- transesterification eliminates the oil extraction step, thus process productivity can be improved. In fact, a FAME yield of 28.98% was achieved in 120 min which is comparable to that of the study of Huynh et al. (2012) and conventional acid catalyzed transester- ification

10**(Mondala et al., 2009; Revellame et al., 2010)**

but required 8 h and 24 h, respectively. However, by extending reaction time to 180 min and 240 min, FAME yield decreased slightly to 25.97% and 25.70%, respectively. This may be because the reaction has reached equilibrium. 3.2.2. Effect of methanol to sludge ratio on FAME yield

12**One of the most important** parameters **affecting the** transester- ification reaction **is the** mass **ratio of methanol to** biomass used in **the** reaction. Theoretically, **transesterification requires three moles of methanol** per **mole of**

triglycerides.

17**The optimum molar ratio of methanol** and Cynara oil **to**

obtain high FAME yield by alkali catalyzed transesterification was between 4.05 and 5.67. Uncom- pleted reaction and difficult separation between methanol and glycerol occurred when

23**molar ratio of methanol to** triglycerides were **less than**

4.05 and higher than 5.67, respectively (Kusdiana and Saka, 2001; Encinar et al., 1999). In this study, the effect of methanol to dry sludge ratio on FAME yield was investigated by varying the ratio from 1:1 to 40:1 mL g 1 at 250 °C for 120 min and the

22**results are depicted in Fig.** 4. **It** can **be observed that**

FAME yield increased from 20.17% to 28.98% as methanol to dry sludge ratio was increased from 1:1 to 30:1 mL g 1. Even at a methanol to dried sludge ratio of 1 mL g 1, FAME yield could reach about 20%.

Biodiesel yield increased as more methanol was used. The best result was obtained at a metha- nol to dried sludge ratio of 30 mL g 1. Since the transesterification is a reversible reaction, excess methanol is required to shift this equilibrium towards the formation of FAME (Encinar et al., 2012). Additionally, in the study of the kinetics of transesterifica- tion of rapeseed oil in supercritical methanol, it was reported that higher molar ratio of methanol to oil resulted in better FAME yield owing to the increase of contact area between oil and methanol (Kusdiana and Saka, 2001). However, further increase in methanol loading tended to have negative effects on FAME yield which decreased slightly to 25.56% as the ratio of methanol to dry sludge was increased to 40 mL g 1. This is possibly the result of dilution effect as more amount of methanol was used. Another reason to avoid using too much methanol is that high methanol loading interferes with the separation between glycerol and FAME because of increase of glycerol in FAME as well as difficulty in washing step and 35 35 30 30 25 25 FAME yield (%) 20 15 FAME yield (%) 20 15 10 10 5 5 0 0 0 30 60 120 180 240 1.0 5.0 7.5 15.0 22.5 30.0 40.0 Reaction time (min) Ratio of methanol to dried sludge (mL.g-1) Fig. 3. Effect of reaction time on FAME yield at 250

13**°C with** a **methanol to** dry **sludge** ratio **of 30 mL g 1.**

Fig. 4. Effect of methanol to dry sludge ratio on FAME yield. Reaction tempera- ture = 250 °C, reaction time = 120 min. contamination of biodiesel product (Encinar et al., 2012). This trend is in agreement with the study of Huynh et al. (2012) which reported that a ratio of methanol to dry activated sludge higher than 30 mL g 1 resulted in lower FAME yield. It may be because excess methanol favors extraction of more polar compounds, such as carbohydrate, proteins and pigments as well as the formation of mono-glyceride as explained in the Section 3.2.1. Excess methanol produces more glycerol which increases the driving force of reverse reaction. In addition, excess methanol

23**increases the cost of methanol recovery.** Following **the** study **of**

Revellame et al. (2011), acid catalyzed transesterification of dry sludge was carried out at 55 °C by using

2**a methanol to** dried **sludge ratio of** 25 **mL g** 1 **and**

4% H2SO4 (v/ v). FAME yield was 11.38% at 2 h and reached a maximum value of 35.28% at 24 h. This maximum FAME yield is higher than the maximum FAME yield achievable (29%) in the subcritical metha- nol transesterification at 250 °C; however much shorter reaction time (2 h) was required in the latter case. Acid catalyst (H2SO4) is required in the former method which requires washing to remove acid from product. On the contrary, the latter process does not require the use of mineral acid.

2**A methanol to** dry **sludge ratio of** 5 **mL g**

1 was selected for the following study since increasing this ratio from 5 to 30 (an increase of 500%), FAME only increased from 25.83% to 28.98% (an increase of 12%). Furthermore, lowering the amount of methanol used is favorable to reduce the cost of biodiesel production. 3.3. Effect of AA on FAME yield Biodiesel productions from sludge using mineral acid, mostly H2SO4, as catalyst have been investigated by Dufreche et al. (2007), Mondala et al. (2009) and Revellame et al. (2010, 2011). However, there is no report on biodiesel

2**production from activated sludge under subcritical methanol condition**

with addition of AA, an organic acid.

4**At a** solvent **(methanol** + AA) **to** dry **sludge ratio of**

5 mL g 1, the effects of the amount of AA added on FAME yield are presented in Fig. 5. The use of 15% AA in the solvent mixture (methanol to AA = 4.25:0.75) enables the reaction to reach a FAME yield of 30.11% in 30 min, which is about 86% of that of the acid catalyzed transesterification (35%) that required a reaction of 24 h. Saka et al. (2010) proposed the kinetics of the transesterification of triglycerides in the presence of AA. At high temperature AA, a weak acid, plays the role of an acid catalyst to react with triglycerides and generate fatty acids, monoacetyl diglyceride, diacetyl mono- glyceride and triacetin. These reaction intermediates then react with methanol to produce FAME. Acid (AA) catalyzed transesterifi- cation of dry sludge was carried out at 55 °C with a solvent (methanol:AA = 4.25:0.75 mL g 1) to dry sludge ratio of 30 mL g 1 resulted in an FAME yield of only 2.61% in 24 h. Apparently, AA shows high catalytic activity only at high temperature. Another possible reason for the improvement on FAME yield was the enhancement of lipids extracted from sludge since lipids have better solubility in an acidic environment (Hensarling and Jacks, 1983). AA could also increase the mutual solubility of reactants in the reaction. However, reaction time longer than 30 min (Figs. 5 and 6) and more AA used (Fig. 4, methanol: AA = 4:1 mL g 1) resulted in lower yields owning to possible degra- dation of products in acidic environment. In this study, a total time of 90 min (60 min for heating and 30 min for reaction) required is significantly shorter than studies on biodiesel production from activated sludge reported in literatures (Table 2). When pure methanol and

2**a methanol to sludge ratio of 30 mL g**

1 were used, it was capable of achieving a FAME yield of 28.98% in 120 min. By using 15% AA in the AA–methanol mixture and a ratio of AA-methanol mixture to sludge of 5 mL g 1, higher yield (30.11%) can be achieved in much shorter time (30 min). 3.4. Advantages of using subcritical methanol and AA Commercial biodiesel production requires the use of acid/base catalyst. Supercritical methanol method has been investigated by many researchers to avoid the use of catalysts. Nevertheless, supercritical methanol has some disadvantages such as

22**high energy consumption and high investment**

of equipment since the reactions are carried out under high temperature and pressure.

17**Co-solvents such as CO2** and alkane **have been** added **in the** super- critical **methanol**

method to reduce the temperature and pressure required for the process, and to reduce the degradation of product (Encinar et al., 2012; Cao et al., 2005). Another possible way is to conduct the reaction under subcritical conditions, with minimum amount of catalysts or without catalyst, at lower temperature and

pressure than that required by the supercritical methanol method (Yin et al., 2008). In terms of reaction time and methanol amount required, the result of in situ transesterification of activated sludge in subcritical methanol and AA obtained in this study is superior to the results of studies that produced biodiesel using conventional acid catalyzed 35 35 30 30 min 45 min 30 FAME yield (%) 25 20 15 25 20 FAME yield (%) 15 10 10 5 5 0 4.75 : 0.25 4.50 : 0.50 4.25 : 0.75 4.00 : 1.00 0 0 15 Methanol to AA ratio (v/v)

5**30 Reaction time (min)** 45 60 **Fig. 5.** Effect **of** AA loading **on**

FAME yield at 250 °C, a solvent (methanol/AA) to dry sludge ration of 5 mL g 1 and reaction time of 30 and 40 min. Fig. 6. Effect of reaction time on FAME yield at 250 °C, a solvent (methanol/AA, 15% acetic acid) to dry sludge ratio of 5 mL g 1. Table 2 Comparison of results of producing biodiesel from sludge by various methods. Sources of activated sludge Lipid In situ transesterification Ratio Temp. Time Pressure FAME yield Conversion References content method (mL g 1) (°C) (h) (MPa) (wt.%)a (%)b (%) Municipal wastewater treatment plant Municipal wastewater treatment plant Primary sludge Secondary sludge Municipal wastewater treatment plant Municipal wastewater treatment plantd Uni-President Enterprises Corp. Ltd., Chung-Li Bakery Factorye Wastewater treatment plant Municipal wastewater treatment plant (greasy, primary and secondary sludge)e Hsin-Tung-Yang LTD Da-Yuan Factory 27.43c Acid catalyzed (H2SO4 1% v/v) n.r.d Acid-catalyzed (H2SO4 5% v/v) n.r.d Acid-catalyzed (H2SO4 4% v/v) n.r.d Acid-catalyzed (H2SO4 10% v/ v) 66.64 Subcritical water-subcritical methanol n.r.d Acid-catalyzed (H2SO4 0.05% v/v, n-hexane as co-solvent) 44.40 Acid-catalyzed (H2SO4 7 wt.%, n-hexane as co-solvent 10% v/ v) 45.42f Subcritical methanol-AA (AA 15%) 5 50 12 75 30 55 30 75 30 175 10 55 20 55 5 250 24 – 8 – 24 – 24 – 8 3.5 8 – 7 – 1.5g 2.5 6.23 14.50 (primary sludge) 2.50 (secondary sludge) 4.79 3.93 45.58 9.68 61.00 30.11 22.60 97.89h – – 66.52 – >100i 65.97 Dufreche

18**et al. (2007)** Mondala **et al. (2009)** Revellame **et al.** (2010) Revellame **et al.** (2011) Huynh **et al.** (2012) Choi **et al.** (2014) Gerhard **et al.**

(2015) This study a Yield based on dry sludge. b Assume that palmitic triglyceride is the major component of lipid and palmitic acid methyl ester is a main component of FAME. c Maximum oil yield, sludge was extracted three times: 60% hexane/20% methanol/20% acetone. d n.r.: not reported. e Wet sludge was used. f Extracted crude oil after SCW treatment for 15 min at 175 °C (Tran-Nguyen et al., 2013). g Total reaction time including heating time. h Estimated by on their kinetic model. i Sludge sample contains greasy, primary-settling and secondary sludge. method and subcritical water-subcritical methanol method. Compared to supercritical methods, this process can reduce the severity of process parameters without sacrificing on biodiesel yield. As shown in Table 2, the 5 mL methanol/AA per gram dry sludge used in this study is lower than most conventional pro- cesses reported in literatures using acid as catalyst which required

2**a methanol to** dry **sludge ratio of** 10–30 **mL g**

1, except for the study of Dufreche et al. (2007) in which a ratio of 5 mL g 1 was also used. Production of biodiesel from activated sludge via subcritical methanol and AA seems feasible and superior to the conventional acid/base catalyzed transesterification method. Dufreche et al. (2007) reported a conversion of 22.60% which is about one third of the conversion obtained in this study although the amount of methanol used is the same. However, this study can reduce the reaction time to 30 min which is much shorter than the

24 h required in the study of Dufreche et al. (2007). Compared to the study of Huynh et al. (2012) which required a reaction time of 8 h, this study required 30 min to achieve the same conversion. Mondala et al. (2009) obtained a conversion of 97.89% which is significantly higher than that of this study (65.97%). However, a reaction time of 10 h and

2**a methanol to** dry **sludge ratio of** 12 **mL g**

1 were required which are much higher than the 1.5 h reaction time and 5 mL g 1 methanol to sludge ratio used in this study. Additionally, the high concentration of sulfuric acid (5%) used in the study of Mondala et al. (2009) required neutralization as well as separation and washing post-treatment. Moreover, the use of co-solvent as hexane was eliminated in in situ transesterification subcritical methanol and acetic acid pro- cess. Since no mineral acid was used, neutralization and separation of catalysts as well as washing step in the traditional biodiesel pro- duction after reaction are not required. Additionally, compared to the acid catalyzed in situ transesterification, this process can dras- tically reduce the reaction time and methanol loading. The failure to meet the sulfur specification from the generation of sulfur- containing compounds in the presence of H2SO4 will no longer be a concern. It can be said that in situ transesterification using sub- critical methanol and AA is an environmentally friendly process. The disadvantage of this process is the reaction has to be carried out at considerably higher temperature than the conventional acid/base catalyzed processes. 4. Conclusions This work studied the biodiesel production from activated sludge in subcritical methanol and AA. The reaction was carried out in short time, acid neutralization after reaction was not required and methanol used was significantly reduced. Results show that AA played an important role in the reaction. A FAME yield of 30.11% was obtained at 250 °C in 30 min using a solvent to dried sludge ratio of 5 mL g 1. This method requires much shorter reaction time and considerably less methanol amount in producing biodiesel from activated sludge than those reported in literatures. Acknowledgement This work was supported by funding from National Science Council of Taiwan (NSC 102-2221-E-011-079). References Ahmad, M., Khan, M.A., Zafar, M., Sultana, S., 2012. Practical Handbook on Biodiesel Production and Properties. CRC Press, Taylor & Francis Group, Florida. Amit, S., 2012. Biodiesel: Production and Properties. The Royal Society of Chemistry, Cambridge. Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H., Mekhilef, S., 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renew. Sustainable Energy Rev. 16, 2070–2093. Cao, W.L., Han, H.W., Zhang, J.C., 2005. Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent. Fuel 84, 347–351. Choi, O.K., Song, J.S., Cha, D.K., Lee, J.W., 2014. Biodiesel production from wet municipal sludge: Evaluation of in-situ transesterification using xylene as a cosolvent. Bioresour. Technol. 166, 51–56. Dufreche, S., Hernandez, R., French, T., Sparks, D., Zappi, M., Alley, E., 2007. Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel. J. Am. Oil Chem. Soc. 84, 181–187. Eevera, T., Rajendran, K., Saradha, S., 2009. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. Renew. Energy 34, 762–765. Encinar, J.M., González, J.F., Sabio, E., Ramiro, M.J., 1999. Preparation and properties of biodiesel from Cynara cardunculus L. oil. Ind. Eng. Chem. Res. 38, 2927–2931. Encinar, M., Pardal, A., Martínez, G., 2012. Transesterification of rapeseed oil in subcritical methanol conditions. Fuel Process. Technol. 94, 40–46. Fan, X., Burton, X., 2009. Recent development of biodiesel feedstocks and the applications of glycerol: a review. Open Fuel Energy Sci. J. 2, 100–109. Gerhard, N.S., Cea, M., Risco, V., Navia, R., 2015. In situ biodiesel production from greasy sewage sludge using acid and enzymatic catalysts. Bioresour. Technol. 179, 63–70. Hensarling, T.P., Jacks, T.J., 1983. Solvent extraction of lipids from soybeans with acidic hexane. J. Am. Chem. Soc. 60, 783–784. Huynh, L.H., Tran-Nguyen, P.L., Ho, Q.P., Ju, Y.H., 2012. Catalyst-free fatty acid methyl ester production from wet activated sludge under subcritical water and methanol condition. Bioresour. Technol. 123, 112–116. Kusdiana, D., Saka, S., 2001. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 80, 693–698.

Kusdiana, D., Saka, S., 2004. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresour. Technol. 91, 289–295. Mata, T.M., Martins, A.A., Caetano, N.S., 2010. Microalgae for biodiesel production and other applications: a review. Renew. Sustainable Energy Rev. 14, 217–232. Mondala, A., Liang, K., Toghiani, H., Hernandez, R., French, T., 2009. Biodiesel production by in-situ transesterification of municipal primary and secondary sludges. Bioresour. Technol. 100, 1203–1210. Mythili, R., Venkatachalam, P., Subramanian, P., Uma, D., 2014. Production characterization and efficiency of biodiesel: a review. Int. J. Energy Res. 38, 1233–1259. Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. J. Am. Oil Chem. Soc. 74, 1457–1463. Olkiewicz, M., Fortuny, A., Stüber, F., Fabregat, A., Font, J., Bengoa, C., 2015. Effects of pre-treatments on the lipid extraction and biodiesel production from municipal WWTP sludge. Fuel 141, 250–257. Revellame, E., Hernandez, R., French, W., Holmes, W., Alley, E., 2010. Biodiesel from activated sludge through in-situ transesterification. J. Chem. Technol. Biotechnol. 85, 614–620. Revellame, E., Hernandez, R., French, W., Holmes, W., Alley, E., Callahan II, R., 2011. Production of biodiesel from wet activated sludge. J. Chem. Technol. Biotechnol. 86, 61–68. Saka, S., Isayama, Y., Ilham, Z., Jiayu, X., 2010. New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel 89, 1442–1446. Tran-Nguyen, P.L., Go, A.W., Huynh, L.H., Ju, Y.H., 2013. A study on the mechanism of subcritical water treatment to maximize extractable cellular lipids. Biomass Bioenergy 59, 532–539. Yin, J.Z., Xiao, M., Wang, A.Q., Xiu, Z.L., 2008. Synthesis of biodiesel from soybean oil by coupling catalysis with subcritical methanol. Energy Convers. Manage. 49, 3512–3516. P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36 31 32 P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36 P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36 33 34 P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36 P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36 35 36 P.L. Tran-Nguyen et al. / Bioresource Technology 197 (2015) 30–36