Turnitin Originality Report

Biomass and Bioenergy by Suryadi Ismadji

From journal (Hippo-hippo)

Processed on 15-Feb-2018 17:45 WIB
ID: 916388226
Word Count: 8901

Similarity Index	Similarity by Source	
18%	Internet Sources:	11%
	Publications:	15%
	Student Papers:	6%

sources:

1. 1% match (Internet from 29-May-2016)
http://tesisenxarxa.net/bitstream/handle/10803/351959/Tesis%20Magdalena%20Olkiewicz.pdf?sequence=1

2. 1% match (publications)
Fedosov, S.N.. "Analysis of biodiesel conversion using thin layer chromatography and nonlinear calibration curves", Journal of Chromatography A, 20110513

3. 1% match (Internet from 04-Nov-2017)
http://kb.psu.ac.th/psukb/bitstream/2016/10702/1/409376.pdf

4. < 1% match (Internet from 11-Nov-2014)
http://pierre.fkit.hr/hdki/cabeq/pdf/27_1_2013/11.pdf

5. < 1% match (publications)
José M. Encinar, Juan F. González, Antonio Rodríguez-Reinares. "Biodiesel from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel", Industrial & Engineering Chemistry Research, 2005

6. < 1% match (Internet from 07-Jul-2013)
http://biofuel.org.uk/first-generation-biofuel.html

7. < 1% match (publications)
Kurniawan, A.. "Utilization of rarasaponin natural surfactant for organo-bentonite preparation: Application for methylene blue removal from aqueous effluent", Microporous and Mesoporous Materials, 201106

8. < 1% match (publications)
A.K. Azad, M.G. Rasul, M.M.K. Khan, S.C. Sharma. "Biodiesel From Queensland Bush Nut (Macadamia integrifolia)", Elsevier BV, 2017

9. < 1% match (Internet from 22-Feb-2015)
http://waset.org/publications/14692/statistical-process-optimization-through-multi-response-surface-methodology

10. < 1% match ()
http://www.restekcorp.com/restek/images/external/59583.pdf

11. < 1% match (publications)
Demirbas, Ayhan. "Energy from Waste Materials and Unconventional Sources", Green Energy and Technology, 2016.

12. < 1% match (publications)
Ramyasree Uppada, Sita; Kumar Gupta, Amit and Dutta, Jayati Ray. "Statistical Optimization Of Culture Parameters For Lipase Production From Lactococcus lactis And Its Application In Detergent Industry", International Journal of ChemTech Research, 2012.

13. < 1% match (student papers from 12-Aug-2013)
Submitted to Universiti Putra Malaysia on 2013-08-12

14. < 1% match (publications)
Emmanuel Revellame. "Production of biodiesel from wet activated sludge", Journal of Chemical Technology & Biotechnology, 01/2011

15. < 1% match (student papers from 08-Feb-2016)
Submitted to University of Hull on 2016-02-08

16 < 1% match (Internet from 03-Aug-2017)
http://iks.ukzn.ac.za/taxonomy/term/14?page=5

17 < 1% match (publications)
Gangadharan, D.. "Response surface methodology for the optimization of alpha amylase production by Bacillus amyloliquefaciens", Bioresource Technology, 200807

18 < 1% match (Internet from 29-Aug-2016)
http://docslide.us/documents/t01-s01.html

19 < 1% match (Internet from 01-Jul-2016)
http://mdpi.com/1996-1073/2/2/362/htm

20 < 1% match (publications)
Jar-Jin Lin, Yu-Wen Chen. "Production of biodiesel by transesterification of Jatropha oil with microwave heating", Journal of the Taiwan Institute of Chemical Engineers, 2017

21 < 1% match (student papers from 10-Sep-2015)
Submitted to Indian Agricultural Research Institute on 2015-09-10

22 < 1% match (publications)
C.Q. Liu. "Response surface methodology for optimizing the fermentation medium of alpha-galactosidase in solid-state fermentation", Letters in Applied Microbiology, 8/2007

23 < 1% match (Internet from 07-Nov-2017)
http://epubs.scu.edu.au/cgi/viewcontent.cgi?article=1485&context=theses

24 < 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.

25 < 1% match (publications)
Urrutia, C., N. Sangaletti-Gerhard, M. Cea, A. Suazo, A. Aliberti, and R. Navia. "Two step esterification–transesterification process of wet greasy sewage sludge for biodiesel production", Bioresource Technology, 2016.

26 < 1% match (Internet from 29-Dec-2017)
http://sphinxsai.com/2014/vol6pt4/5/(2568-2576)Jul-Aug14.pdf

27 < 1% match (publications)
Jena, Umakanta, Alex T. McCurdy, Andrew Warren, Hailey Summers, Rhesa N. Ledbetter, S. Kent Hoekman, Lance C. Seefeldt, and Jason C. Quinn. "Oleaginous yeast platform for producing biofuels via co-solvent hydrothermal liquefaction", Biotechnology for Biofuels, 2015.

28 < 1% match (Internet from 27-Mar-2016)
http://www.omicsonline.org/open-access/in-situ-transesterification-of-wet-activated-sludge-under-subcritical-conditions-2157-7463.1000182.pdf

29 < 1% match (publications)
Siddiquee, M.N.. "Lipid extraction and biodiesel production from municipal sewage sludges: A review", Renewable and Sustainable Energy Reviews, 201102

30 < 1% match (publications)
Fang, Tao, Wahyudiono, Bushra Al-Duri, Yusuke Shimoyama, Yoshio Iwai, Mitsuru Sasaki, and Motonobu Goto. "Supercritical Methanol Process of Modifying Oil Byproduct for Concentrating Natural Tocopherols", Industrial & Engineering Chemistry Research, 2007.

31 < 1% match (publications)
Nascimento, Iracema Andrade, Sheyla Santa Izabel Marques, Iago Teles Dominguez Cabanelas, Gilson Correia de Carvalho, Maurício A. Nascimento, Carolina Oliveira de Souza, Janice Isabel Druzian, Javid Hussain, and Wei Liao. "Microalgae Versus Land Crops as Feedstock for Biodiesel: Productivity, Quality, and Standard Compliance", BioEnergy Research, 2014.

32 < 1% match (publications)
Biofuels and Biorefineries, 2014.

33 < 1% match (student papers from 05-Oct-2017)
Submitted to Australian Catholic University on 2017-10-05

34 < 1% match (student papers from 15-Aug-2014)
Submitted to Durban University of Technology on 2014-08-15

35 < 1% match (student papers from 06-Oct-2017)
Submitted to Manchester Metropolitan University on 2017-10-06

36 < 1% match (Internet from 26-Dec-2017)
https://d-nb.info/1120120608/34

37 < 1% match (publications)
Zhu, Fen Fen, Juan Juan Qi, Xiang Wei, Lu Yao Zhao, and Yi Qun Xiong. "*In Situ* Transesterification of Sewage Sludge for Biodiesel Production", Applied Mechanics and Materials, 2015.

38 < 1% match (publications)
Rakopoulos, C.D.. "Comparative performance and emissions study of a direct injection Diesel engine using blends of Diesel fuel with vegetable oils or bio-diesels of various origins", Energy Conversion and Management, 200611

39 < 1% match (publications)
Navia, R., and M. Mittelbach. "Could sewage sludge be considered a source of waste lipids for biodiesel production?", Waste Management & Research, 2012.

40 < 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%3A240

41 < 1% match (publications)
Biofuels and Biorefineries, 2015.

42 < 1% match (publications)
Sawangkeaw, R.. "A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001-2009)", The Journal of Supercritical Fluids, 201011

43 < 1% match (student papers from 13-Jul-2017)
Submitted to Unviersidad de Granada on 2017-07-13

44 < 1% match (Internet from 21-Dec-2017)
http://repository.its.ac.id/44003/1/A%20new%20approach%20in%20maximizing%20and%20direct%20utilization%20of%20whole%20jatropha

45 < 1% match (publications)
G.Q. He. "Response surface methodology for optimizing the fermentation medium of Clostridium butyricum", Letters in Applied Microbiology, 10/2004

46 < 1% match (publications)
de Almeida, Vanessa F., Pedro J. García-Moreno, Antonio Guadix, and Emilia M. Guadix. "Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties", Fuel Processing Technology, 2015.

47 < 1% match (publications)
Christoph Strauß, Armin Vetter, A. Von Felde. "Chapter 313 Biogas biogas Production biogas production and Energy Crops biogas energy crops", Springer Nature, 2012

48 < 1% match (publications)
Poljanek, Ida, and Bla Likozar. "Influence of Mass Transfer and Kinetics on Biodiesel Production Process", Mass Transfer in Multiphase Systems and its Applications, 2011.

49 < 1% match (student papers from 15-May-2013)
Submitted to University of the West Indies on 2013-05-15

50 < 1% match (publications)
Atabani, A.E.. "A comprehensive review on biodiesel as an alternative energy resource and its characteristics", Renewable and Sustainable Energy Reviews, 201205

51 < 1% match (publications)
Tom Burr. "Performance of Variable Selection Methods in Regression Using Variations of the Bayesian Information Criterion", Communications in Statistics - Simulation and Computation, 03/2008

52 < 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%3A1210

53 < 1% match (Internet from 29-Jul-2016)
http://jehse.biomedcentral.com/articles/10.1186/s40201-015-0232-9

54 < 1% match (publications)
Emmanuel Revellame. "Biodiesel from activated sludge through in situ transesterification", Journal of Chemical Technology & Biotechnology, 2009

55 < 1% match (publications)
Zhu, Fenfen, Luyao Zhao, Huimin Jiang, Zhaolong Zhang, Yiqun Xiong, Juanjuan Qi, and Jiawei Wang. "Comparison of the Lipid Content and Biodiesel Production from Municipal Sludge Using Three Extraction Methods", Energy & Fuels, 2014.

56 < 1% match (publications)
A. Hussain. "Contributions to the investigation of inorganic non-stoichiometric compounds. XXXI. A New NbOx Phase with ß-ZrNb24O62 structure", Zeitschrift für anorganische und allgemeine Chemie, 04/1986

57 < 1% match (publications)
Ianatul Khoiroh. "Isothermal Vapor−Liquid Equilibrium for Binary Mixtures of Polyoxyethylene 4-Octylphenyl Ether with Methanol, Ethanol, or Propan-2-ol", Journal of Chemical & Engineering Data, 04/14/2011

58 < 1% match (publications)
Olkiewicz, Magdalena, Carmen M. Torres, Laureano Jiménez, Josep Font, and Christophe Bengoa. "Scale-up and economic analysis of biodiesel production from municipal primary sewage sludge", Bioresource Technology, 2016.

59 < 1% match (publications)
Yanti, Asnida, Mohd Azlan Mohd Ishak, and Khudzir Ismail. "Production of Biodiesel via In-Situ Supercritical Methanol Transesterification", Biodiesel - Feedstocks and Processing Technologies, 2011.

60 < 1% match (student papers from 16-Nov-2011)
Submitted to National University of Singapore on 2011-11-16

61 < 1% match (Internet from 20-Dec-2015)
http://lait.dairy-journal.org/articles/lait/pdf/2003/02/L3207.pdf

62 < 1% match (Internet from 05-Jul-2016)
http://mdpi.com/2227-9717/4/1/2/htm

63 < 1% match (Internet from 21-Sep-2017)
http://uvadoc.uva.es/bitstream/10324/18034/1/Tesis1074-160720.pdf

64 < 1% match (Internet from 02-Dec-2016)
http://dalspace.library.dal.ca/bitstream/handle/10222/45049/maqbool-rizwan-PhD-Biol-December-2013.pdf?isAllowed=y&sequence=5

65 < 1% match (publications)
Sajjadi, Baharak, Abdul Aziz Abdul Raman, and Hamidreza Arandiyan. "A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models", Renewable and Sustainable Energy Reviews, 2016.

< 1% match (publications)

66 Ramalingam Subramaniam. "Microbial lipids from renewable resources: production and characterization", Journal of Industrial Microbiology & Biotechnology, 12/2010

67 < 1% match (publications)
Kakkad, Hardik, Mahesh Khot, Smita Zinjarde, and Ameeta RaviKumar. "Biodiesel Production by Direct In Situ Transesterification of an Oleaginous Tropical Mangrove Fungus Grown on Untreated Agro-Residues and Evaluation of Its Fuel Properties", BioEnergy Research, 2015.

68 < 1% match (publications)
Wang, Ting, Ning Wang, Xin Jin, Kai Zhang, and Tiefu Li. "A novel procedure for preparation of submicron liposomes-lyophilization of oil-in-water emulsions", Journal of Liposome Research, 2009.

69 < 1% match (publications)
David M. Kargbo. "Biodiesel Production from Municipal Sewage Sludges", Energy & Fuels, 05/20/2010

70 < 1% match (publications)
Chen, Xiaolin, Linfeng Hu, Ronge Xing, Song Liu, Huahua Yu, Yukun Qin, Kecheng Li, Rongfeng Li, and Pengcheng Li. "Ionic liquid assisted subcritical water promotes the extraction of lipids from wet microalgae Scenedesmus sp .", European Journal of Lipid Science and Technology, 2015.

71 < 1% match (publications)
Shi, Wenying, Mingxia Yang, Hongbin Li, Rong Zhou, and Haixia Zhang. "Preparation and Characterization of Sulfonated Poly (Ether Sulfone) (SPES)/Phosphotungstic Acid (PWA) Hybrid Membranes for Biodiesel Production", Catalysis Letters, 2015.

paper text:

43**Available online at www.sciencedirect.com ScienceDirec t http://www.elsevier.com/locate/biombioe**

5**Synthesis of biodiesel from vegetable oils wastewater sludge by in-situ subcritical methanol transesterification: Process evaluation and optimization**

Farrel Gunawan a, **Alfin Kurniawan** a, **Iwan Gunawan** a, **Yi-Hsu Ju** b,***, **Aning Ayucitra** a,**, **Felycia E. Soetaredjo**

7**a, Suryadi Ismadji a,* a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b Department of Chemical Engineering, National Taiwan University of Science and Technology,** No. 43, **Sec. 4, Keelung Rd., Taipei 106-** 07, **Taiwan,**

ROC

16**article info Article history: Received 7 May 2013 Received in revised form** 3 July **2014 Accepted** 5 **July 2014 Available online Keywords:**

Wastewater sludge Subcritical methanol In-situ transesterification Biodiesel Statistical design abstract

Biodiesel

60**are gaining increased public and scientific attention as an alternative to**

petro- leum diesel fuel,

26**driven by factors such as oil price** spikes, **energy security and**

environ- mental concerns. In this study, low grade wastewater sludge originated from wastewater treatment unit of vegetable oil factory as a viable alternative lipid source

25**for biodiesel production** was evaluated. **The lipid** mass **fraction of** the dry **and** ash-free **sludge was**

12.44 ± 0.87%, which mainly comprised of C16eC18 fatty acids. The in-situ trans- esterification process under subcritical water and methanol conditions was applied as a green pathway to convert lipids into fatty acid methyl esters (FAMEs). The reaction pa- rameters investigated were temperatures (155e215 C), pressures (5.5e6.5 MPa) and methanol to lipid mass ratios (1:1, 5:1 and 9:1). The highest FAME yield of 92.67 ± 3.23% was obtained

15**at 215** C, **6.5 MPa** and **methanol to lipid** mass **ratio of 5:1.**

Statistical analysis based on response surface methodology in 3-factor-3-level central composite designed experiments and analysis of variance were applied to examine the relation between input parameters and the response and to locate the optimum condition. Results showed that 98%

22**of the variability in the response could be** adequately **explained by the second-order polynomial**

model. The optimum FAME yield (90.37%) was obtained at 215 C, 6.5 MPa and methanol to lipid mass ratio of 5.12:1. Experimental validation (N ¼ 3) demonstrated satisfactory agreement between the observed and predicted values with an error of at most 3.3%. ©

16**2014 Elsevier Ltd. All rights reserved. * Corresponding author. Tel.:**

þ62 31 389 1264; fax: þ62 31 389 1267. ** Corresponding author. ***

57**Corresponding author. Tel.: þ886 2 2737** 6612; **fax: þ886 2 2737 6644.**

44**E-mail addresses:** alfin_kur **@yahoo.com** (A. Kurniawan), **yhju@mail.ntust.edu.tw (Y.-H. Ju),**

aayucitra@yahoo.com (A. Ayucitra), suryadiismadji@yahoo.com (S. Ismadji).

33**http://dx.doi.org/10.1016/j.biombioe.** 2014.07 **.005 0961-9534/©** 2014 **Elsevier Ltd. All rights reserved.**

41**1. Introduction The development of sustainable** biofuels **is**

vitally crucial to global transportation and many industrial operations to generate electricity and heat. Such today's concern is driven by long-term supply issue associated with fossil fuels and their environmental impacts due to the release of carbon di- oxide, SOx and NOx pollutants during fuel combustion. One of potential alternative and sustainable biofuels which have been extensively studied and now commercially produced is biodiesel. Although biodiesel produces less air pollutants and is fast becoming a currently recognized substitute and/or blending agent for petroleum diesel, yet it still possesses key limitations include a heavy price, life-cycle assessment and the necessity of a vast land to produce enough biofuel without threatening food supplies and biodiversity.

11**There are a number of factors affecting high variable costs in the production of biodiesel, limiting the fuel's widespread use.**

In this light, the cost of biodiesel feedstock is the most burdensome, which accounts for 70e85% of total cost of pro- duction [1]. Palm

35**oil [2],** soybean **oil [3],** corn **oil [4], rapeseed oil [5],** sunflower **oil [6], sesame oil [7],** rice bran **oil [8]**

6**and a number of other food crops have all**

6**served as feedstock for** biodiesel, **however they all suffer from the same problems including threatening the food chain, increasing carbon emissions when planted outside traditional agricultural** set- tings **and intense growth requirements.**

Animal fats such as beef tallow [9], poultry fat [10], fish oil [11] and pork lard [12] have been investigated to produce biodiesel. Although much of animal fats are not considered edible by humans and

65**their cost is substantially lower than the cost of vegetable**

oils, yet their applications can be challenging because they frequently contain contaminants (e.g., phospholipids and gums) that should be removed before the fuel is used in an engine and also animal fat-based biodiesel typically has higher viscosity and sulfur content. Therefore, it is necessary to gain a new perspective on the production of biodiesel by seeking an alternative feedstock, which is non-food crops and easily obtainable in large quantities. Recently, municipal waste- water sludge is being explored for its untapped potential as a cheap and readily available lipid

39**feedstock for** sustainable **biodiesel production. The sewage sludge is a by-product generated** after **wastewater treatment and**

usually a blend of thickened primary and secondary sludges. This sludge con- tains considerable mass fraction of lipids (up to 30%) either as

29**a composite organic matrix (oils, greases,** sterols, **fats and long-chain fatty** acids) originated **from direct adsorption of lipids** in municipal **and industrial**

wastewater or from phos- pholipids

1**in the cell** membrane **of microorganisms, their metabolites and by-** products **of cell lysis** [13]. **The**

conven- tional technology

58**to produce biodiesel from** sewage **sludge** is by a **two-step process** involving **lipid extraction** using organic **solvents**

and then alcoholysis of extracted lipids. However, this usual approach poses a great challenge for industrial practice. The lipid recovery process from sewage sludge is tedious and costly because it

11**requires huge** amounts **of organic** solvents **and large vessels with stirring and heating systems.**

Also, most of organic solvents used for extracting lipids are not environmentally acceptable. In addition, the alcoholysis either by esterification or transesterification using liquid or solid catalysts often creates limitations in the cata- lyst recovery, yield and purity of biodiesel and treatment of wastewater. Kwon et al. [14] had demonstrated a thermo- chemical approach to transform lipids to biodiesel employing a catalyst-free, continuous flow system. However, non- catalytic thermochemical process suffers from the drawback of intense energy consumption due to the use of high tem- peratures (350e500 C) although nearly complete conversion reaction is achieved within a short period of time.

4**Subcritical water (SubCW),** that **is, pressurized water at temperatures above** the **boiling point at ambient pressure and below critical point** (TC ¼ 374 **C),** is considered as a unique and green reaction medium for various applications including catalytic/non-catalytic reactions, biomass trans- formation to chemicals and materials and extraction of bioactive compounds from natural matrices. Several

4**relevant properties of SubCW as a reaction** medium **are miscibility, ionic product, electrolytic solvent power,** dielectric constant and **transport properties** (e.g., **viscosity,** diffusivity **and ion mobility).**

The physicochemical properties of interest of SubCW

32**can be tuned** through **changes in pressure and** tem- perature. With **the**

increase of temperature, there is a marked and systematic decrease in

63**permittivity, viscosity and surface tension** while **the diffusion rate** increases [15]. In **the** extrac- tion **of**

lipids by SubCW, the process is feasible at mild tem- peratures (typically 150e200 C)

32**due to reduced dielectric constant of water,** making it capable **to**

extract weakly polar to non-polar compounds. A successful implementation of SubCW as a green alternative solvent to recover lipids from wet algae [16] and dewatered activated sludge [17] has been reported and the possibility of producing biodiesel

1**from wet activated sludge** without any catalyst **under subcritical water and methanol condition**

has been investigated by Huynh et al. [18]. In their recent paper, dried activated sludge was used instead of wet activated sludge as the lipid feedstock and water was added prior to methanolysis. Drying of wet activated sludge is a time-consuming as well labor- and energy-intensive process and for large-scale operation, this process is not economically feasible due to large fuel con- sumption in drying machine or huge land area for sun drying process. To date, limited studies on the production of biodiesel from wet activated sludge can be found in literature. In most cases, transesterification is performed under catalytic action of acidic or base homogeneous/heterogeneous catalysts, either in single or two-step processes. In contrast to such method, the in-situ transesterification procedure under subcritical alcohol condition is an ongoing area of intense research. Therefore, the aims of this study are to evaluate

28**in-situ transesterification of wet** wastewater **sludge** to fatty esters **under subcritical** water and methanol **conditions**

along with the influencing

42**parameters (temperature, pressure and methanol to** lipid mass **ratio)**

and to determine the optimum reaction condition by employing response surface methodo- logical approach (RSM)

46**and analysis of variance (ANOVA).** Several key properties **of**

biodiesel is also investigated and compared to ASTM D6751 standard.

55**2. Materials and methods 2.1. Materials** Fresh wastewater **sludge was** collected **from a**

vegetable oil wastewater treatment unit located at Surabaya city, East Java. Distilled water was obtained from a local supplier. Anhydrous methanol (99.8%) and n-hexane (95%) was supplied from Merck, Germany while ultra pure N_2 gas (99.9%) was supplied from a local company. The fatty acid methyl esters (FAMEs) reference standard mix (Supelco) consisting of C14eC22 fatty acids

53**was purchased from Sigma Aldrich Co.,** Singapore **and used without** any **further purification.**

2.2. In-situ subcritical methanol transesterification The experimental setup of a lab-scale high pressure batch reactor in this work (150 cm3, temperature limit: 273e473 K, pressure range: 0e10 MPa) is shown in Fig. 1. The reactor was made of Type 316 stainless steel and equipped with an external heater, a pressure gauge, a Type K thermocouple and M8 screws for tightening the reactor with its cap. The reaction vessel was charged with a given quantity of wet sludge and methanol (methanol to sludge mass ratios of 1:1, 5:1 and 9:1). Here, mass ratio was used instead of molar ratio to represent methanol loading due to the difficulty in calculating exact molecular weight of the sludge containing numerous com- ponents. N_2 was then flowed into the reactor to remove air and build a bit of pressure prior to heating. The reactor was heated at 20 K min 1 from room to desired temperatures (155e215 C) and kept at final temperatures for 12 h. To maintain an isothermal and isobaric condition, temperature was controlled by a PID-type controller with uncertainty of ±1 C and pressure was monitored in real time by a pressure gauge. During the reaction period, the mixture was magneti- cally stirred at a constant rate of 13.33 Hz. When final tem- perature was reached, the pressure inside the reaction vessel ranged between 5.5 and 6.5 MPa. After completion of

30**the reaction, the reactor was** immersed **in** a **cold water**

bath for immediate cooling and the vapor Fig. 1 e Schematic diagram of the subcritical reactor system: N_2 cylinder (1); relief valve (2); electric heating element (3); RPM controller (4); magnetic bar (5); high- pressure reactor (6); release valve (7). mixture was vented to the condenser inlet. The condensate was collected in a conical flask and extracted with n-hexane. The liquid contents were placed in the separatory funnel and after addition of n-hexane and shaking; the mixture was allowed to settle for 24 h to ensure complete separation be- tween ester-rich (organic) and glycerol-rich (aqueous) phases. The aqueous phase (bottom phase) was removed and left in a separate container. The organic phase was evaporated in vacuum to remove n-hexane. The solid fraction was removed and a given amount of n-hexane was added to extract fatty esters and unreacted lipids. The extraction process was con- ducted in a stirred borosilicate cylindrical glass vessel for 2 h with a constant stirring rate of 13.33 Hz. The solid was removed using a Buchner filtering funnel. The retained solid was washed three times with 50 cm3 n-hexane. The removal of n-hexane was conducted in vacuum using a rotary evapo- rator flask and the mass of biodiesel (FAMEs) was weighed using an analytical balance (Mettler Toledo). 2.3. Analysis of FAME mass fraction The FAME mass fraction was assayed by gas chromatography, in a Shimadzu GC 2014

31**equipped with a flame ionization detector (FID) and an** Agilent DB **-WAX capillary column (30 m** length, **0.25 mm**

i.d., 0.25 mm film thickness). Highly pure he- lium (99.9%)

27**was used as the carrier gas** at **a** linear **velocity of** 40 **cm s 1. The injector temperature was set at** 250 **C**

running

68**in splitless mode** and **the detector temperature was** kept **at** 300 **C** for **the**

duration of analysis. The oven temperature program was started at 50 C with a holding time of 2 min, then ramped

37**to 250 C at 10** K **min** and held constant **at** 1 250 **C for** 8 **min. The injection volume** of the samples **was 1**

mm3.

54**Calibration of the instrument was** conducted **using a** 10 **-component FAMEs standard** mix **with** methyl heptadeca- noate as internal standard.

40**All calibration curves were linear with a correlation coefficient of 0.** 98 **or better.** Peaks **of**

FAMEs

61**were identified by comparing retention** time **with those of** FAMEs **standard mix.**

FAMEs not included in this standard were compared with the peaks of well-recognized materials under similar analytical conditions. The FAME mass fraction was determined by the following equation: P Fcð%Þ ¼ 100 AFAME Aint VintCint Aint m (1) P where Fc is the FAME mass fraction, AFAME is total peak area of FAMEs,Aint

3**is the peak area of methyl heptadecanoate,** Vint **is the volume of methyl heptadecanoate internal standard solution added to sample** (cm3), Cint **is the concentration of methyl heptadecanoate** internal standard **solution (g** cm 3) **and m is the mass of** sample **(g). The**

percent yields of FAMEs based on lipid mass fraction of the dry and ash-free sludge were calculated as follows: 100 mp Fc Yieldð%Þ ¼ ml (2) where mp is the mass of biodiesel (g), ml is the mass of lipids in the dry and ash-free sludge (g) and Fc is the FAME mass frac- tion obtained from Eq. (1). Thin-layer chromatography (TLC) was carried out for qualitative analysis of fatty esters, employing

2**silica gel TLC plates (Polygram® Sil G) on** polyester **support**

(20 cm 20 cm, 0.20 mm). The product was

1**dissolved in** n **-hexane and spotted on a TLC plate which was then developed using a** solvent mixture **of** n **-hexane,** ethyl acetate and **acetic acid**

(volume ratios of 90:10:1) in a covered glass vessel

2**until the solvent front reached the top of the plate. After a brief drying, the**

plate was dipped in a water bath for 1e2 min. The

2**wet plate was stained in** 100 cm3 **of 1%** KMnO4 **solution** in **4% NaOH for approximately** 20 s **with constant agitation**

for visualization [19]. Then,

2**the stained plate** was **extensively washed with water** (3e4 **changes for** 3e4 min) **and dried.**

The individual fractions as spots on the plate were identified by comparing Rf values with authentic standards of known masses. 2.4. Biodiesel fuel properties For commercial applications in the compression-ignition en- gines, biodiesel should meet ASTM D6751 standard specifica- tion. The key properties of biodiesel were analyzed as per standard methods described in ASTM D613 for cetane num- ber, ASTM D93 for closed-cup flash point, ASTM D445 for ki- nematic viscosity, ASTM D1480 for relative density, ASTM D664 for acid number, ASTM D2500 for cloud point and ASTM D97 for pour point. 2.5. Statistical

71**experimental design and optimization** Statistical experimental design **was** applied **to optimize the** reaction **conditions for** maximum FAME production. Here, a statistical method called response surface methodology (RSM) coupled with a 3-factor-3-level central composite design (CCD) was adopted to obtain maximum response by optimizing three independent variables namely temperature (C), pressure (MPa) and methanol to lipid mass ratio.

22**Table 1** shows **the coded and** actual **values of** reaction parameters used **in**

the design of experiments. The selection of pressure, temperature and methanol to lipid mass ratio as reaction parameters to be optimized was based on the fact that these parameters are directly relevant to process economics and safety concerns. The experiments were conducted in random order and after finishing the experiments, a suitable mathe- matical model was developed for prediction of the response based on experimental factors. A 95% confidence level was applied for model development and analysis of variance (ANOVA). The analysis of variance was performed using Minitab software (Version 16.2.1) and the response surface plots were obtained using MatLab R2013b software. All ex- periments were repeated three times and the results are averaged. The central data point (0, 0, 0) was replicated five times. Table 1 e 3-factor-3-level experimental design. Parameters Coded values 1 0 1 Temperature (C) Pressure (MPa) Methanol to lipid mass ratio 155 185 5.5 6.0 1 5 215 6.5 9 3.

25**Results and discussion 3.1.** Characteristics **of** vegetable oil wastewater **sludge The characteristics of**

as-received (wet) vegetable oil waste- water sludge are given in Table 2. The dry and ash-free sludge contains quite significant amounts of lipid fractions (12.44 ± 0.87%) include triglycerides, diglycerides, mono-glycerides, sterols, phospholipids and free fatty acids. The fatty acids in the sludge based on gas chromatography anal- ysis consist of

8**myristic acid (C14:0,** 5.7%), **palmitic acid (C16:0,** 31.6%), **palmitoleic acid (C16:1,** 24.8%), **stearic acid (C18:0,** 10.4%), **oleic acid (C18:1,** 16.3%), **linoleic acid (C18:2,** 7.4%), eicosanoic **/arachidic acid (C20:0, 2.**

2%) and docosanoic/

8**behenic acid (C22:0, 1.** 6%). Similar fatty **acid**

compositions had

66**been reported by** Olkiewicz **et al.** [20] **and** Mondala **et al.** [21] **for** primary **and**

secondary sludges originated from munic- ipal wastewater treatment facilities (Table 3). The distribution of fatty acids is also in good agreement with sludges origi- nated from

3**sunflower oil** [24] **and palm oil** [25] industries, **which mainly** comprised **of** C16eC18 **fatty acids**

(~90%). High moisture content of the sludge is necessary to conduct in-situ transesterification process where fatty acids are simulta- neously extracted and transesterified to fatty esters. Compared to conventional process employing solid or liquid catalysts, water content should be taken into consideration because water can hydrolyze

69**fats to form free fatty acids, which then form soap**

and consequently decrease biodiesel yield and cause difficulty in product separation (for base- catalyzed transesterification). 3.2. Process optimization

12**RSM is a** collection **of mathematical and statistical** tech- niques **for empirical model building and optimization,** which **examines the** relation **between one or more response** pa- rameters **and a set of experimental input parameters.**

The design procedure of RSM to locate the optimum value of response (output parameter) from

12**a set of experimental input parameters**

can be divided into four steps [26]:

9**(i) designing a series of experiments for** reliable **and** adequate measurements **of the response of interest, (ii)** constructing **a mathematical model of the second order response surface with best fittings, (iii) finding the optimal set of experimental**

Table 2 e The characteristics of as-received (wet) wastewater sludge. Parameters Mass fraction, % Water contenta Dry matters Lipidic fractionsa (dry basis) Wax and gum Oil components - Fatty acids - Acylglycerols - Unsaponifiable matters 85.51 ± 2.38 14.49 ± 2.38 10.78 ± 1.22 62.13 ± 4.61 37.87 ± 2.35 82.05 ± 3.18 10.73 ± 1.64 7.22 ± 0.51 a The values represent the averages of the results for three repli- cate runs. Table 3 e Distributions of fatty acids in various industrial wastewater sludges. Origin of sludge Type of sludge Fatty acids

23**C12:0 C14:0 C15:0 C16:0** C16:1 **C18:0 C18:1 C18:2 C20:0 C20:** 1 **C22:0 C24:0**

Municipal WWTP [20,21] Primary Secondary Blended Stabilized tracea

56**e , trace e e , , , , , e trace e e** trace **e e , , , , , , , e**

, Pulp & paper mill Blended e trace e , , , , , WWTP [22] Swine manure WWTP [23] Sunflower oil WWTP [24] Secondary Composite , , e , NR trace NR , trace , NR , , , , , Palm oil Secondary , , e , trace , , , WWTP [25] Vegetable oil Secondary e , e , , , , , WWTP (this work) e trace

18**e e** NRa **NR NR** , trace , , e **NR NR NR e NR NR NR , NR NR** NR **e** trace **e e , e** , trace , **e** NR **e e e e NR NR e e , e**

Fatty acids:

10**C12:0 (lauric acid), C14:0 (myristic acid), C15:0 (pentadecanoic acid), C16:0 (palmitic acid), C16:1 (palmitoleic acid), C18:0 (stearic acid), C18:1 (oleic acid), C18:2 (linoleic acid),** C20:0 (eicosanoic **acid),**

C20:1 (gadoleic acid), C22:0 (behenic acid), C24:0 (lignoceric acid). a Trace (concentration below 1%), NR (not reported), , (detected), (not detected or zero).

36**parameters that** give **a maximum or minimum response** and **(iv) representing direct and interactive effects** between input **parameters and**

response as 2D or 3D surface or contour plots. It is realized that the energy requirement of in-situ transesterification process under subcritical water and methanol conditions is higher compared to that of acidic- or base-catalyzed transesterification. However, the in-situ technique offers ancillary advantages than the conventional ones since this technique does not require any solid or liquid catalyst to achieve relatively high FAME yield and elimi- nating the need for pretreatment steps. In order to imple- ment this method for large-scale operation, optimization of reaction condition is important to give maximum benefit from an economic viewpoint. In this light, RSM was applied to obtain the optimum condition for production of fatty es- ters by integrating

42**temperature, pressure and methanol to** lipid mass **ratio** simultaneously. **The**

designed experiments based on 3-factor-3-level CCD model are presented in Table 4. The fitting model,

62**as a function of independent variables,** was expressed as **a** quadratic **(second-order) polynomial** regression form using least squares analysis: X3 X3X3 Y ¼ k0 þ kiXi þ kijXiXj (3)

13i¼1 i¼1 j¼ 1 **where Y is the** predicted **response,** k0, ki, kii **and** kij **are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively** and **Xi and Xj are the coded** levels of **independent variables. The** second term **of**

Eq. (3) represents linear effect of single process variables while the cross-product term represents an interaction effect between two variables Xi and Xj. After developing the response surface plots, the multiple

64**regression coefficients of the model** was **estimated using the** method of **least squares**

at a significance level of 0.05

52**and the results are** listed **in Table** 5. **As shown in Table** 5, it **is**

evident that the main linear effects of temperature (T) and pressure (P) are significant factors toward FAME production. Results also suggested that the square interaction of methanol to lipid mass ratio (M2) and an inter- action effect between temperature and pressure (T*P) signifi- cantly affects FAME yield. The main linear effect of methanol to lipid mass ratio (M), square interaction of pressure (P2) and temperature (T2), interaction effects between pressure and methanol to lipid mass ratio (P*M) and temperature and methanol to lipid mass ratio (T*M) are not significant toward the dependent variable (Y) therefore all these terms except the linear term of methanol to lipid mass ratio (M) and quadratic term of temperature (T2) could be removed from the model without affecting the accuracy of predictions. The variables M and T2 still preserved in the model because after elimination of the insignificant terms, the p-value of linear term M be- comes approximately same to the a-level (0.05) thus methanol to lipid mass ratio has significance toward FAME yield. Simi- larly, the p-value of quadratic temperature term (T2) satisfies 95% confidence level. By inserting the values of significant regression coefficients into Eq. (3), the following second-order polynomial coded model for prediction of FAME yield is obtained: Yieldð%Þ ¼ 67:58 þ 9:89ðTÞ þ 5:12ðPÞ þ 1:64ðMÞ þ 4:41 T2 30:87 M2 þ 3:36ðT$PÞ (4) The above coded model fits the data very well with coef- ficient of determination (R2) of 0.98. This indicates that 98% of

45**the variability in the response could be** adequately inter- preted **by the** developed **second-order polynomial prediction**

model. Additionally, all linear, quadratic and interaction terms in the model are significant at 95% confidence level (Table 5). The response surface plots of the interaction effects be- tween two independent variables are represented in Fig. 2aec. As displayed in Fig. 2a, the positive linear influence for both temperature and pressure indicates that FAME yield increases Table 4 e The designed experiments based on 3-factor-3-level central composite design. Run Input parameters P/MPa (X1) T/ C (X2) M (X3) Response (FAME yield, %) Experimental (N ¼ 3) Prediction 1 1 (5.5) 1 (215) 1 (9:1) 42.35 ± 2.28 44.17 2 0 (6.0) 0 (185) 0 (5:1) 67.92 ± 2.58 67.58 3 1 (6.5) 1 (215) 1 (1:1) 58.12 ± 4.33 57.85 4 1 (5.5) 1 (155) 1 (1:1) 27.77 ± 2.02 27.83 5 1 (6.5) 1 (155) 1 (9:1) 36.12 ± 0.89 34.63 6 0 (6.0) 0 (185) 0 (5:1) 68.15 ± 1.24 67.58 7 0 (6.0) 1 (155) 0 (5:1) 56.33 ± 3.65 62.10 8 0 (6.0) 0 (185) 0 (5:1) 67.32 ± 2.09 67.58 9 1 (6.5) 0 (185) 0 (5:1) 70.96 ± 4.12 72.70 10 0 (6.0) 0 (185) 1 (9:1) 37.12 ± 2.23 38.35 11 0 (6.0) 1 (215) 0 (5:1) 84.02 ± 4.54 81.88 12 0 (6.0) 0 (185) 1 (1:1) 32.67 ± 1.81 35.07 13 1 (5.5) 0 (185) 0 (5:1) 65.77 ± 2.15 62.46 14 1 (6.5) 0 (185) 1 (9:1) 40.38 ± 2.57 43.47 15 1 (6.5) 1 (155) 1 (1:1) 34.02 ± 1.12 31.35 16 0 (6.0) 0 (185) 0 (5:1) 68.25 ± 4.68 67.58 17 1 (5.5) 1 (215) 1 (1:1) 40.35 ± 2.54 40.89 18 1 (6.5) 1 (155) 0 (5:1) 58.24 ± 2.88 63.86 19 1 (6.5) 1 (215) 1 (9:1) 61.02 ± 3.63 61.13 20 1 (6.5) 1 (215) 0 (5:1) 92.67 ± 3.23 90.37 21 1 (6.5) 0 (185) 1 (1:1) 38.49 ± 3.28 40.19 22 0 (6.0) 0 (185) 0 (5:1) 67.44 ± 3.51 67.58 23 1 (5.5) 0 (185) 1 (1:1) 31.21 ± 1.65 29.95 24 0 (6.0) 1 (215) 1 (1:1) 43.72 ± 3.25 49.37 25 1 (5.5) 1 (155) 1 (9:1) 32.77 ± 1.53 31.11 26 0 (6.0) 1 (215) 1 (9:1) 47.11 ± 1.33 52.65 27 1 (5.5) 1 (215) 0 (5:1) 83.11 ± 1.92 73.40 28 0 (6.0) 1 (155) 1 (1:1) 30.11 ± 2.47 29.59 29 1 (5.5) 1 (155) 0 (5:1) 55.15 ± 3.08 60.34 30 1 (5.5) 0 (185) 1 (9:1) 35.21 ± 2.42 33.23 31 0 (6.0) 1 (155) 1 (9:1) 33.21 ± 1.79 32.87 as the level of both factors increases. It was observed that the curve line of pressure vs. temperature vs. FAME yield rose sharply by changing the levels of one independent variable from lowest (1) to highest (1) while keeping another inde- pendent variable in the highest level.

14**It is expected that the increase in** FAME **yield would be greater for** temperature rather than pressure since the coded coefficient of Table 5 e Results of significance test on the multiple regression coefficients of the quadratic polynomial model for estimation of the response (coded form). No Full Partiala Term p-Value Coefficient p-Value Coefficient 1 Intercept

51**2 X1 3 X2 4 X3 5** X21 **6** X22 **7** X23 8 **X1*** X2 9 X2 ***X3** 10 **X1***

X3 0.00 67.78 0.00 5.12 0.00 9.89 0.09 1.65 0.07 1.65 0.35 3.46 0.00 31.82 0.01 3.36 0.78 0.28 0.80 0.25 0.00 67.58 0.00 5.12 0.00 9.89 0.05 1.65 0.01 e e 4.41 0.00 30.87 0.00 3.36 e e e e a Partial means the insignificant terms (p-values > 0.05) of the model are eliminated. temperature is higher than that of pressure.

14**This is also evident on the main effect plots, showing** a **steeper slope for**

temperature than for pressure (Fig. 3). Response surface plots in Fig. 2b and c shows that FAME yield tends to have a maximum level for

14**interaction effects** between **temperature** and **methanol to** lipid mass **ratio and**

pressure and methanol to lipid mass ratio. Maximum FAME

17**production was** noticed **in the middle levels of both factors while further increase in the** factor **levels resulted in a gradual decrease in yield.**

A consistent result was verified on the main effect plot of methanol to lipid mass ratio in Fig. 3. It can be seen the contribution of each parameter investigated has signifi- cant effect on FAME yield in the order of temperature > pressure > methanol to lipid mass ratio. After constructing variable design, the optimal levels of process variables were determined. The

17**optimal levels of process variables for**

28**in-situ transesterification of wet sludge under subcritical** water and methanol **conditions**

are temperature of 215 C, pressure of 6.5 MPa and methanol to lipid mass ratio of 5.12:1. The predicted FAME yield under this condition was 90.37% with a model desirability of 0.97. To further assess the reliability of prediction, three replicate experiments were performed under the condition predicted by the model. Re- sults show that FAME yield of 91.63 ± 1.72% was obtained; giving an error of at most 3.3% and evidencing that the model prediction is highly reliable. Fig. 2 e 3D response surface plots of FAME yield, showing interaction between pressure and temperature (a), pressure and

24**methanol to** lipid **mass ratio** (b) **and temperature** and **methanol to** lipid **mass ratio**

(c). 3.3. Effect of methanol to lipid mass ratio on FAME yields Methanol is the most widely used alcoholic reactant

26**in the production of** methyl **esters from oils or fats.**

Stoichiometri- cally, three moles of methanol are required to produce

20**three moles of methyl esters and one mole** of **glycerol.** Since **transesterification is a reversible reaction, excess** amounts **of methanol** are **required to shift the reaction to the right-hand side.**

Excess methanol to lipid molar ratio, to a certain extent, seems favor the equilibrium position moving to the right-hand side. However, the addition of highly excess methanol has a tendency to give negative effects on FAME yields. According to the results obtained, the addition of methanol greater than five times the mass of wet sludge lowers biodiesel yield. A reasonable explanation is that a further increase in methanol amount

(9:1), aside from shifting the equilibrium to the right-hand side, would promote the extraction of more polar compounds in the sludge, such as phenols, pigments, carbohydrates and proteins [18], which retards the formation of fatty esters. Excess methanol in the reaction mixture would also interfere with glycerol separation due to increased solubility. Encinar et al. [27] showed

19**there is a slight recombination of** fatty **esters and glycerol to** mono-glycerides because **their concentration keeps increasing** dur- ing **the course of reaction**

when an excess alcohol is present. From the equilibrium point of view, excess glycerol concen- tration could

19**drive the equilibrium back to the left, lowering** FAME yields. **In**

addition, increasing methanol amount above the optimal value not only decreases yield but also raises cost for excess reactant recovery.

1**3.4. Effect of reaction temperature** on FAME yields **Reaction temperature is**

the major factor influencing neutral lipids extraction from the sludge and transesterification pro- cesses. In the extraction of neutral lipids, temperature changes under isobaric condition vary the polarity and thus solvation properties of water. With increasing temperature, the dielectric constant of water drastically decreased due to weakening of hydrogen bonding between water molecules, allowing greater miscibility between lipids and water [28]. This property of water also makes separation between lipid and water very easy when temperature is reduced to room temperature. The presence of water in the reaction system also initiates hydrolysis of triglycerides to form free fatty acids due to triglyceridesewater reactive system. As the hydrolysis proceeds, more free fatty acids are formed which increases the solubility of water in the oil-rich phase and thus the re- action rate. The resulting free fatty acids are esterified by methanol to form methyl esters and glycerol, increasing the product

70**yield. The effect of** reaction **temperature on** FAME **yield is** depicted **in Fig.**

4. The results show that increasing reaction temperature causes an increase in FAME yield. At room tem- perature,

34**methanol and oil do not mix well and poor** methanol and **oil** miscibility **means the reaction rate is** very **slow.**

From a kinetic viewpoint, an increase in FAME yield was attributed to enhanced reaction rate at higher temperatures as a result of increased solubility of methanol in the oil-rich phase and higher energy state of the molecules to undergo useful colli- sions. Also,

48**the time** for **the mass transfer-controlled region is shortened as temperature is increased**

[29]. The percent of FAME yields ranged between 34.02% and 92.67% at tempera- tures of 155e215 C. It is well-known that transesterification between triglycerides and methanol is a reversible and high activation energy reaction. Thus, increasing temperature would favor transesterification of triglycerides to diglycerides, diglycerides to monoglycerides and monoglycerides to methyl esters [29]. In addition, the formation of H3Oþ and OH ionic products from dissociation of water molecules increased with increasing temperature and these ionic products could act either as acid or base catalysts to promote hydrolysis and methanolysis reactions. Below the critical point of mixture, both H3Oþ and OH ionic products promote transesterification reaction under the same catalytic mechanisms using Bronsted acids and alkali catalysts [30].

59**The increase in temperature** also **causes the polarity of methanol to decrease**

by the same phenomenon of that water and it leads to increasing amount Fig. 3 e Main effect plots of reaction parameters investigated and the response at optimal levels (D e composite desirability; y e predicted response; d e desirability). of fatty acids that are soluble in the methanol phase. As the system continues to rise in temperature, the initial two-phase oil and methanol mixtures become more homogeneous (single phase) thus facilitates the conversion of triglycerides to fatty esters. 3.5. Effect of reaction pressure on FAME yields Since transesterification and esterification reactions occur in the liquid phase, the pressure inside the reaction vessel should be sufficient to keep methanol and water both in the liquid state at all temperatures. The applied pressures of the in-situ transesterification process under subcritical water and methanol conditions are 5.5, 6.0 and 6.5 MPa. Generally speaking, pressure has only minor effects on the solvent strength of liquid water and methanol. By increasing pressure, the yields of FAME slightly increased as shown in Fig. 4. In the wastewater sludge, the lipids are attached to protein, mineral or carbohydrate structures [18]. When pressure and temper- ature of the system are increased to subcritical condition, water could enter more easily into the solid matrices where the lipids are trapped in the complex-bonded structures.

41**Chen et al.** [31] **had** also reported **similar** results **in their**

recent paper for extraction of lipids from wet Nannochloropsis sp. micro- algae paste. The ability of subcritical water to extract lipids was due to that the solubility parameter of water becomes closer to the solubility parameter of lipids at elevated pressure and temperature. Also, subcritical water provides enhanced mass-transfer properties of solutes compared to liquid water at room temperature and pressure [15]. In the vicinity of critical point of methanol at 239 C (TC) and 8.09 MPa (PC), methanol is highly compressible and the density is a strong function of pressure. The solubility of methanol in the oil-rich phase becomes higher at elevated pressure under critical temperature while only minor amount of oil present in the vapor methanol-rich phase. According to vaporeliquid phase equilibria data reported by Glisic et al. [32], the mole fraction of methanol in the liquid phase at 503 K and 3.0 MPa was 0.82 and this value increases to 0.98 when pres- sure is increased to 5.6 MPa. Meanwhile, the mole fraction of methanol in the vapor phase remains constant at values close to one, indicating pure methanol

30**in the vapor phase** [32]. **The** higher solubility **of** methanol **in the** oil-rich **phase**

with increasing pressure could overcome the interphase mass- transfer resistance arising from dissimilarity in size and po- larity between lipids and methanol. Thus, this phenomenon can enhance reaction rate of transesterification. The presence of vapor phase in the reaction mixture also contributes on the enhanced chemical kinetics at pressures and temperatures correspond to lower densities of subcritical methanol [32,33]. The highest FAME yield (92.67 ± 3.23%)

24**was obtained at a methanol to** lipid **mass ratio of** 5 **:1**

and under condition in the vicinity of critical point of methanol (6.5 MPa and 215 C). 3.6.

67**Fuel properties of biodiesel The fuel properties of biodiesel are**

varied quite widely, depending upon the quantity and types of fatty acids in the lipid sources and also the refining method. In this regard, the quality of biodiesel produced from wastewater sludge was judged according to ASTM D6751 specification and the results are given in Table 6.

21**Several parameters directly depend upon the fatty** ester **composition**

21**are cetane number,** oxidative stability, **kinematic viscosity and cold-flow properties in form of** the **cloud point,** pour point and **cold filter plugging point**

(CFPP) [34]. Density is one of the properties of biodiesel that Fig. 4 e Variation of FAME yields with reaction temperatures at different mass ratios of methanol to lipid (1:1, 5:1 and 9:1) and pressures (5.5, 6.0 and 6.5 MPa). can be used to indicate contamination by unwanted compo- nents such as residual alcohol, water and sediment (refers to any substance that is higher in density than biodiesel, such as unreacted monoglycerides and diglycerides). The presence of these contaminants, particularly water could make the fuel becomes rancid, corrode metal parts in fuel lines, accelerate fuel gelling in cold weather and reduce the heat and power of combustion. The density of biodiesel produced in this study is about 885 kg m 3. Although the density requirement is not specified in ASTM D6751, the value satisfies EN 14214 stan- dard. Kinematic viscosity is associated with the injection and atomization of the fuel

47**in the combustion chamber of the engine** and **is** also known **to** impact **the engine** life **and the** rate of injector fouling. The sludge-based biodiesel has kinematic viscosity of 2.91e3.17 mm2 s 1, which is an acceptable vis- cosity range based on ASTM D6751 standard specification.

50**The flash point of biodiesel** samples **is**

generally over 150 C,

50**which is** much **higher than ASTM specification**

re- quires. High flash point of biodiesel confirms that this fuel is safer to handle than regular diesel fuel in high temperature environment. Cetane number indicates how well a fuel will combust inside a compression engine and is an important quality parameter for engine performance. Knothe [34] re- ported that cetane number of biodiesel depends upon the nature of fatty esters comprising the fuel and this combustion-related parameter increases with an increasing fatty acid carbon chain and increasing saturation of compo- nents. The cetane number of biodiesel samples in this study exceeds the minimum standard value specified in ASTM D6751, characterizing good ignition and combustion quality. Moreover, high cetane number minimizes soot (carbon) par- ticles and white smoke emissions from the engine during cold start operation. The cetane number obtained in this study agreed well with those of vegetable oils-based biodiesel such as peanut

38**oil methyl ester** [35], sunflower **oil methyl ester** [6], soybean **oil methyl ester** [3], cottonseed **oil methyl ester** [6] and rapeseed **oil methyl ester**

[6]. This result may be ascribed to similar distribution of fatty acids in the feedstock from which biodiesel fuel was made. Acid value is a crucial property for biodiesel quality check due to its relevancy with oxidative stability of the fuel during long-term storage. This parameter is commonly used to indicate free fatty acid content of finished biodiesel. During long-term storage, biodiesel can absorb water which can lead to the formation of free fatty acids from hydrolysis of tri- glycerides. Biodiesel with an acid value as KOH higher than 500 mg kg 1 has a greater tendency to corrode fuel tank, lin- ings and pipelines. The vegetable oil sludge methyl esters have acid values as KOH in the acceptable range of 280e410 mg kg 1. The cloud point is a measure of low- temperature operability of the fuel and is well-correlated with filter plugging point. This cold-flow property depends mostly on the fatty acid composition and also the type and quantity of impurities in the fuel. Biodiesel made from satu- rated fatty acid chains has a higher cloud point compared to biodiesel made from mono- or poly-unsaturated fatty acid chains. From Table 6, it can be seen that vegetable oil sludge methyl esters which mainly comprised of methyl palmitate (29.8%), methyl palmitoleate (23.4%) and methyl oleate (15.4%) have a moderate cloud point about 8 C. The pour point, a

49**temperature at which the fuel contains many agglomerated crystals** and **will no longer flow**

was about 7 C. The cloud point and pour point of biodiesel can be further lowered by a winterization technique [36], using a branched-chain alcohol Table 6 e

46**Fuel properties of biodiesel produced from** vegetable **oil**

wastewater sludge. (D e density; KV e kinematic viscosity; FP e flash point; PP e pour point; CP e cloud point; CN e cetane number; AN e acid number). Samplea D @ 15 C (kg m 3) KV @ 40 C (mm2 s 1) FP (C) PP CP (C) (C) CN AN as KOH (mg kg 1) 155/1/5.5 885.7 2.97 163 7.2 8.2 52.8 342.5 185/1/5.5 886.4 2.96 155 7.1 8.0 51.7 378.3 215/1/5.5 886.2 3.04 158 6.8 7.6 52.7 322.6 155/5/5.5 886.2 3.08 161 6.9 7.8 52.6 335.2 185/5/5.5 885.9 3.02 157 7.1 7.9 51.7 364.1 215/5/5.5 885.9 3.06 156 7.0 8.1 51.1 391.2 155/9/5.5 884.9 2.94 165 6.8 8.0 54.0 285.4 185/9/5.5 885.0 2.92 162 7.2 7.8 53.7 314.8 215/9/5.5 884.9 2.91 165 7.1 8.0 53.5 348.6 155/1/6.0 885.9 2.98 160 6.9 7.7 52.4 363.0 185/1/6.0 886.4 2.97 155 7.0 7.9 51.6 412.7 215/1/6.0 886.1 3.02 157 6.8 8.2 52.5 357.8 155/5/6.0 885.8 3.07 159 6.7 8.1 53.0 310.6 185/5/6.0 885.7 3.02 157 7.2 7.9 51.9 282.5 215/5/6.0 885.9 3.07 154 6.9 7.8 51.0 347.2 155/9/6.0 884.9 2.97 170 6.6 7.6 53.9 354.4 185/9/6.0 885.1 2.99 165 7.0 8.1 53.4 339.1 215/9/6.0 884.8 2.93 162 7.1 8.0 53.5 307.3 155/1/6.5 885.9 2.98 158 6.9 7.7 52.4 344.9 185/1/6.5 886.5 3.03 157 6.6 7.6 51.8 305.8 215/1/6.5 886.1 3.02 160 6.8 7.9 52.5 338.5 155/5/6.5 886.3 3.17 163 6.7 7.5 53.1 319.8 185/5/6.5 885.7 3.02 160 7.1 7.7 51.9 340.2 215/5/6.5 885.9 3.10 156 6.9 7.6 51.0 371.3 155/9/6.5 885.1 2.95 165 6.9 8.1 53.9 356.6 185/9/6.5 885.2 3.00 168 7.2 8.3 53.7 323.5 215/9/6.5 884.9 2.96 172 7.0 8.0 53.8 388.1 ASTM D6751 na 1.9e6.0 min 93 report report >47 max 500 a Biodiesel samples codes: T (C)/methanol to lipid mass ratio/P (MPa). instead of methanol during transesterification [37], adding polymeric cold-flow improvers [38] or blending with other methyl esters having a lower cloud point or No.1/No.2 diesel fuels [39]. The first and

second authors also acknowledge partial support provided by the Directorate of Higher Education (DIKTI) through Student Creativity Research Program 2013. 4. Conclusions This study demonstrated the

5**synthesis of biodiesel from** low grade **vegetable** oil **wastewater sludge**

with lipid mass fraction of 12.44 ± 0.87% (dry and ash-free basis) by a catalyst-free transesterification method. Effects of temperature and pres- sure show that increasing these parameters contributed positively on FAME yields. The highest FAME yield of 92.67 ± 3.23% was obtained

15**at 215** C, **6.5 MPa** and **methanol to lipid** mass **ratio of 5:1.** The optimum **reaction** condition for **in- situ** subcritical methanol **transesterification of**

sludge to fatty esters was 215 C, 6.5 MPa and 5.12:1 of methanol to lipid mass ratio with a predicted FAME yield of 90.37%. The predicted FAME yield was in good agreement with experimental results under the optimum reaction condition. Acknowledgments The authors wish to acknowledge the support from Indonesia Toray Science Foundation through ITSF 2012 Research Grant. references [1] Haas MJ, Foglia TA. Alternate feed stocks and technologies for biodiesel production. In: Knothe G, Krahl J, Gerpen JV, editors. Biodiesel handbook. Urbana, IL: AOCS Press; 2005. pp. 54e61. [2] Bo X, Guomin X, Lingfeng C, Ruiping W, Lijing G. Transesterification of palm oil with methanol to biodiesel over a KF/Al2O3 heterogeneous base catalyst. Energy Fuels 2007;21(6):3109e12. [3] Tao G, Hua Z, Gao Z, Chen Y, Wang L, He Q, et al. Synthesis and catalytic activity of mesostructured KF/CaxAl2O(xþ3) for the transesterification reaction to produce biodiesel. RSC Adv 2012;2(32):12337e45. [4] Mata TM, Sousa IRBG, Vieira SS, Caetano NS. Biodiesel production from corn oil via enzymatic catalysis with ethanol. Energy Fuels 2012;26(5):3034e41. [5] Hajek M, Skopal F, Capek L, Cernoch M, Kutalek P. Ethanolysis of rapeseed oil by KOH as homogeneous and heterogeneous catalyst supported on alumina and CaO. Energy 2012;48(1):392e7. [6] Rakopoulos CD, Antonopoulos KA, Rakopoulos DC, Hountalas DT, Giakoumis EG. Comparative performance and emissions study of a direct injection diesel engine using blends of diesel fuel with vegetable oils or bio-diesels or various origins. Energy Convers Manag 2006;47(18e19):3272e87. [7] Saydut A, Duz MZ, Kaya C, Kafadar AB, Hamamci C. Transesterified sesame (Sesamum indicum L.) seed oil as a biodiesel fuel. Bioresour Technol 2008;99(14):6656e60. [8] Sinha S, Agarwal AK, Garg S. Biodiesel development from rice bran oil: transesterification process optimization and fuel characterization. Energy Convers Manag 2008;49(5):1248e57. [9] Bhatti HN, Hanif MA, Qasim M, Ata-ur-Rehman. Biodiesel production from waste tallow. Fuel 2008;87(13e14):2961e6. [10] Shi W, Li J, He B, Yan F, Cui Z, Wu K, et al. Biodiesel production from waste chicken fat with low free fatty acids by an integrated catalytic process of composite membrane and sodium methoxide. Bioresour Technol 2013 July;139:316e22. [11] Fadhil AB, Dheyab MM, Saleh LA. Conversion of fish oil into biodiesel fuels via acid-base catalyzed transesterification. Energy Sources Part A 2014;36(14):1571e7. [12] Dias JM, Alvim-Ferraz MCM, Almeida MF. Production of biodiesel from acid waste lard. Bioresour Technol 2009;100(24):6355e61. [13] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: a review. Renew Sustain Energy Rev 2011;15(2):1067e72. [14] Kwon EE, Kim S, Jeon YJ, Yi H. Biodiesel production from sewage sludge: new paradigm for mining energy from municipal hazardous material. Environ Sci Technol 2012;46(18):10222e8. [15] Kronholm J, Hartonen K, Riekkola ML. Analytical extractions with water at elevated temperatures and pressures. Trends Anal Chem 2007;26(5):396e412. [16] Reddy HK, Muppaneni T, Sun Y, Li Y, Ponnusamy S, Patil PD, et al. Subcritical water extraction of lipids from wet algae for biodiesel production. Fuel 2014 October;133:73e81. [17] Huynh LH, Kasim NS, Ju YH. Extraction and analysis of neutral lipids from activated sludge with and without sub-critical water pretreatment. Bioresour Technol 2010;101(22):8891e6. [18] Huynh LH, Nguyen PLT, Ho QP, Ju YH. Catalyst-free fatty acid methyl ester production from wet activated sludge under subcritical water and methanol condition. Bioresour Technol 2012 November;123:112e6. [19] Fedosov SN, Brask J, Xu X. Analysis of biodiesel conversion using thin layer chromatography and nonlinear calibration curves. J Chromatogr A 2011;1218(19):2785e92. [20] Olkiewicz M, Fortuny A, Stuber F, Fabregat A, Font J, Ch Bengoa. Evaluation of different sludges from WWTP as a potential source for biodiesel production. Procedia Eng 2012;42:634e43. [21] Mondala A, Liang K, Toghiani H, Hernandez R, French T. Biodiesel production by in situ transesterification of municipal primary and secondary sludges. Bioresour Technol 2009;100(3):1203e10. [22] Upadhyaya KL, Mondala A, Hernandez R, French T, Green M, McFarland L, et al. Biocrude production by activated sludge microbial cultures using pulp and paper wastewaters as fermentation substrate. Environ Technol 2013;34(13e16):2171e8. [23] Loughrin JH, Szogi AA. Free fatty acids and sterols in swine manure. J Environ Sci Health B 2006;41(1):31e42. [24] Saatci Y, Arslan EI, Konar V. Removal of total lipids and fatty acids from sunflower oil factory effluent by UASB reactor. Bioresour Technol 2003;87(3):269e72. [25] Hayyan A, MdZ Alam, Mirghani MES, Kabbashi NA, Hakimi NINM, Siran YM, et al. Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. Fuel Process Technol 2011;92(5):920e4. [26] Myers RH, Montgomery DC, Anderson-Cook CM. Response surface methodology: process and product optimization using designed experiments. 3rd ed. John Wiley & Sons; 2009. [27] Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Biodiesel from used frying oil: variables affecting the yields and characteristics of the biodiesel. Ind Eng Chem Res 2005;44(15):5491e9. [28] Peterson AA, Vogel F, Lachance RP, Froling M, Antal Jr MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy Environ Sci 2008;1(1):32e65. [29] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Chem Oil Soc 1997;74(11):1457e63. [30] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification e a review. Renew Sustain Energy Rev 2006;10(3):248e68. [31] Chen M, Liu T, Chen X, Chen L, Zhang W, Wang J, et al. Subcritical co-solvents extraction of lipid from wet microalgae pastes of Nannochloropsis sp. Eur J Lipid Sci Technol 2012;114(2):205e12. [32] Glisic S, Montoya O, Orlovic A, Skala D. Vapor-liquid equilibria of triglycerides-methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol. J Serb Chem Soc 2007;72(1):13e27. [33] Bulgarevich DS, Otake K, Sako T, Sugeta T, Takebayashi Y, Kamizawa C, et al. Hydrogen bonding in supercritical methanol studied by infrared spectroscopy. J Chem Phys 2002;116(5):1995e2003. [34] Knothe G. “Designer” biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuels 2008;22(2):1358e64. [35] Kaya C, Hamamci C, Baysal A, Akba O, Erdogan S, Saydut A. Methyl ester of peanut (Arachis hypogea L.) seed oil as a potential feedstock for biodiesel production. Renew Energy 2009;34(5):1257e60. [36] Kerschbaum S, Rinke G, Schubert K. Winterization of biodiesel by micro process engineering. Fuel 2008;87(12):2590e7. [37] Giraldo SY, Rios LA, Suarez N. Comparison of glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold flow improvers for palm biodiesel. Fuel 2013 June;108:709e14. [38] Wang J, Cao L, Han S. Effect of polymeric cold flow improvers on flow properties of biodiesel from waste cooking oil. Fuel 2014 January;117(Part A):876e81. [39] Serrano M, Oliveros R, Sanchez M, Moraschini A, Martinez M, Aracil J. Influence of blending vegetable oil methyl esters on biodiesel fuel properties: oxidative stability and cold flow properties. Energy 2014 February;65:109e15. biomass and bioenergy 69 (2014) 28e38 biomass and bioenergy 69 (2014) 28e38 29 30 biomass and bioenergy 69 (2014) 28e38 biomass and bioenergy 69 (2014) 28e38 31 32 biomass and bioenergy 69 (2014) 28e38 biomass and bioenergy 69 (2014) 28e38 33 34 biomass and bioenergy 69 (2014) 28e38 biomass and bioenergy 69 (2014) 28e38 35 36 biomass and bioenergy 69 (2014) 28e38 biomass and bioenergy 69 (2014) 28e38 37 38 biomass and bioenergy 69 (2014) 28e38