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1**Feasibility study of nanocrystalline cellulose as adsorbent of steryl glucosides from palm-based biodiesel**

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, d, Phuong Lan Tran-Nguyen e, Maria Yuliana a, * a Department of Chemical Engineering, Widya Mandala Catholic University Surabaya, Kalijudan 37, Surabaya, 60114, Indonesia b Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Sec 4, Taipei, 10607, Taiwan

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1**National Taiwan University of Science and Technology, 43 Keelung Road, Sec 4, Taipei, 10607, Taiwan** d **Taiwan Building Technology Center, National Taiwan University of Science and Technology, 43 Keelung Road, Sec 4, Taipei, 10607, Taiwan e Department of Mechanical Engineering, Can Tho University, 3-2 Street, Can Tho City, Viet Nam**

article info Article history: Received 16 October 2019 Received in revised form 3 February 2020 Accepted 1 March 2020 Available online 4 March 2020 Keywords: Biodiesel Steryl glucosides removal Nanocrystalline cellulose Adsorption isotherm Adsorption mechanism Feasibility study abstract Increasing the content of biodiesel in the diesel fuel mixture faces some challenges

13**due to the presence of steryl glucosides** (SG) compounds, **which**

causes the filter clogging and the reduction of engine power. In this study, coarse filter paper-based nanocrystalline cellulose (CFP-based NCC) with the crystallinity of 85.73% is selected as a potential adsorbent to separate SG compounds in palm-based biodiesel (PO eB100). The adsorption experiments were carried out at various CFP-based NCC to PO-B100 mass ratio (1:50, 1:75, 1:100, 1:125, 1:150, 1:175, 1:200) and temperature (65, 75, 85 C). The maximum SG removal was 91.81%, obtained at 75 C for CFP-based NCC to PO-B100 mass ratio of 1:50. The adsorption treat- ment also improves the cold stability of PO-B100 by reducing the cloud point from 13.2 C to 11.5 C. Langmuir isotherm model is best-fitted to the equilibrium adsorption data

3**and thermodynamic studies** suggested **that the adsorption of** SG onto **the**

CFP-based NCC

18**surface is spontaneous and endothermic. The**

isotherm and

18**thermodynamic study showed that the** mechanism governing the **adsorption process**

may be driven by both dipole-dipole interactions and ion exchange. The adsorption results showed that CFP-based NCC has great affinity and selectivity to SG and can be considered as a promising adsorbent of SG. © 2020 Elsevier Ltd. All rights reserved. 1. Introduction To date, petroleum diesel is used worldwide for transportation, manufacturing, power generation, construction and farming in- dustries. However, disruption in crude market price and the long- term availability along with the nature deterioration due to its gas emission have become the major concerns for environmental sustainability [1]. Therefore, it is necessary to develop alternative fuels that are environmentally friendly, especially as a substitute for diesel fuel. Of the several alternative fuels available, biodiesel is an alter- native diesel fuel made from renewable biological resources [2]. * Corresponding author. E-mail address: mariayuliana@ukwms.ac.id (M. Yuliana).

71**1 These authors contributed equally to this work**

. https://doi.org/10.1016/j.renene.2020.03.001 0960-1481/© 2020 Elsevier Ltd. All rights reserved. Biodiesel is generally derived from transesterification of agricul- tural or animal lipids and

20**short-chain alcohols in the presence of** a **catalyst**

. Conventional base-catalyzed transesterification in a batch stirred-tank reactor is the most common technique used to produce the commercially available biodiesel [3]. Several modifications on the conversion route as well as the reactor configuration and design have been performed

19**in order to** create, **optimize and intensify the continuous production of biodiesel**

. The transesterification using catalyst-free subcritical [4e6] or supercritical alcohol [7,8], as well as heterogeneous [9] or enzymatic catalyst [9,10], gain wide attention in improving the continuity of biodiesel production. Likozar et al. (2016) also introduced

19**a simple and robust design of** a **tubular** reactor **with** a **static**

mixer to intensify the mass transfer rate between the reactants and increase the biodiesel conversion rate. Their work also studied the chemical equilibrium and reaction kinetics at different operating parameters to optimize the product Abbreviation SG MG DG TG CFP NCC FAME PO-B100 Steryl glucoside(s) Monoacylglyceride(s) Diacylglyceride(s) Triacylglyceride(s) Coarse filter paper Nanocrystalline cellulose Fatty Acid Methyl Ester(s) Palm-based biodiesel yield [11]. While biodiesel is currently mass-produced and a large number of studies have been carried out to improve its performance in various aspects, the white precipitates are still a challenge for its manufacturers. Although biodiesel distributed around the country must conform to the fuel property specifications as controlled by ASTM D6751, white precipitates were often detected in biodiesel and its blends during storage [12]. Several cases even showed that suspended particles in biodiesel have been found shortly after the production and at a rather high temperature (slightly below 60 C) [13]. The white precipitates may cause filter plugging in engine systems [13,14]. This phenomenon was also observed in many biodiesel plants and hence frequent maintenance and process modification are often essential to maintain plant effectiveness and efficiency.

13**The presence of steryl glucosides** (SG), **which**

is one of the plant sterols, has

13**been identified as the major component of**

the white precipitates. It mostly presents in biodiesel with a concentration of 35 ppm or higher [15]. The existence of this dispersed particles of SG promotes the aggregation of other components in biodiesel, saturated monoacylglycerides (MG) and diacylglycerides (DG), and subsequently affects the cold flow stability of fuel and widespread use [16]. Several techniques have been conducted to minimize the SG content in the biodiesel product, namely enzymatic hydrolysis [17,18], adsorption using magnesium silicate and bleaching earth [16] and ultrafiltration [19]. SG removal by enzymatic hydrolysis resulted in 81% removal efficiency with the addition of

13**a synthetic codon-optimized version of the** LacS **gene**

expressed from E. coli with the total operating time of 7 h [17]. Na-Ranong et al. (2015) reported that the conventional adsorption using magnesium sili- cate and bleaching earth in temperature of 65e80 C yielded in 81.4e82.5% removal efficiency of SG [16]. Tremblay and Montpetit (2017) stated that the highest separation for SG (86%) by ultrafil- tration was obtained when the biodiesel was transesterified using 0.7% (w/w) catalyst and 4:1 methanol:soybean oil molar ratio [19]. Based on the removal efficiency and economic feasibility, the adsorption treatment is a potential method to reduce SG content as well as to improve the cold flow properties of the fuel in the in- dustrial scale because it is found to be effective and facile, time-saving and energy-efficient. The development of adsorbent for effective adsorption has been conducted using various types of materials. Currently, the devel- opment of cellulosic adsorbent received major interest because it

11**is renewable, biodegradable**, low cost, **and non-toxic**

[20].

11**Cellulosic adsorbents have the** ability **to meet the requirement** of **being**

a biosorbent, as it is abundantly available as a natural biopolymer. Cellulose in the form of nanocrystalline cellulose (NCC)

11**has been** widely **studied due to its** extensive **industrial application**, namely **enzyme immobilization, adsorption, catalysis, drug delivery**, bio- sensors **and bio-imaging**

[21]. NCC, with a large

11**specific surface area and** plenty **of surface**

hydroxyl and anionic sulfate ester group for physical and chemical reactions [22e24],

18**can be considered as a** new **promising adsorbent for** SG **removal**

. As the Indonesian government plans to increase the

7**use of biodiesel in diesel blend from B20 to B30**

in the time span of 5 years, the use of NCC for SG removal and improvement of the cold stability

1**is an interesting topic to be studied. The** objective **of this study is to observe the** feasibility **of**

coarse filter paper-based NCC (CFP-based NCC) as the adsorption agent for SG. Various operating parameters, namely temperature, and the mass ratio of CFP-based NCC to palm- based biodiesel (POeB100) will be monitored. The adsorption mechanism was also proposed based on the isotherm and ther- modynamics study.

1**2. Materials and methods 2.1. Materials** PO-B100 **was collected from a local** palm oil manufacturer **in Gresik, Indonesia, and**

stored for 3 days at room temperature prior to the adsorption experiment. Coarse filter paper (CFP) as the cellulosic material

6**was obtained from a local supplier in** Surabaya, **Indonesia**

. Sulphuric acid, sodium hydroxide, ethyl acetate, and

5**n- hexane were purchased from Merck, Germany. FAMEs standard 47885 U contains 37 components FAME mix**

and SG standard 1117 were

7**procured from Supelco (Bellefonte, PA, USA**

) and Matreya (State College,

5**PA, USA**), respectively. **Nitrogen gas (99.9% purity) was purchased from Aneka Gas Industry Pty. Ltd., Surabaya. All reagents were of analytical grade and** required **no further purification**

. 2.2. Preparation of NCC CFP was ground into fibrous powder before use. The non- cellulosic material of CFP was subsequently removed to obtain purified cellulose using the modified method of Putro et al. (2017) [25]: 12 g of the CFP powder was delignified using 0.1 g/ml sodium hydroxide aqueous solution (40 ml). The delignified product was washed with distilled water and filtrated three times through a Whatman 1 (11 mm pore size) filter paper before being dried under vacuum at 80 C for 12 h. CFP-based NCC was prepared by using acid hydrolysis following the procedure conducted by Putro et al. (2017) [25]. 1 g of delignified cellulose was hydrolyzed with 20 ml sulphuric acid 64% at 45 C for 75 min under constant agitation. The reaction time was selected to ensure high reaction efficiency. After the specified duration, the reaction was immediately quenched using 20-fold of cold distilled water. The suspension

3**was centrifuged at 4500 rpm for** 10 **min to** remove **the** excess acid solution. **The**

resulting pre- cipitates were dialyzed against distilled water until neutral pH was achieved. The colloidal suspension was subjected to sonication treatment for 30 min in a cooling bath to avoid overheating and subsequently subjected to vacuum drying at 80 C for 6 h to obtain CFP-based NCC powder. 2.3.

1**Characterization of** CFP-**based** NCC **The surface morphologies of**

the CFP-based NCC particles were analyzed on a field emission scanning electron microscope (

1**FESEM) JEOL JSM**-6500F (**Jeol Ltd., Japan), with an accelerating voltage of** 5e10 **kV and**

9.5e9.6 mm working distance. The CFP-based NCC powder was attached to a stub, sputtered and coated with gold prior to analysis. Fourier Transform Infrared (FTIR) analysis was performed by an FTIR-8400S spectrophotometer (Shimadzu, Japan) in the range of 400e4000 cm?1 at a 4 cm?1 scanning resolution. L. Widdyaningsih et al. / Renewable Energy 154 (2020) 99e106 101 XRD analysis was conducted by

1**an X’PERT Panalytical Pro X-Ray diffractometer (Philips-FEI, Netherlands) with monochromatic Cu Ka1 radiation at wavelength** (l) ¼ **0.154 nm, 40 kV of voltage and 30 mA of tube current. The**

diffraction pattern was acquired in the range of 5 e60 (2q angle). The

12**crystallinity index (CrI) was** expressed **according to the following equation**

, as proposed by Segal et al. (1959) [26]. CrI ð%Þ ¼ ðI200 ? IamÞ x100 (1) I200

12**Where I200 is the maximum intensity of the 200 lattice diffraction at** 2q around **22 , Iam is the** maximum **intensity of** the **amorphous** region **at** 2q ¼ **18**

. The crystallite size (nm) was calculated using the Scherrer analysis. 2.4. Compositional study of SG in PO-B100 using GC-FID analysis The analysis of SG composition in PO-B100

1**was carried out using GC**-17A (**Shimadzu, Japan), completely equipped with a split/splitless injector and a flame ionization detector (FID). The separation was performed using** nonpolar capillary column **DB**

- 5HT (5 %-phenyl)-methylpolysiloxane (15 m 0.32 mm ID, Agi- lent

1**Technology, CA). The column temperature was initially set**

at 80 C, then subsequently ramped to 365 C at the rate of 15 C/ min, and held constant for 19

1**min. The temperature of the injector and detector were adjusted constant at** 370 **C**

4**100 mg of** SG **was dissolved in** 1 **ml**

ethyl acetate

1**and subjected to filtration using polyvinylidene difluoride (PVDF) filter prior analysis. The prepared sample (1** ml) **was injected into the GC with a split ratio of 1:50. The velocity of nitrogen (N2, 99.9%) as the carrier gas was fixed at 30 cm/s at 80 C**

. 2.5. Removal of SG using adsorption The adsorption of SG from PO-B100 was conducted in a batch mode according to the study conducted by Na-Ranong et al. (2015) with a few modifications [16]. A various mass ratio of CFP-based NCC to PO-B100 (1:50, 1:75, 1:100, 1:125, 1:150, 1:175, 1:200) was introduced into a series of beakers, where the mixture will be

3**subjected to a** 1-h **adsorption process at constant temperature and** agitation speed (250 **rpm). The** selection **of adsorption** duration **was based on the** preliminary experiment conducted to find the equi- librium time. Several adsorption temperatures (65, 75 and 85

3**C) were** used **to study the** effect **of temperature on the** adsorption **of**

SG. The solution was separated from the adsorbent by using centrifugation at the rotational speed of 4900 rpm for 10 min. The SG contents in PO-B100 before and after adsorption were analyzed using UV-mini 1240 spectrophotometer (Shimadzu, Japan) at 240 nm, according to the modified technique conducted by Moreau et al. (2008), Nystro€m (2007) and Araújo et al. (2013) [14,27,28]. The

24**percentage of** SG **removal was** determined **by using the following equation**

. SG removal ð%Þ ¼ Ci ? Cf x100 (2) Ci Where Ci is the concentration of SG in untreated PO-B100 (mg/kg) and Cf is

2**the concentration of SG in** treated (after adsorption) **PO- B100**

(mg/kg). The results of SG removal were verified by using GC-FID analysis (see section 2.4) and its statistical approach was performed using Minitab software (version 18.1) to identify the significance order of the parameters affecting the adsorption. 2.6. Isotherm and thermodynamics study of the SG adsorption The adsorption isotherm was conducted at the temperature of 65, 75 and 85 C with various CFP-based NCC to PO-B100 mass ratio (1:50, 1:75, 1:100, 1:125, 1:150, 1:175, 1:200). It was performed using a similar procedure as previously mentioned in subsection 2.5. At the equilibrium condition, the amount of adsorbed SG per unit mass of CFP-based NCC as the adsorbent (Qe) was calculated by the equation below. mg Qe g ¼ Co ? Ce x V m (3) Where Co

9**and Ce** are **the initial and** final (**equilibrium**) concentra- tion **of** SG **in** PO-B100 (**mg/L), respectively, m** is **the mass of adsorbent (g) and V** is **the volume of** PO-B100 (L). **The**

equilibrium data obtained at various temperature

6**were fitted to** the three **isotherm models**, namely **Langmuir, Freundlich and Dubinin**-Radushkevich (**D-R**). Meanwhile, **the**

thermodynamic

16**parameters such as** Gibbs **free energy change (DG), enthalpy (DH) and entropy (DS) were** further **determined**

from the results of isotherm study using equations (4) and (5). D G ¼ ? RTln KL:MSG:103:Co (4) DG ¼DH ? TDS (5) Where

15**R is the gas constant** with the value **of 8.314 J**/mol.**K, T is the** absolute **temperature** in Kelvin, **KL is Langmuir**

equilibrium con- stant in L/mg, MSG is the molecular weight of SG in g/mol and Co is the reference concentration in standard state with the value of 1 mol/L.

1**3. Results and discussions 3.1. Characterization of** CFP-**based** NCC **The**

27**X-ray diffraction** pattern **of the** CFP **and** its NCC **are shown**

in Fig. 1, and the corresponding crystallinity index is presented in Table 1. Both XRD patterns showed the cellulose I characteristic peaks at 2q around 15e17 (110 crystal plane) and 22e23 (200 crystal plane) [26,29]. The crystallinity index of CFP and its NCC were calculated using equation (1) and recorded to have the cor- responding value of 57.60% and 85.73%. The change of crystallinity has occurred

27**because of the** progressive **removal of** amorphous **hemicellulose and lignin**

during acid hydrolysis. The highly crys- talline product is more efficient to improve the mechanical prop- erties of the composite material, particularly as an adsorbent, since crystallinity positively corresponds to the tensile strength of the material [30]. The scanning electron micrograph in Fig. 2 shows the shape and size of the CFP-based NCC. The distribution of NCC products derived from CFP was estimated to have approximately 200e400 nm in length (Fig. 2). The prepared CFP-based NCC has a homogenous needle-shaped with crystallite size in the range of 2e4 nm, ob- tained from the combination of X-ray diffraction data and Scherrer analysis. The homogenous CFP-based NCC particles are likely caused by the swollen of cellulose fibers due to NaOH delignifica- tion pretreatment [25]. Fig. 3 (a) e (b) illustrated the FTIR spectra of CFP-based NCC before and after adsorption. As shown in Fig. 3 (a), several peaks representing certain functional groups in CFP-based NCC were found in the spectra. The broad

14**band in the range of** 3008e3459 **cm?1** represents **the**

OeH stretching vibrations, while Fig. 1. X-ray diffraction patterns of (a) CFP, (b) CFP-based NCC. Table 1 The crystallinity index of CFP and CFP-based NCC. Samples 2-theta ( ) Crystallinity (%) 110 crystal plane 200 crystal plane CFP 15.44 22.63 57.60 CFP-based NCC 16.52 22.60 85.73 Fig. 2. SEM image of the rod-like CFP-based NCC particles.

15**Fig. 3. FTIR** spectrum **of (a**) CFP-based NCC **before adsorption** and (**b**

) CFP-based NCC after adsorption.

14**the peaks in the range of** 2802e2925 **cm?1** correspond **to**

CeH

21**stretching vibrations. The absorption at** 936e1137 **cm?1 is related to the**

functional group of CeOeC, and the peak at 1640 cm?1 in- dicates the

21**presence of abundant hydrophilic hydroxide** group **in the cellulose**

[31]. A peak at 1382 cm?1 represents the CeH asym- metric deformations [32]. Meanwhile, Fig. 3 (b) showed strong peaks in the wavenumbers of around 1019e1376 cm?1 and 2602e3160 cm?1, which represent the CeO moiety, and CH2 and CH3 stretching vibrations. These two specific peaks are known as the fingerprint areas for SG. Another

14**peak at** 1750 **cm?1** corresponds **to the** typical **C]O stretching** band **of the**

methyl ester, while an OeH band around 3110 - 3700 cm?1 indicates the presence of hydroxyl groups in SG and CFP-based NCC [33]. Therefore, based on the FTIR

20**spectra, it can be concluded that** SG is **the major component of the**

adsorbate on the surface of CFP- based NCC, which is consistent with the GC-FID results discussed in section 3.2. 3.2. Properties of PO-B100 The properties of PO-B100 have been analyzed according to the standard method of ASTM for its content of FAME, acid value (AV), MG, DG and triglycerides (TG). As reported in Table 2, the purity of FAME in PO-B100 is 98.7%, while the AV, MG, DG, and TG values are 0.12 mg KOH/g, 0.23%, 0.09%, and 0.06%, respectively. Furthermore,

2**PO-B100 feedstock contained** 194.1 **mg/kg of SG**

with the cloud point of 13.2 C and a clear initial appearance. Based on the GC-FID analysis, the SG profile in PO-B100 consists of 34.79% of campes- teryl glucoside, 23.73% of stigmasteryl glucoside and 41.48% of b- sitosteryl glucoside. The results met the requirements of ASTM D6751 and SNI 7182:2015. However, white precipitates could be found within a few hours after production. After the adsorption using the parameters giving the highest SG removal (1:50, 75 C, 1 h; see section 3.3), the sample of treated PO-B100 was collected for the properties measurement

2**in order to** monitor **the effect of** the **adsorbent**

. According to the results, the

2**treated PO-B100 contained FAME with** a purity **of**

98.8% and AV

2**value of 0.**11 **mg KOH/g**

. The concentration of SG reduced signifi- cantly to 15.9 mg/kg with the composition of 24.81% campesteryl glucoside, 25.07% stigmasteryl glucoside and 50.12% b-sitosteryl glucoside, while the other glycerides components, MG, DG, and TG, were slightly decreased to 0.22%, 0.09%, 0.05%, respectively. The cloud point of the treated PO-B100 was also found to be decreased to 11.5 C. These results indicated that CFP-based NCC has selec- tivity to adsorb SG, particularly campesteryl glucoside and L. Widdyaningsih et al. / Renewable Energy 154 (2020) 99e106 103 Table 2 The properties of untreated and treated PO-B100 (1:50, 75 C, 1 h), and the comparison with ASTM D6751 and SNI 7182:2015. Parameters ASTM D6751 SNI 7182:2015 Untreated PO-B100 Treated PO-B100 (1:50, 75 C, 1 h) FAME (%) AV (mg KOH/g) MG (%) DG (%) TG (%) SG (mg/kg) Cloud point (C) 96.5 96.5 0.50 0.50 0.80 0.80 0.20 e 0.20 e N/Aa N/Aa e 18.0 98.7 0.12 0.23 0.09 0.06 194.1 13.2 98.8 0.11 0.22 0.09 0.05 15.9 11.5 a Not available. stigmasteryl glucoside, as compared to the other minor compo- nents, such as MG, DG, and TG. It also subsequently lowered the cloud point significantly, which is advantageous for storage and transportation purposes [34]. 3.3. Adsorption of SG using CFP-based NCC Fig. 4 summarized the SG removal rate at the various temper- ature and mass ratios of CFP-based NCC to PO-B100. The highest value of the SG removal rate (91.81%) was obtained at the following conditions: 75 C, CFP-based NCC to PO-B100 mass ratio of 1:50, and 1 h adsorption time. Based on the results

2**shown in Fig. 4, the** lowest **removal** rate **of SG**

in every adsorption temperature was seen at 1:200 of CFP-based NCC to PO-B100 mass ratio. It was likely due to insufficient binding and active adsorption sites and the adsorption required more time to reach the equilibrium stage. The

3**removal percentage of** SG **was observed to have amplified**

with the increase of CFP-based NCC to PO-B100 mass ratio from 1:200 to 1:50 at all temperatures in the tested range. Greater amounts of CFP-based NCC provide greater adsorption surface area and active sites in CFP-based NCC, leading to an adequate SG binding area and certainly, a higher percentage of SG removal [35]. It was also monitored that the SG removal rate exponentially increased when the CFP-based NCC to PO-B100 mass ratio was increased from 1:100 to 1:50 in the all adsorption temperature. The phenomenon indi- cated the good dispersion ability of CFP-based NCC in PO-B100, where constant diffusion path length of SG binding to CFP-based NCC surface was found regardless of the amount of adsorbent [36]. As depicted in Fig. 4, temperature also remarkably affected the SG reduction. A temperature elevation from 65 C to 75 C improves the reduction of SG, regardless of CFP-based NCC to PO-B100 mass ratio. Chowdhury et al. (2011) stated that the adsorption enhancement along with the temperature increase may be asso- ciated with the increase of the number of active sites available for adsorption. The diffusion rate of the adsorbate across the external boundary layer also escalates with the rise in temperature, due to lower solution viscosity and enhancement in the mobility and ki- netic energy of the adsorbate [37]. Therefore, the

4**collision between particles intensifies with the temperature** elevation so that **the activation energy of the** adsorption process **is easier to achieve**

. As a result, the amount of the adsorbed SG enhances along with the temperature increase. However, it was also observed that the SG removal rate

2**decreased when the temperature was further** esca- lated **from** 75 C **to** 85 **C**

. More (2018) mentioned that after reaching a certain temperature, excessive particle collision causes the removal of adsorbates from the adsorbent, leading to lower adsorption capacity [38]. Lee et al. (2019) also stated that the NCC surface binding generally weakens along with the temperature enhancement [36]. The fluctuations of the SG uptake observed with the change in temperature suggests that the SG adsorption is governed by both physical attraction and chemical bonding, indi- cating that the sorption of SG by CFP-based NCC is both driven by physical and chemical sorption [37,39]. Fig. 5 presented the

4**Pareto chart of the standardized effect generated** using statistical analysis (**Minitab version 18.1). The**

figure showed that both independent parameters (temperature and the mass ratio of CFP-based NCC to PO-B100) were

4**found to be prominent with the significance order of**

the mass ratio of CFP- based NCC to PO-B100 > temperature. The other quadratic and two-way interaction terms were also found to significantly affect the SG removal rate. 100 80 65°C 75°C 85°C SG removal (%) 60 40 20 0 1:200 1:175 1:150 1:125 1:100 1:75 1:50 Mass ratio of CFP-based NCC to PO-B100 Fig. 5. The Pareto chart of the standardized effect showing the significance order of the Fig. 4. SG removal rate varied with the mass ratio of CFP-based NCC to PO-B100 at two independent variables (temperature and mass ratio of NCC to PO-B100) on the SG three different temperatures. removal, generated by ANOVA. 3.4. Study of adsorption isotherm and thermodynamic parameters In this study, three isotherm equations

8**were fitted to the experimental equilibrium data for** SG **at**

three temperature points (65 C, 75 C and 85 C). The results are presented in Table 3 and the isotherm models are plotted in Fig. 6. The Langmuir isotherm constant, KL and maximum absorption capacity, Qm(L) were calcu- lated from the nonlinear curve fitting between Qe and Ce. The value of Qm(L) was found to be increased from 12.50 mg/g at 65 C to 12.93 mg/g at 75 C before declining to 11.24 mg/g at the highest tested temperature (85 C). The Qm(L) results are quite comparable to the adsorption capacity of magnesium silicate and bleaching earth on the SG (~13 mg/g) [16]. The

6**Langmuir constant (KL**) also increases **along with the temperature, from 0**.11 **L/mg at**

the lowest temperature (65

6**C) to 0**.26 **L/mg at**

the highest temperature point (85 C), indicating that the adsorption of SG to CFP-based NCC is an endothermic

8**process. The** isotherm **data were further analyzed** by **the Freundlich model. The Freundlich** constant KF **and 1**/n were obtained **from the**

non-linear regression analysis. Table 3 showed that the values of 1/ n are all under unity, ranging from 0.03 at 75 C to 0.16 at 65 C. The extent of 1/n represents the favorability degree of adsorption. The value of 1/n less than unity corresponds to favorable sorption. It was also observed that the Freundlich constant greatly escalates along with the temperature, implying that the adsorption was favorable at high temperature and the process is certainly endo- thermic. de Sa et al. (2017) mentioned that 1/n value between 0 and 1 is associated with a chemisorption process [40]. Another isotherm equation, the

9**Dubinin-Radushkevich (D-R) model**, was further applied **to** analyze **the equilibrium data**

, particularly to determine the nature of SG adsorption onto CFP- based NCC surface. The D-R

29**constant (b) gives an idea about the mean** sorption **energy, E, and** their correlation **can be** expressed by **the following**

equation: E ¼ p1ffi2ffiffiffifibffiffi (6) where E represents sorption energy (kJ/mol) and b is the D-R constant (mmol2/J2). The value of sorption energy provides infor- mation to determine the type of adsorption mechanism, as chem- ical ion exchange or physical adsorption. Li et al. (2009) and Zhu et al. (2009) stated that if the sorption energy ranges from 8 to

25**16 kJ/mol, the** sorption **process** is supposed **to** be **chemisorption, while for** energy **value lower than 8 kJ/mol, the** sorption is of **physical**

nature [41,42].

5**Based on the results** provided **in Table 3, the**

adsorption mechanism is physical attraction since the E values for all tested temperatures are lower than 8 kJ/mol. The highest Qm(D-R) was found at 75 C with a value of 12.13 mg/g, which was similar to Table 3 Isotherm parameters of SG adsorption onto CFP-based NCC surface. Isotherm Parameters Temperature (K) 338 348 358 Langmuir Freundlich Dubinin-Radushkevich Qm(L) (

22**mg/g) KL (L/mg) r2** c2 **KF ((mg/g) (L/mg)1/n**) 1/**n r2** c2 **Qm**(D-R) (**mg/g**

) E (kJ/mol) r2 c2 12.50 12.93 0.11 0.16 0.8587 0.8580 0.2329 0.2865 5.59 6.48 0.16 0.03 0.8408 0.7986 0.2624 0.4064 11.58 12.13 0.18 0.25 0.8094 0.8387 0.3147 0.3254 11.24 0.26 0.7039 0.2487 7.31 0.09 0.6079 0.3293 10.86 0.29 0.7555 0.2053 14 12 Qe (mg/g) 10 Langmuir Freundlich Dubinin-Radushkevich (D-R) 8 0 50 100 Ce (mg/L) Fig. 6. The modelled isotherm profiles for the adsorption of SG to CFP-based NCC surface (temperature 75 C, mass ratio of CFP-based NCC to PO-B100 1:50, ¼ ¼ time ¼ 1 h, agitation speed ¼ 250 rpm). the result obtained using Langmuir isotherm. The effect of tem- perature previously studied also provides similar results where the temperature of 75 C gives the highest SG removal rate compared to the other tested temperatures. The

8**correlation coefficient (r2) and chi-square** (c2) **values of the** three **isotherms are also listed**

17**in Table 3. It** could **be concluded that** the **adsorption of** SG **onto**

the CFP-based NCC surface is

17**best fitted to the Langmuir isotherm equation under the temperature range studied**. Based on **the**

three isotherm models studied, the adsorp- tion mechanism is predicted to be driven by both physical and chemical sorption due to its sorption energy value and endo- thermic nature, respectively. The overall results of this study showed that NCC has a particular affinity for SG and is an effective adsorbent for SG removal from PO-B100. Table 4 listed the thermodynamics parameters of the SG adsorption onto the surface of NCC,

16**such as** Gibbs **free energy change (DG), enthalpy (DH) and entropy (DS**

). The values of Gibbs free energy (DG) for the adsorption of SG were negative at all tested temperatures. These values confirm the spontaneous nature of SG adsorption onto the CFP-based NCC. Enhancement of the DG value along with the increasing temperature implies

9**that the affinity of** SG **on** CFP-based NCC **was higher at high** tempera- ture. **Positive** DH **value**

(42.90 kJ/mol) verifies that the adsorption is indeed an endothermic process, while the absolute value of D S (219.80 J/mol.K) reflects the increased randomness at the solid- solution interface during the adsorption process [37,43]. 3.5. Adsorption mechanism study The study of the adsorption mechanism was used to further illustrate the interaction between SG and CFP-based NCC surface. Two important points have to be considered to understand the

24**Table 4 Thermodynamic parameters of adsorption of** SG **onto**

CFP-based NCC surface.

6**Temperature (K) Thermodynamic parameters** DG (**kJ/mol**) DH (**kJ/mol**) DS (**J/mol.K**

) 338 348 358 ?31.44 ?33.46 ?35.84 42.90 219.80 L. Widdyaningsih et al. / Renewable Energy 154 (2020) 99e106 105 mechanism, namely the

3**surface properties of** the **adsorbent** and **the structure of adsorbate. The**

NCC molecule was constructed by a substantial

23**number of hydrogen bonds between glucose units or glucose chains inside the molecule** to **form a very stable structure**

[44,45]. NCC contains the majority of oxygen functional groups such as hydroxyl, ether, and sulfonate. While the hydroxyl and ether groups are originally present in the cellulosic material, the sulfonate group existed due to the acid hydrolysis to produce NCC. On the other hand, SG was built by a steryl cation (SCþ) and a glucose unit, with a positive charge on the cationic steryl part. According to the findings of this study, the adsorption was temperature-dependent and the isotherm modeling showed an equal contribution of physical attraction and chemical binding. Therefore, the mechanism of SG removal by adsorption on the CFP- based NCC surface

26**may be** presumed **to involve** these **following steps: Migration of** SG **from the bulk of** PO-B100 to **the** CFP-based NCC **surface** Diffusion **of** SG through **the**

8**boundary layer to the** CFP-based NCC **surface** Adsorption **of** SG on **the** surface **of**

CFP-based NCC, which may be caused by physical interaction of dipole-dipole coupling be- tween the positively charged SCþ and the negatively charged NCC surface as suggested in Fig. 7; and through a possible chemical binding mechanism of ion exchange as shown below: NCC ? OH4NCC ? O? þ Hþ NCC ? SO?34NCC ? SO?3 NCC ? O? þ SCþ4NCC ? O ? SC NCC ? OH4NCC ? O? þ Hþ Intraparticle diffusion of SG into the pores of CFP-based NCC OH- SO3- OH- SO3- Nanocrystalline cellulose SO3- OH O HO HO OH OH- -O3S -HO dipole-dipole coupling NCC surface sc+ O Fig. 7. Schematic representation of the proposed adsorption mechanism of SG onto CFP-based NCC surface. 4. Conclusions CFP-based NCC was successfully used as an adsorbent for reducing SG in PO-B100. The content of SG was able to be reduced from 194.1

2**mg/kg to as low as** 15.9 **mg/kg**

(91.81% removal rate) within 1 h at the temperature of 75 C using CFP-based NCC to PO- B100 mass ratio of 1:50. The study proved that CFP-based NCC has great affinity and selectivity to SG, particularly on the campesteryl glucoside and stigmasteryl glucoside. The adsorption treatment greatly improves the cold stability of PO-B100 by reducing the cloud point from 13.2 C to 11.5 C, while slightly affected the purity of FAME, AV and other minor components, such as MG, DG, and TG, which were still

2**in the acceptable range according to** ASTM D6751. **The adsorption** process was endothermic and may be driven by both physical attraction and chemical ion exchange. The adsorption treatment using CFP-based NCC

2**should be a** prospective **method used to remove SG from**

PO-B100 since it possesses high efficiency, time-saving and energy-efficient.

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. Albert Setiawan:

7**Conceptualization, Methodology, Investigation, Software, Writing - original draft. Shella Permatasari Santoso: Conceptualization, Data curation, Supervision**. Felycia Edi Soetaredjo: **Resources, Visualization**

. Suryadi Ismadji: Resources, Validation. Sandy Budi Hartono:

1**Software, Validation. Yi-Hsu Ju: Writing - review & editing. Phuong Lan Tran-Nguyen: Writing - review editing**

. &

7**Maria Yuliana: Conceptualization, Resources, Visualization, Writing - review & editing, Supervision**

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