PAPER • OPEN ACCESS

The increase of biodiesel B20 oxidation stability using antioxidant obtained from soursop leaves extraction through microwave assisted extraction technique

To cite this article: Megawati *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **625** 012026

View the article online for updates and enhancements.

The increase of biodiesel B20 oxidation stability using antioxidant obtained from soursop leaves extraction through microwave assisted extraction technique

Megawati[1], W Astuti[1], U M Arief[2], R R Ginting[3] and W Sammadikun[1]

[1] Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Indonesia
[2] Electrical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Indonesia
[3] Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Japan

Email: megawati@mail.unnes.ac.id

Abstract. The purpose of this research is to study the performance of soursop leaves extract as an antioxidant to inhibit biodiesel B20 oxidation. The antioxidant extraction was conducted with ethanol as the solvent (1:13 v/v) using microwave assisted extraction at powers of 300, 450, and 600 W for 2-10 min. In addition, the biodiesel oxidation was performed with air (2.3 L/min) at temperatures of 100, 110, and 120 $^{\circ}$C for 0-70 min. The extraction results show that microwave power and extraction time strongly influence the extraction yield. The highest total phenolic concentrations of soursop leaves extract antioxidant obtained at 600 W and 8 min is about 0.608 mg/mL. From the oxidation results, it can also be seen that temperature and time influence the acid numbers of biodiesel B20. In 10 min, at 100, 110, and 120 $^{\circ}$C, the acid numbers of biodiesel B20 are 0.09, 0.12, and 0.13 g NaOH/g. The mixture acid numbers of biodiesel B20 and soursop leaf extract are 0.126, 0.13, and 0.15 g NaOH/g. The optimization result shows that the activation energy of biodiesel B20 oxidation is 37.7 kJ/mol and the mixture of biodiesel B20 and soursop leaf extract is 41 kJ/mol. Therefore, it can be concluded that antioxidant additional is proven to inhibit the oxidation of biodiesel B20, as much as 47%.

1. Introduction

Soursop (*Annona muricata* L.) is the easiest type of plant to grow among other types of *Annona* in a warm and humid tropical climate [1]. The leaf themselves contain bioactive compounds, tannins, phenols, phytosterols, flavonoids, and saponins [2]. Flavonoids are phenolic compounds that can act as antioxidants, because they have a molecular structure that can transfer electrons to free radical molecules [3]. Conventional extraction methods like maceration and Soxhlation are the most common methods used to extract antioxidants, but they have several disadvantages; they need a large amount of solvents and long process, while the yield obtained is few [4]. A modern method which has been developed is microwave assisted extraction (MAE) [5]. MAE is an extraction method which utilizes microwave as a heating medium. This technology is suitable for extracting thermolabile antioxidants, because it has better temperature control than conventional heating methods. In addition, MAE also has several advantages [6]. This research used MAE to extract soursop leaf antioxidant efficiently and economically. The antioxidant obtained was used to increase the oxidation stability of biodiesel B20.

Indonesia has produced biodiesel B20 (20% v/v biodiesel + 80% v/v diesel fuel) as an alternative fuel for energy conservation. Biodiesel compounds produced from unsaturated fatty acids, especially methyl esters from vegetable and animal oils can cause oxidative degradation in biodiesel [7-9]. If biodiesel is exposed to high temperature, sunlight, metals and air, it will be oxidized to acid and alcohol [10]. The alcohol formed will increase the total acid and reduce the flash point, so it will be a problem on combustion engines, especially in the injection system [11]. During the oxidation process, acid numbers, kinematic viscosity, peroxide numbers, and ester levels in biodiesel deteriorate, so biodiesel oxidation needs to be inhibited [12]. In order to inhibit oxidation reactions, antioxidants need to be added [13].

A study on the performance of natural antioxidants from pepper extract, coffee leaf, bacupari leaf, and sage to inhibit biodiesel B100 oxidation has been conducted. Its performance was studied through an oxidation kinetics approach called pseudo-homogeneous first-order model. The effect of temperature on the oxidation kinetics was approached by the Arrhenius equation [14]. Meanwhile, in this research, the performance of antioxidant obtained from soursop leaf extraction on the oxidation kinetics will be evaluated based on the activation energy. This study aims to investigate the performance of soursop leaf extract as an antioxidant for biodiesel B20 through its oxidation kinetics using pseudo-homogeneous first-order model approach.

2. Materials and methods

2.1 Antioxidant extraction of soursop leaf using microwave assisted extraction

The materials used for this study were soursop leaf obtained from Perumahan Sapta Marga, Semarang. The chemicals used were 70% ethanol and gallic acid, folin ciocalteau reagent, Na_2CO_3, methanol, NaOH, and distilled water. Before being used, the soursop leaves were dried using an oven at 90 ^{o}C for 2 hours, blended using a blender until they became powder, and sifted using a 500 µm sieve. The soursop leaf extraction through MAE method was done by putting in 20 g of soursop leaf powder into a glass extractor and adding 70% ethanol as much as 260 mL. The extractions were conducted at 300, 450, and 600 W for 10 min. In every 2 min, 5 mL of the sample was taken in order to analyze its phenolic concentration. After the extraction was complete, the mixture was vacuum filtered to separate the filtrate and residue. The solvent in the filtrate was recovered by distillation at 78 ^{o}C until the extract volume was 20 mL. The extract obtained was purified again using an oven at a temperature of 100 ^{o}C to obtain pure extract.

The phenolic concentration analysis was conducted using UV-Vis spectrophotometer by adding 0.5 mL samples with 0.5 mL folin ciocalteau reagent (v/v) and 4 mL Na_2CO_3 7.5% (w/v). The solution was left for 60 min. Absorbance was determined at a wavelength of 765 nm. The phenolic concentration of antioxidant extract was calculated based on the absorbance produced using a calibration curve. In each power, total phenolic levels can be calculated from data on antioxidant phenolic concentrations obtained every 2 min and expressed as mg gallic acid equivalent (GAE)/g extract.

2.2 Oxidation of biodiesel B20

Biodiesel was obtained from PT. Pertamina. Before being used, physical and chemical properties of biodiesel B20 and the mixture of biodiesel B20 and soursop leaf extract were analyzed. The density analysis was conducted by Pyrex glass pycnometer (volume of 5 mL) while the kinematic viscosity analysis was done by viscometer (Stanhope-Seta - KV6 Viscometer Bath). In The first step of biodiesel oxidation, biodiesel B20 sample and antioxidant (5% v/v), were put into a flask and then heated and stirred at 600 rpm for 20 min using a speed regulator hotplate. After reaching 100 ^{o}C (being kept constant) air with a speed of 2.5 L/min was injected. Sampling was carried out in every 10 min for seven times. This treatment was repeated for different temperatures (110 and 120 ^{o}C). This oxidation was conducted for both biodiesel B20 and the mixture of biodiesel B20 and antioxidant.

2.3 Kinetic of biodiesel B20 oxidation

Oxidation conversion (*x*) can be calculated using equation (1), with AV_t = acid number when *t* (mg NaOH/g sample) and AV_0 = initial acid number.

$$x = \frac{AV_t - AV_0}{AV_0} \tag{1}$$

The performance of antioxidant was analysed through its oxidation reaction kinetics. Assumptions taken to solve the reaction rate were: 1) The reaction runs in batches with a fixed volume; 2) decrease in oxygen can be ignored because it is injected continuously [14,15]; 3) the kinetics were approached using pseudo-homogeneous first-order model.

3. Results and discussion

3.1 The influences of time and microwave power on antioxidant extraction of soursop leaves using microwave assisted extraction

The influence of extraction times (2-10 min) on phenolic concentration resulted from soursop leaf extraction using MAE can be seen in Table 1. The longer the extraction time, the higher the phenolic concentration will be. However, after reaching a certain time, the phenolic concentration decreases. The longer the extraction time, the more effective the breakdown or degradation of cell walls will be [16]. According to Ghafoor et al., during extraction, the solute will continue to dissolve in the solvent and stop when the solvent is saturated with the solute [17]. In addition, according to Chew et al., the longer the extraction time, the phenolic compounds from *Centella asiatica* extraction can be degraded [18]. It can be concluded that, at 600 W and 10 min, phenolic compounds extracted from soursop leaf have been damaged. In the processes of using microwave as the energy source, the power parameters represent temperatures. Mario et al. stated that some phenolic compounds are sensitive to high temperature changes, so they can be damaged [19]. Meanwhile, in this study, the effect of power can be studied. At 2 min, the higher the power (300, 450, and 600 W), the higher the phenolic concentration (10.01, 12.20, and 17.08 mg/mL, respectively) and at 8 min, the higher power, phenolic concentrations also increased (0.393, 0.443, and 0.603 mg/mL, respectively). It is obvious that antioxidant obtained from extraction is influenced by microwave power. Power shows the amount of heat as the driving force for destroying the pore cells of the leaf powder, so that antioxidants can diffuse out. Therefore, if the power is high, the antioxidants will quickly get out [20].
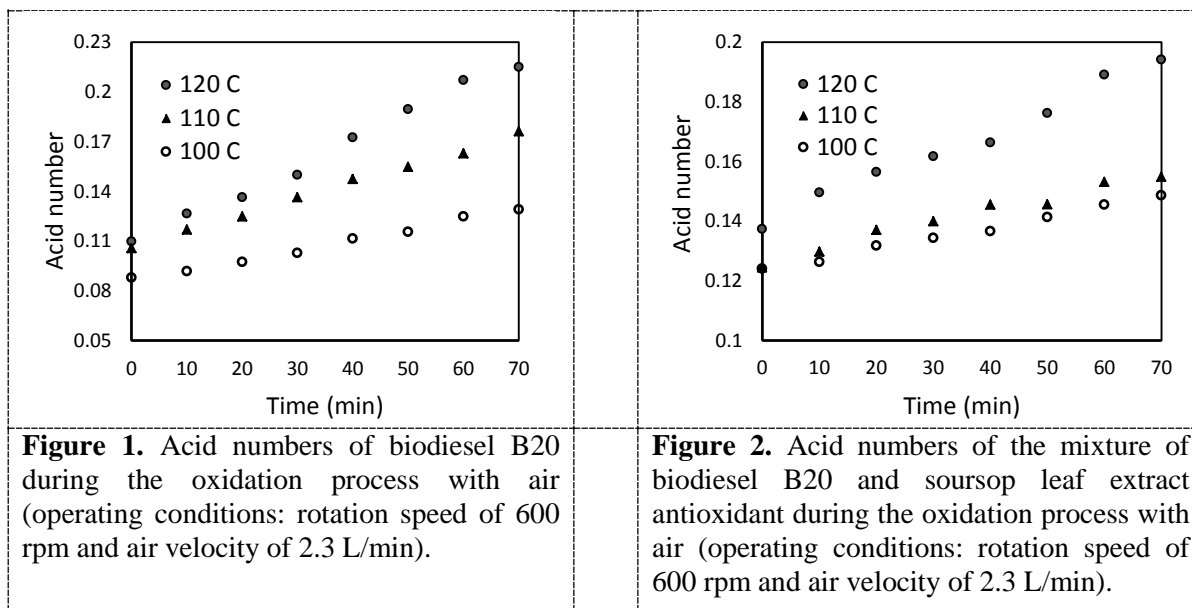
Table 1. Total phenolic concentration as well as phenolic content of soursop leaf extraction using microwave assisted extraction (operating condition: raw material weight of 20 g, raw material size of 500 µm, and 70% ethanol volume as solvent of 260 mL)

Time (min)	Concentration Phenolic (mg/mL)			Total Phenolic Content (mgGAE/g)		
	300 W	450 W	600 W	300 W	450 W	600 W
2	0.250	0.305	0.427	10.006	12.196	17.078
4	0.303	0.358	0.469	12.128	14.312	18.769
6	0.373	0.399	0.600	14.919	15.957	24.011
8	0.393	0.443	0.603	15.702	17.716	24.105
10	0.418	0.507	0.589	16.723	20.298	23.554

3.2 Physical and chemical properties of biodiesel B20 and the mixture of biodiesel B20 and soursop leaf extract antioxidant

The addition of antioxidants increases the density of biodiesel B20, because antioxidants have more density than biodiesel [21]. In this study, the density of biodiesel B20 obtained from PT Pertamina was 824 kg/m³ and the mixture of biodiesel B20 and soursop leaf extract antioxidant was 834 kg/m³.

Meanwhile, the viscosity of biodiesel B20 was 2.92 mm^2/s and the mixture of biodiesel B20 and soursop leaf extract antioxidant was 2.89 mm^2/s. This is in line with a research conducted by Kivevele and Huan in which the addition of antioxidant additives can reduce the viscosity of biodiesel [22]. On top of that, the viscosity of biodiesel will increase due to oxidation reactions [8,23]. Thus, oxidation of biodiesel must indeed be prevented. In this study, biodiesel B20's acid numbers during the oxidation can be seen in Figure 1 and 2. It can be seen that the higher the temperatures, the higher the acid numbers will be. Soursop leaf extract antioxidant can prevent the oxidation of biodiesel B20 by 46.90%. It can also be said that antioxidant obtained from soursop leaf extraction is promising to be applied on a large scale in which biodiesel B20 oxidation kinetics data is needed.

| **Figure 1.** Acid numbers of biodiesel B20 during the oxidation process with air (operating conditions: rotation speed of 600 rpm and air velocity of 2.3 L/min). | **Figure 2.** Acid numbers of the mixture of biodiesel B20 and soursop leaf extract antioxidant during the oxidation process with air (operating conditions: rotation speed of 600 rpm and air velocity of 2.3 L/min). |

Oxidation kinetics are solved using the pseudo-homogeneous first-order reaction kinetics approach. The biodiesel oxidation rate constants (k_{bio}) are greater than those in the mixture of biodiesel and antioxidant (k_{mix}). That means that biodiesel oxidation is faster than the oxidation of the mixture of biodiesel and antioxidant. This shows that antioxidants can inhibit biodiesel oxidation. The comparison values of the oxidation rate constants (k_{mix}/k_{bio}) are as follows: 0.0026:0.0056; 0.0034:0.0076; 0.0051:0.0104, for 100, 110, and 120°C, respectively. The same result was also stated by Xin et al. and Gregorio et al. [14,15]. It is also seen that the reaction rate constant of each temperature follows the Arrhenius theory. From the results of linear regression, the activation energy values obtained were 37 and 41 kJ/mol for biodiesel B20 and the mixture of biodiesel B20 and soursop leaf extract antioxidant. From the increase in activation energy, it can be concluded that antioxidants play an important role in inhibiting oxidation reactions [14].

4. Conclusions

Soursop leaf extraction with 70% ethanol using microwave assisted extraction obtained a maximum yield of 33.98% (with total phenol of 24.10 mgGAE/g extract) at 600 W and 8 min. The extraction kinetics of soursop leaf were approached using the mass transfer from the particle's surface to the bulk of the solution, that can be expressed by second-order rate law. The soursop leaf extract antioxidant could inhibit biodiesel B20 oxidation by 47%. Biodiesel oxidation kinetics are strongly influenced by temperature with activation energy of 37 and 41 kJ/mol for biodiesel and the mixture of biodiesel and the soursop leaf extract antioxidant.

Acknowledgments

References

[1]   Coria-Téllez A V, Montalvo-Gónzalez E, Yahia E M and Obledo-Vázquez E N 2018 *J. Chem.* **11** 662-691

[2]   Baskar R, Rajeswari V and Kumar T S 2007 *J. Indian. Exp. Biol.* **45** 480–485

[3]   Adeyemi D O and Komolafe O A 2009 *J. Afr. Trad.* **6** 62–69

[4]   Megawati, Wulansarie R, Faiz M B, Adi S and Sammadikun W 2018 *AIP Conf. Proc.* **1941** 020016 1-7

[5]   Farida R and Nisa F C 2015 *Jurnal Pangan dan Agroindustri* **2** 362-373

[6]   Megawati and Murniyawati F 2015 *Jurnal Bahan Alam Terbarukan* **4** 14-20

[7]   Domingos A K, Saad E B, Vechiatto W D, Wilhelm H M and Ramos L P 2007 *J. Braz. Chem. Soc.* **18** 416-423

[8]   Knothe G 2007 *Fuel Proc. Technol.* **88** 669–677

[9]   Anis S, Budiandono G N, Saputro D D, Zainul Z A 2018 *Jurnal Bahan Alam Terbarukan* **7** (in progress)

[10]   Chan H W S 2005 *Autoxidation of Unsaturated Lipid*, ed H W S Chan (New York: Academic Press) p 1

[11]   Sarin R, Sharma M, Sinharay S and Malhotra R K 2007 *Fuel* **86** 1365-1371

[12]   Galvan D, Orives J R, Coppo R L, Silva E T, Angilelli K G and Borsato D 2013 *Ener. & Fuel* **27** 6866−6871

[13]   Mittelbach M and Schober S 2003 *J. Am. Oil Chem. Soc.* **80** 817-823

[14]   Gregorio A P H, Borsato D, Moreira I, Silva E T, Romagnoli E S and Spacino K R 2017 *Biofuels* **8** 1-8

[15]   Xin J and Imahara H S 2009 *Fuel* **88** 282–286

[16]   Handayani P A and Juniarti E R 2012 *Jurnal Bahan Alam Terbarukan* **1** 1–7

[17]   Ghafoor K and Yuan H C 2009 *J. Korean Soc. Appl. Biol.* **52** 295-300

[18]   Chew K K, Ng S Y, Thoo Y Y, Khoo M Z,Wan A W M, Ho C W 2011 *Internat. Food Res. J.* **18** 571-578

[19]   Mário R M J, Alice V L, Nathalia R V D 2010 *The Open Chem. Eng. J. Brazil.* **4** 51-60

[20]   Calinescu I, Ciuculescu C, Popescu M, Bajenaru S and Epure G 2001 *Romanian. Internat. Conf. Chem. Chem. Eng.* **12** 1-6

[21]   Fattah I M R, Masjuki H H, Kalam M A, Mofijur M and Abedin M J 2014 *Ener. Convers. Manage.* **79** 265–72

[22]   Kivevele T T and Huan Z 2013 *Ener. Tech.* **1** 537-543

[23]   Fernandes D M, Serqueira D S, Portela F M, Assunção R M N, Munoz R A A and Terrones M G H 2012 *Fuel* **97** 658–661