Chapter 2
Mangosteen Peel Antioxidant Extraction and Its Use to Improve the Stability of Biodiesel B20 Oxidation

Megawati, Rizqy Romadhona Ginting, Ratna Dewi Kusumaningtyas, and Wahyudi Budi Sediawan

Abstract Antioxidants can be extracted from mangosteen peel with ethanol as solvent using microwave assisted extraction (MAE) efficiently and economically. The mangosteen peel antioxidant can be used to inhibit the biodiesel B20 oxidation. The microwave power gives a great factor of antioxidant conversion in mangosteen peel extraction. At 35 min and 300, 450, 600 W, the antioxidant conversions obtained were 15.45, 17.00, 18.33%, respectively. The total phenolic concentration was about 156–202 mg GAE/g. In addition, the extraction kinetic can be quantitatively described by antioxidant diffusivity from inside the solid to the solid's surface and antioxidant mass transfer from the solid's surface into solution with diffusion coefficient (D_e) of 2.81×10^{-11}, 3.42×10^{-11}, 3.8×10^{-11} cm^2/s, mass transfer coefficient (k_c) of 6.36×10^{-8}, 8.97×10^{-8}, 1.05×10^{-7} cm/s for 300, 450, 600 W, respectively, and Henry equilibrium constant (H) of 0.032. In the oxidation, the mangosteen extract antioxidant can improve 26.32% of the oxidative stability of biodiesel B20. Theoretically, the performance of mangosteen peel extract antioxidants in biodiesel B20 oxidation can be evaluated from its oxidation kinetic which can be approached using the pseudo-homogeneous first-order model. The reaction rate constant follows the Arrhenius equation with activation energy (E_a) of 54.34 and 56.27 kJ/mol as well as collision factors (A) of 348,711 1/min, for the oxidation of biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidant, respectively. The activation energy of the mixture of biodiesel B20

Megawati (✉) · R. D. Kusumaningtyas
Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang, Indonesia
e-mail: megawati@mail.unnes.ac.id; ratnadewi.kusumaningtyas@mail.unnes.ac.id

R. R. Ginting
Department of Chemical Engineering, Graduate School of Engineering, Faculty of Engineering, Universitas Gadjah Mada, Hiroshima, Japan

W. B. Sediawan
Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia

Z. A. Zakaria et al. (eds.), *Valorisation of Agro-industrial Residues – Volume II: Non-Biological Approaches*, Applied Environmental Science and Engineering for a Sustainable Future, https://doi.org/10.1007/978-3-030-39208-6_2

and mangosteen peel antioxidant was higher, so that the mixture of biodiesel B20 and antioxidant is more difficult to oxidize.

Keywords Antioxidant · Biodiesel B20 · Mangosteen peel · Microwave assisted extraction · Oxidation

2.1 Introduction

Indonesia is an agricultural country which is rich in various kinds of fruit plants; one of them is mangosteen (*Garcinia mangostana* L.) (BPS 2017). The biggest component of mangosteen lies in the skin, about 70–80%. Accordingly, mangosteen peel waste contains polyphenol compounds with high total phenolic concentration, which can be used as antioxidants (Zarena and Udaya Sankar 2009; Suttirak and Manurakchinakorn 2012; Naczk et al. 2011). Theoretically, antioxidants work by donating one electron to oxidant compounds, so that its oxidation activity can be inhibited (Borsato et al. 2014; Gregorio et al. 2017; Nimse and Pal 2015; Zarena and Udaya Sankar 2011; Walker 2007). Moreover, mangosteen peel extract contains IC_{50} of 44.49 mg/L (<50 mg/L), so the antioxidant activity level is very strong (Wibawanti et al. 2019).

The most commonly used method to extract antioxidants from mangosteen peel is conventional method which still has several disadvantages; it needs a lot of solvents and long extraction process, while the yield obtained is low (Tjahjani et al. 2014). Certainly, to solve this problem, it is mentioned that an underdeveloped method called microwave assisted extraction (MAE) can be used as an alternative (Bagherian et al. 2011; Buanasari et al. 2017; Guo et al. 2012; Megawati et al. 2018). MAE is a nonconventional extraction method that utilizes microwave radiation as a heating medium. This is convenient to extract thermolabile antioxidant compounds, because this method has better temperature control compared to conventional heating methods (Thirugnanasambandham and Sivakumar 2017; Chuyen et al. 2017; Karami et al. 2015).

The most important thing in extraction is the solute mass transfer from solid to solution which can be approached using two main phases; they are solute diffusivity from inside the solid to the solid's surface and solute mass transfer from the solid's surface into solution (Fernando and Soysa 2015). It is important that the data obtained from antioxidant extraction experiment is developed to find out the mass transfer phenomena.

In fact, biodiesel fuel is easily oxidized by oxygen, light, high temperature, and metals (Bouaid et al. 2009; Leung et al. 2006; Kivevele and Huan 2013; Park et al. 2008). Recently, antioxidants added into biodiesel have one function—to capture free radicals formed during oxidation and stop chain reactions in fuel degradations (Spacino et al. 2016). Moreover, natural antioxidants can inhibit biodiesel oxidation (Coppo et al. 2013; Spacino et al. 2015). Mangosteen peel antioxidant extract can inhibit biodiesel oxidation. The performance of mangosteen peel extract as an antioxidant for biodiesel can be investigated through its oxidation kinetics. Pseudo-

homogeneous rate law was used to do the oxidation kinetics. Some researchers have successfully used pseudo-homogeneous first-order model to investigate antioxidant performance in biodiesel oxidation (Gregorio et al. 2017; Xin et al. 2009).

2.2 The Composition of Mangosteen Peel Antioxidant Extract

Mangosteen is one of the plants of the genus *Garcinia* and the Guttiferae family. Mangosteen is an annual fruit plant that grows naturally in tropical forests in the Asian region, such as Indonesia, India, Myanmar, Sri Lanka, and Thailand (Jung et al. 2006). Mangosteen is often called as the "Queen of Fruits" because it contains high antioxidants (Gutierrez-Orozco and Failla 2013). The description of mangosteen can be seen in Fig. 2.1. Mangosteen productivity in Indonesia continues to increase every year. In 2016, the production of mangosteen was 162,864 tons/year (BPS 2017). The biggest component of mangosteen lies in the skin (about 70–80%), so that mangosteen peel waste in Indonesia is about 114,000–130,000 tons/year. Mangosteen skin contains water and high organic compounds (Tjahjani et al. 2014), polyphenol compounds. Mangosteen peel antioxidant extract contains antioxidants (Suttirak and Manurakchinakorn 2012; Naczk et al. 2011). Phenolic compounds in

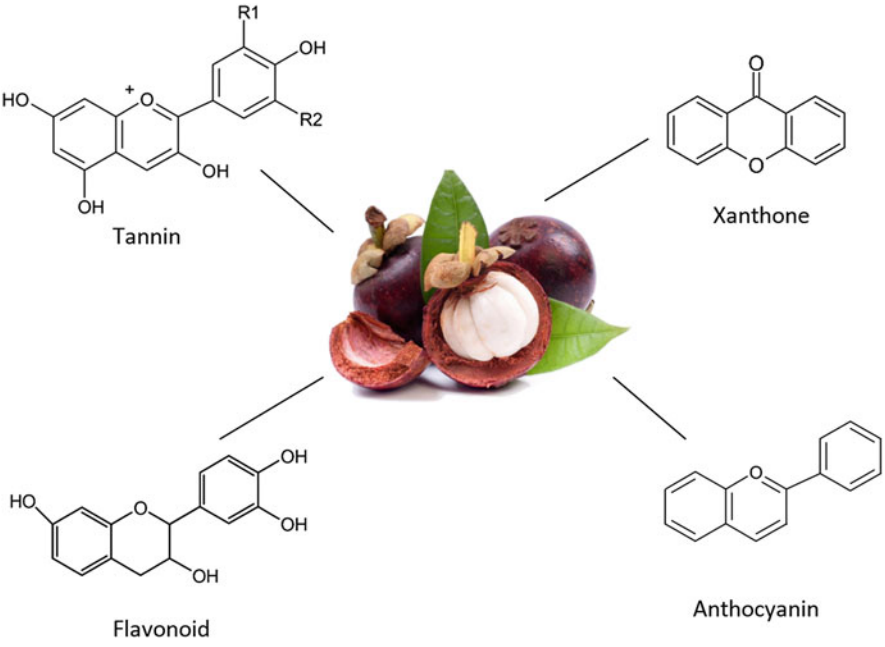


Fig. 2.1 Mangosteen fruit

mangosteen peel antioxidants consist of xanthones, flavonoids, anthocyanins, and tannins (Zarena and Udaya Sankar 2011).

Xanthones are the largest compounds, which include 3-iso mangostin, alpha-mangostin, beta-mangostin, gamma-mangostin, 8-desoxygartanin, gartanin, and garsinon (Walker 2007). Xanthone ($C_{13}H_8O_2$) is a polar compound that has a molecular weight of 196.19 g/mol, boiling point of 351 °C, and melting point of 174 °C. Xanthone's high melting point causes difficulties in its physical transformation even though the environment's temperature is very hot (Palapol et al. 2009). Meanwhile, flavonoids (C6-C3-C6) are polar compounds and included in the group of phenolic compounds, so they will dissolve in polar solvents such as ethanol and methanol (Dai and Mumper 2010). Flavonoids are divided into several groups according to their chemical structure, such as flavones, flavanols, and anthocyanins (Moraes et al. 2013). Whereas tannins are polyphenol compounds found in plants, which taste bitter and chelate and can clump proteins (Paryanto et al. 2017). Tannin monomers are digallic acid and D-glucose. Tannin has the molecular formula $C_{76}H_{52}O_{46}$ (Zalacain et al. n.d.). The last compound found in large quantities in mangosteen peel is anthocyanin. The term "anthocyanin" itself was derived from Greek words, "anthos" which means flower and "kyanos" which means blue. Anthocyanin is a compound that can give red, blue, and purple color to fruits, vegetables, and ornamental plants. Anthocyanin ($C_5H_{11}O$) has a molecular weight of 207.08 g/mol. Most anthocyanins are found in six forms; they are pelargonidin, cyanidin, peonidin, delphinidin, petunidin, and malvidin (Khoo et al. 2017).

Apart from its utilization as biodiesel additive, antioxidants from mangosteen also have an eminent prospect to be used in the food industry, primarily as a preservative in edible oil. As an additive for edible oil preservation, the mangosteen antioxidants act as lipid peroxidation resistors (Chong et al. 2015). Lipid peroxidation is a process when free radicals (oxidants) invade the double bond carbon-contained lipids such as polyunsaturated fatty acids which leads to food quality deterioration (Ayala et al. 2014). Unlike the use of synthetic antioxidants such as butylated hydroxytoluene (BHT); butylated hydroxy anisole (BHA); and tert-62 butylhydroquinone (TBHQ), which have a potential health risk, natural antioxidants from mangosteen peel are safe to human health (Maisuthisakul et al. 2007). In addition to its safety and ability to stabilize the edible oils and extend the shelf life, antioxidants from mangosteen peel are also known to contribute to the nutritional value of the oil (Chong et al. 2015; Bera et al. 2006).

2.3 Antioxidant Extraction of Mangosteen Peel

Extraction is a method used to separate a component in a material using a solvent (Zhang et al. 2018a; Dean 2009; Ramaswamy and Marcotte 2008). The solvent used must be able to extract the desired component without dissolving the other components. Broadly speaking, extraction is divided into two types; they are solid–liquid extraction and liquid–liquid extraction. In the solid–liquid extraction, like

mangosteen peel antioxidant extraction, contact occurs between two phases that causes the solvent diffusion from solids to liquids or solvents. The mechanism that occurs during the solid–liquid extraction can be described as follows:

(a) Mass transfer of the solvent to the material's surface, so the material's surface is coated with the solvent.
(b) There is a mass diffusion of the solvent from the material's surface into the material's pore.
(c) Solute contained in the material dissolves in the solvent.
(d) The solute solution in the material will be diffused out to the material's surface.
(e) The mass transfer of the solute solution from the material's surface to the solvent.

The extraction methods can be divided into two types, conventional and nonconventional. Conventional extraction is the simplest method because it uses solvents and conventional heaters which still has several disadvantages; it needs a lot of solvents and long extraction time, while the yields obtained are few (Tjahjani et al. 2014). Moreover, in a long period of time, the yield produced is not maximal. Recently, this method can cause thermolabile compounds to be degraded. In contrast to the conventional methods, nonconventional or modern methods have advantages, higher yields, faster extraction times, and fewer solvent volumes. This modern method has been carried out on an industrial scale. An example of a nonconventional method is MAE (Bagherian et al. 2011; Buanasari et al. 2017; Guo et al. 2012; Megawati et al. 2018).

The most commonly used conventional methods are maceration and Soxhlation. Maceration is a simple extraction method that is commonly used. This method is suitable for both laboratory and industry scale. This method can be done by adding materials in solvents with tightly closed state at room temperature (Damayanti and Fitriana 2015). The extraction is stopped when the equilibrium between the concentration of the component (extract) in the solvent and its concentration in the material is reached. To separate the extract solution with material, filtering should be done. A pure extract is obtained by evaporating the solvent and/or liquid–liquid extraction. The disadvantage of this method is that some compounds are difficult to extract at room temperature (Handayani and Nurchayati 2015). Some studies using this method are mangosteen peel antioxidant extraction (Jung et al. 2006), rose essential oil extraction (Damayanti and Fitriana 2015), and zodiac leaf essential oil extraction (Handayani and Nurchayati 2015).

As a matter of fact, recently there is one other choice of method to extract the antioxidants which used biotechnology. This method makes use of enzyme assistance in order to obtain the bioactive compound. Enzymes such as pectinases, cellulases, glucanases, and amylases can be used to disrupt the plant or fruit cell membranes, hence the bioactives can be released more effectively (Arnous and Meyer 2010). In comparison with previously mentioned methods, this enzyme-assisted extraction is far more ecofriendly as it does not use either high amount of solvent or energy (Puri et al. 2012). However, this method also has some drawbacks, for instances, longer extraction time; lower yield obtained; and limited information

about suitable type of enzymes for various kind of plants (Meini et al. 2019). Thus, further studies about enzyme-assisted extraction are still needed to develop a highly efficient and ecofriendly antioxidant method.

There are several factors that can affect the solid–liquid extraction; they are:

Solvent The solvents used in extraction should have the following properties:

(a) The solvent used must be adjusted to the polarity of the compound to be extracted, so that a purer extract can be obtained.
(b) The solvent used should not cause a chemical change in the components of the extract.
(c) Solvents must have a low boiling point, so that the solvent is easily evaporated even in low temperatures.
(d) The solvent used must not be corrosive, so that the equipment used is not corroded.

The solvents that have been used in extracting antioxidants are ethanol and water. Ethanol solvents are used for antioxidant extraction of petai leaves and basil leaves (Buanasari et al. 2017; Warsi and Sholichah 2017). Whereas water solvents were used for extraction of dragon fruit antioxidants (Thirugnanasambandham and Sivakumar 2017) and antioxidant extraction of green tea leaves (Ziaedini et al. 2010).

Particle Size Solid–liquid extraction process will be better if the particle diameter size is smaller. A smaller particle size will expand the contact surface with the solvent, so that the diffusion rate increases. However, it is not desirable that the particle size is too small, because the smaller the particle size, the more expensive the operating costs and the more difficult the separation process will be. Thus, obtaining pure extracts will be difficult (Sun et al. 2012). The particle size used in antioxidant extraction of mangosteen peel was 80 mesh (Ghasemzadeh et al. 2018) and the extraction of antioxidant dragon fruit was 40 mesh (Thirugnanasambandham and Sivakumar 2017).

Extraction Time A longer extraction time can lead to longer contact materials with solvents, so more extracts will be obtained (Handayani and Nurchayati 2015). The extraction has an optimum time, that is the time when the increase in the amount of extract is high, so that the amount of extract is high in an efficient time. The saturated solvent can no longer extract or decrease in its ability to extract because the thrust is getting smaller. As a result, the extraction time is longer and the resulting extract is no longer increasing (Buanasari et al. 2017). The time that has been used in antioxidant extraction using MAE was at least 2 min (Chong et al. 2015) and at the longest was 50 min (Buanasari et al. 2017).

Temperature In general, increasing extraction temperature will increase the amount of substances dissolved in the solvent. The solubility of the extracted material will increase with increasing temperature. In addition, the diffusivity coefficient is also increasing, so reaction rate will also be increasing (Damayanti and Fitriana 2015). In extraction using MAE, the effect of temperature is represented by power.

2.3.1 Antioxidant Extraction of Mangosteen Peel Using Soxhlation Method

Soxhlation is the most commonly used extraction method in a laboratory scale. This method can be done by adding a material on the filter paper placed in the extractor. The solvent used is put into the boiling flask and the temperature of the heater is set below the reflux temperature. This extraction will be done with several cycles determined by the researcher. The advantage of this method is the continuity of the extraction process; it does not require a lot of solvents and time. However, this process has a disadvantage. Thermolabile compounds can be degraded, because the extract is obtained continuously at the boiling point (Zhang et al. 2018b; Handayani and Juniarti 2012). This method was used in some studies on extractions of several components, such as coriander oil, frangipani leaves essential oil, and clove flower essential oil (Handayani and Juniarti 2012; Megawati and Saputra 2012; Hadi 2012).

In the antioxidant extraction of mangosteen peel using Soxhlation, before being used, 1 kg mangosteen peel was dried using an oven (Mammert™) at 50 °C for 24 h. The dried mangosteen peel was blended using a blender (Philips) until it became powder which was then sieved using a 500 μm strainer (Endecotts). Drying mangosteen peel was done to prevent the fungal growth, so the peel will still be in a good shape when it is stored before being used. Moreover, drying the peel also eases the blending process (Zhang et al. 2018b). The mangosteen peel is dried at low temperatures so that the components are not damaged, the quality is not reduced. The purpose of blending the mangosteen peel was to enlarge its contact area with ethanol solvents.

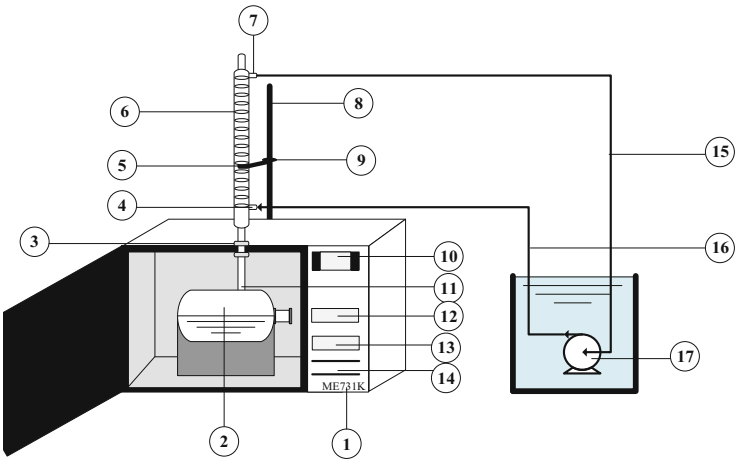
The antioxidant content of mangosteen peel was tested through an extraction using Soxhlet and methanol as solvent (material mass of 40 g and solvent volume of 400 mL). The heater used was a 200 W Electrothermal M575370/03. The extraction was done for 25 cycles (12.5 h). After the extraction, the solvent was recovered using distillation at 68 °C and until the volume was 20 mL. For further purification, the extract obtained was heated in the oven at 68 °C until constant weight was obtained. The phases of the process are depicted in Fig. 2.2. The extract was then measured using a digital scale and its phenolic concentration was tested using UV–Vis spectrophotometer (Genesys 10 UV).

From the experiment, the phenolic content of mangosteen peel extract obtained from Soxhlation method is about 23.16% (9.264 g). Accordingly, mangosteen peel has a phenolic content of 28.88% (Suttirak and Manurakchinakorn 2012). Differences in climate, geography, and other environmental factors affect the phenolic contents of the same material. The energy needed to produce 1 g phenolic compound was about 0.3 kWh. It is assumed that 1 kWh is IDR 1350, so the production cost of 1 g phenolic compound using Soxhlation method is Rp 364.

Fig. 2.2 Phases of change from mangosteen peel to antioxidant extracts

2.3.2 Antioxidant Extraction Using MAE Method

MAE is an extraction method which utilizes microwave radiation as a heating medium. The basic mechanism of heating using MAE involves molecules in dipole material. If a molecule is exposed to microwave radiation, the dipole will align itself with each other. In addition, when microwaves are continuously emitted, there is a movement between molecules that cause heat because of the friction between one molecule and another. This heat serves as a heating to the sample in the microwave (Kapoore et al. 2018). This is convenient to extracting thermolabile antioxidant compounds, because this method has better temperature control compared to conventional heating methods (Thirugnanasambandham and Sivakumar 2017; Megawati et al. 2019). Moreover, MAE is seen to be more advantageous, because the extraction process is shorter and higher yields can be obtained (Chuyen et al. 2017; Karami et al. 2015). MAE has been used to extract the sweet orange peels essential oil (Megawati and Kurniawan 2015), dragon fruit pectin (Megawati and Ulinuha 2015), *Chorella* sp. microalgae oil (Barqi 2015), dragon fruit peel betalain pigment (Thirugnanasambandham and Sivakumar 2017), *Parkia speciose* "petai" leaves antioxidant (Buanasari et al. 2017), basil leaves antioxidant (Dean 2009), tea



1. Microwave oven, 2. Glass extractor, 3. Hanger, 4. Water inlet nozzle, 5. Cast iron clamp, 6. Spiral condenser, 7. Water outlet nozzle, 8. Cast iron static, 9. Cast iron boss head, 10. Monitor, 11. Vapor outlet nozzle, 12. Power regulator, 13. Timer, 14. Power switch, 15. Water outlet hose, 16. Water inlet hose, 17. Cooling water pump

Fig. 2.3 The equipment of microwave-assisted extraction of mangosteen peel antioxidant

leaf caffeine (Pan et al. 2003), and chestnut saponins (Buanasari et al. 2017; Thirugnanasambandham and Sivakumar 2017; Arnous and Meyer 2010; Megawati and Kurniawan 2015; Megawati and Ulinuha 2015; Barqi 2015; Pan et al. 2003; Kerem et al. 2005). MAE has great potential to be a good technique for extracting organic materials (Olalere et al. 2019). Compared to conventional methods, MAE can also accelerate extraction rates (Megawati et al. 2019). The amount of phenolic compounds obtained from the MAE method in 1–3 min is almost the same as that obtained by the maceration method within 15 h (Li et al. 2012). The lowest microwave power used in antioxidant extraction was 100 W (Thirugnanasambandham and Sivakumar 2017) and the highest was 900 W (Zhang et al. 2018b).

The antioxidant extraction of mangosteen peel using MAE method can be performed by putting 40 g mangosteen peel powder into a 600 mL glass extractor, in which 400 mL ethanol was then added. The equipment used is depicted in Fig. 2.3. The microwave oven used was Samsung ME731K and the reflux condenser used was Leibig with a diameter of 4.1 cm and length of 30 cm. The extraction was performed at 300, 450, and 600 W for 5–35 min. Sampling was carried out every 5 min and the phenolic concentration was analyzed using a UV–Vis spectrophotometer. After the extraction was completed (35 min), the antioxidant solution was vacuum filtered to separate the filtrate and residue; the solvent in the filtrate was recovered using distillation at 78 °C until the extract volume was 20 mL; the extract obtained was purified by evaporating the solvent in the filtrate using the oven at

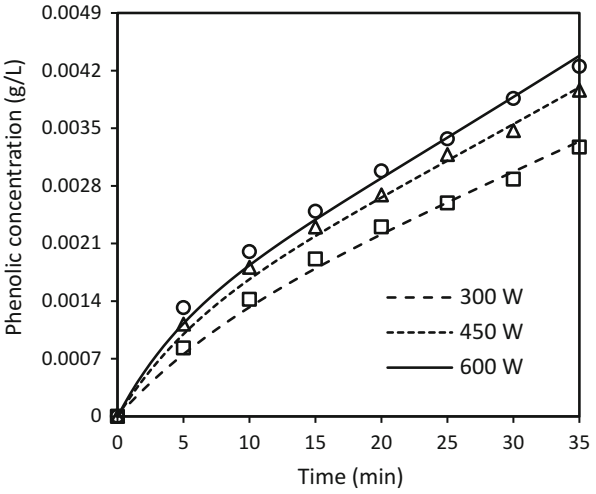


Fig. 2.4 The effect of power and time on antioxidant concentration of mangosteen peel extraction using MAE

78 °C until constant weight was obtained. The extract obtained was used as an antioxidant solution.

The effect of extraction times (5–35 min) on phenolic concentration obtained from mangosteen peel extraction using MAE can be seen in Fig. 2.4. The longer the time, the more the phenolic concentrations of mangosteen peel extraction will be. In addition, until 35 min, the concentrations were still increasing. At 300, 450, and 600 W, the highest increase of phenolic concentrations occurred when the extraction times were 5–10 min, which was 0.59, 0.68, and 0.68 mg/mL, respectively, and after 10 min, the phenolic concentration steadily increased. A similar observation was conducted for alpha-mangostin extraction from mangosteen pericarp, in which with an increase in extraction time from 2 to 4 min, the α-mangostin value increased significantly (Ghasemzadeh et al. 2018).

Phenolic concentration of mangosteen peel extract is also affected by microwave power. At 15 min and 300, 450, 600 W, the phenolic concentrations obtained were 1.91, 2.30, 2.49 mg/mL, respectively. The highest phenolic concentrations were obtained at 35 min; they were 3.28, 3.96, 4.25 mg/mL at 300, 450, 600 W, respectively. The increase in power can provide more heat as a driving force to destroy the pore cells of mangosteen peel, so that antioxidants can be diffused out (Megawati et al. 2019). Extraction conversion can be calculated from the values of phenolic concentrations and the result showed that at 300, 450, 600 W, the conversion values were 15.45, 17.00, 18.33%, respectively. Meanwhile, generally, the greater the microwave power used, the greater the conversion will be (Li et al. 2017). Accordingly, at 40–120 °C, the increase in total vitamin E was 59.63% in rice bran oil extracted using isopropanol as a solvent through microwave assisted method (Zigoneanu et al. 2008).

After the solvent was separated, a very concentrated antioxidant solution was obtained, which would be used for biodiesel B20 oxidation. The concentrated antioxidant solutions had total phenolic concentrations in mg GAE/g extract; they

were 155.77, 188.32, and 202.20 mg GAE/g extract at 300, 450, and 600 W, respectively. These values are in accordance with research conducted by Uslu and Ozcan (Uslu and Ozcan 2017). In their research, the highest phenolic concentration was at 720 W (107 mg GAE/g extract) and the lowest was at 180 W (33.38 mg GAE/g extract).

In 35 min, the phenolic compound produced from extractions using MAE at 300, 450, and 600 W was about 6.18, 6.8, and 7.33 g, respectively. Therefore, the energy needed to produce 1 g phenolic compound at 300, 450, and 600 W were about 0.028, 0.039, and 0.047 kWh. Hence, the production cost to produce 1 g phenolic compound using MAE method at 300, 450, and 600 W are IDR 38; 53; and 65. It can be concluded that MAE method is more economical and effective for mangosteen peel antioxidant extraction, with about 82.14% energy efficiency.

2.4 Kinetics on Antioxidant Extraction of Mangosteen Peel Using MAE

Extraction kinetics is important to facilitate the design of unit operation. In the solid–liquid extraction, the mass transfer of solute from solid to liquid will undergo through two main stages; they are diffusion from the solid to its surface and mass transfer from the surface to the liquid. Both processes go simultaneously. If one of the processes is relatively much faster, then the extraction speed is determined by the slow one. However, if both processes have similar extraction speeds, then the extraction speed is determined by both processes. If the solid is relatively small, the diffusion of solute from solid to its surface will be very fast, so that the extraction speed is determined by the speed of the solute mass transfer from the solid's surface to the liquid. In contrast, when the solid is relatively large, then the diffusion of solute from the solid to the surface will be very slow. Therefore, the extraction speed is determined by the solute diffusion speed from the solid to the surface.

Accordingly, in the case of very small particles, the diffusion of solute in the inner particles was assumed very fast that can be negligible (Sayyar et al. 2009). Hence, the rate-limiting step is only the mass transfer from the particle surface to the bulk of solution. The mass transfer of solute in the solid–liquid extraction can be expressed by homogeneous reaction rate law. In addition, the extraction kinetics of *Jatropha* seeds with hexane and petrochemical ether solvents using MAE has been studied. The kinetic study results stated that the mass transfer from the solid's surface to the solution is controlling the rate of process that followed the second order of homogeneous reaction model. Krishnan dan Rajan (2016) also did the same study on flavonoid extraction on *Terminalia bellerica* using MAE.

In this section, the three models above will be studied, they are:

1. Mathematical model for the intra-particle diffusion-controlled rate (Model 1)
2. Mathematical model for the intra-particle diffusion and mass transfer-controlled rate (Model 2)

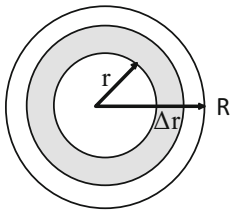


Fig. 2.5 Element of solute volume in a sphere-shaped material item. *Rate of Input – Rate of output = Rate of Accumulation*

3. Mathematical model for mass transfer-controlled rate (Model 3)

Solute diffusion from the inside the material to its surface can be explained as follows.

Intra-particle Diffusion The mass balance *A* in the volume element in Fig. 2.5 is expressed as Eq. (2.1) and is simplified into Eqs. (2.2)–(2.5).

$$\left(-D_e.4.\pi.r^2.\left.\frac{\partial C_A}{\partial r}\right|_r\right) - \left(-D_e.4.\pi.(r+\Delta r)^2.\left.\frac{\partial C_A}{\partial r}\right|_{r+\Delta r}\right) = 4.\pi.r^2.\Delta r.\frac{\partial C_A}{\partial t} \tag{2.1}$$

$$\frac{(r+\Delta r)^2.\left.\frac{\partial C_A}{\partial r}\right|_{r+\Delta r} - r^2.\left.\frac{\partial C_A}{\partial r}\right|_r}{\Delta r} = \frac{1}{D_e}.r^2.\frac{\partial C_A}{\partial t} \tag{2.2}$$

with:

D_e: Effective diffusivity (cm^2/s)
r: radius, cm
t: time, s

If $\Delta r \to 0$, then,

$$\frac{\partial}{\partial r}\left(r^2.\frac{\partial C_A}{\partial r}\right) = \frac{1}{D_e}.r^2.\frac{\partial C_A}{\partial t} \tag{2.3}$$

$$r^2.\frac{\partial^2 C_A}{\partial r^2} + 2.r.\frac{\partial C_A}{\partial r} = \frac{1}{D_e}.r^2.\frac{\partial C_A}{\partial t} \tag{2.4}$$

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}.\frac{\partial C_A}{\partial r} = \frac{1}{D_e}.\frac{\partial C_A}{\partial t} \tag{2.5}$$

Mass Transfer in Extraction Mass transfer in extraction is affected by operating conditions. To calculate the mass transfer rate, mass transfer coefficient is needed. Theoretically, several factors can influence the mass transfer rate; they are contact time and operating temperature. For extraction using MAE, the operating

temperature can be represented by power. The speed of mass transfer from the grain surface to the liquid follows Eq. (2.6) (Scott Fogler 2016; Levenspiel 1999).

$$N_A\left(\frac{\text{mass}A}{\text{time} \times \text{area}}\right) = K_C\left(C_f^* - C_f\right) \tag{2.6}$$

with:

K_C: Mass transfer coefficient
C_f^*: The level of A in the liquid which is balanced with the concentration of A on the surface of the grain.
C_f: The level of A in the liquid (mass A/free solvent mass A) at any time

At certain times, the concentration of antioxidants in solids will balance the concentration of antioxidants in the solvent. The equilibrium relationship follows an equation similar to Henry's Law (Eq. 2.7).

$$C_A = H.C_f^* \tag{2.7}$$

with:

C_A: The concentration of solute in solids, g solut/solid's volume
H: Henry's equilibrium constant

2.4.1 *Mathematical Model for Intra-particle Diffusion-Controlled Rate of Antioxidant Extraction of Mangosteen Peel Using MAE (Model 1)*

In extraction, the initial level of A is C_{AO} with radius R, as many as Np pieces that are in the extractor, they will be dissolved in pure solvent with volume V. Equation (2.5) can be solved by finite difference approximation. In this way, the equation is changed to an algebraic equation. Solid radius and time are divided into small intervals as thick as Δr, number N, interval boundaries are indexed $i = 1, 2, 3, \ldots, N$, for radius, while for time divided by Δt, a number of T and given an index $j = 1, 2, 3, \ldots, T$. The approach is done using an explicit method, Eqs. (2.8)–(2.10).

$$\frac{\partial C_A}{\partial r} = \frac{(C_A)_{i+1,j} - (C_A)_{i-1,j}}{2.\Delta r} \tag{2.8}$$

$$\frac{\partial^2 C_A}{\partial r^2} = \frac{(C_A)_{i-1,j} - 2(C_A)_{i,j} + (C_A)_{i+1,j}}{(\Delta r)^2} \tag{2.9}$$

$$\frac{\partial C_A}{\partial t} = \frac{(C_A)_{i,j+1} - (C_A)_{i,j}}{\Delta t} \tag{2.10}$$

Thus, by substituting Eqs. (2.8)–(2.10) to Eq. (2.5), Eq. (2.11) is obtained.

$$\frac{(C_A)_{i-1,j} - 2(C_A)_{i,j} + (C_A)_{i+1,j}}{(\Delta r)^2} + \frac{2}{i.\Delta r} \cdot \frac{(C_A)_{i+1,j} - (C_A)_{i-1,j}}{2.\Delta r} = \frac{1}{D_e} \cdot \frac{(C_A)_{i,j+1} - (C_A)_{i,j}}{\Delta t} \tag{2.11}$$

By multiplying Δr (Zarena and Udaya Sankar 2009) on the left and right segments, Eq. (2.12) is obtained. If M is expressed by Eq. (2.13), the Eq. (2.12) can be simplified to Eq. (2.14).

$$(C_A)_{i-1,j} - 2(C_A)_{i,j} + (C_A)_{i+1,j} + \frac{1}{i}\left((C_A)_{i+1,j} - (C_A)_{i-1,j}\right) = \frac{(\Delta r)^2}{D_e.\Delta t}\left((C_A)_{i,j+1} - (C_A)_{i,j}\right) \tag{2.12}$$

$$M = \frac{(\Delta r)^2}{D_e.\Delta t} \tag{2.13}$$

$$(C_A)_{i,j+1} = \frac{\left(1 - \frac{1}{i}\right)(C_A)_{i-1,j} + (-2 + M)(C_A)_{i,j} + \left(1 + \frac{1}{i}\right)(C_A)_{i+1,j}}{M} \tag{2.14}$$

Eq. (2.14) applies to $i = 1, 2, 3, \ldots, N-1$ and boundary conditions such as Eqs. (2.15)–(2.17). The boundary condition as in Eq. (2.16) was obtained by assuming that the solute mass transfer from the solid's surface to the liquid was relatively quick, so the solute level on the solid surface was in proportion with the solute level in the liquid, and the proportion relationship can be approached by an equation similar to Henry's law.

$$C_A(r, 0) = CAO \tag{2.15}$$

$$C_A(R, t) = C_f\, H \tag{2.16}$$

$$\frac{\partial C_A}{\partial t}(0, t) = 0 \tag{2.17}$$

with:

C_{AO}: The concentration of solute in the original material, g solut/g volume of solids
R: Radius, cm

To solve Eq. (2.14) with limitations as in Eqs. (2.15)–(2.17), one equation was still needed to correlate C_f with C_A. The correlation between C_f and C_A can be

obtained by generating the total mass balance of A (antioxidant) in solid particles during extraction, as depicted in Eq. (2.18). The integral equation can be solved using the Simpson's Rule method.

$$N.\frac{4}{3}.\pi.R^3.C_{AO} = N.\int_0^R 4.\pi.r^2.C_A.dr + V.C_f \tag{2.18}$$

Equations (2.13)–(2.16) and total phenolic concentration data were then applied to curve-fitting method to evaluate the values of D_e and H. For a set of values of D_e and H, the values of C_f can be calculated. The values of C_f were evaluated and the values of D_e and H were optimized. The values chosen were the ones presenting the minimum value of the Sum of Squared Error (SSE). The *SSE* was defined in Eq. (2.19). Optimization was done using a solver tool of Microsoft Excel.

$$\text{SSE} = \sum \left(C_{f(\text{calc})} - C_{f(\text{data})}\right)^2 \tag{2.19}$$

Calculation Steps:

1. Determine C_{AO}, Δt, Δr, R, V, and N.
2. D_e and H values trial.
3. Calculating the value of M.
4. Calculating the value of C_A when $j = 0$.
5. Calculating C_f as $C_{f(\text{calc})}$.
6. Repeat steps 4–5 for $j = 1$ to $j = T$.
7. $C_{f(\text{calc})}$ is compared with $C_{f(\text{data})}$ until the smallest SSE value is obtained.
8. Calculating the average of error using Eq. (2.19).

$$\%\text{Average Error} = \frac{\sum\left(C_{f(\text{calc})} - C_{f(\text{data})}\right)}{C_{f(\text{data})}}\frac{1}{n}100\% \tag{2.20}$$

In the study described in the mangosteen peel extraction using MAE (Fig. 2.4), the solvent volume used was 400 mL; the mass of mangosteen peel powder 40 g; total solids 428; initial antioxidant concentration 0.232 g/cm^3; the material powder size was 50 μm (0.05 cm), so that the radius was 0.025 cm. Experimental data and results of calculations every time can be seen in Table 2.1 and Fig. 2.6. Based on calculations using Model 1 at power variations of 300, 450, and 600 W, it can be concluded that the antioxidant extraction of mangosteen skin using MAE with the Model 1 approach is less appropriate, especially at 300 W. Model 1 is also relatively more difficult to solve.

Table 2.1 Antioxidant concentration with intra-particle diffusion model-controlled rate approach (Model 1) of mangosteen peel extraction using MAE with ethanol as solvent ($V = 400$ mL, $m = 40$ g, $N_p = 428$, $C_{AO} = 0.232$ g/cm^3, $R = 0.025$ cm)

t (min)	Antioxidant concentration (g/cm^3)					
	300 W		450 W		600 W	
	Data	Calculation	Data	Calculation	Data	Calculation
0	0.0000	0.0000	0.00000	0.0000	0.00000	0.0000
5	0.0008	0.0016	0.00112	0.0016	0.00132	0.0016
10	0.0014	0.0018	0.00181	0.0020	0.00200	0.0020
15	0.0019	0.0021	0.00230	0.0024	0.00249	0.0025
20	0.0023	0.0023	0.00269	0.0028	0.00298	0.0030
25	0.0026	0.0026	0.00318	0.0032	0.00337	0.0034
30	0.0029	0.0028	0.00347	0.0036	0.00386	0.0039
35	0.0033	0.0030	0.00396	0.0039	0.00425	0.0043
SSE		1.17×10^{-06}		1.45×10^{-06}		1.03×10^{-06}
Average error (%)		11.51		18.29		13.53

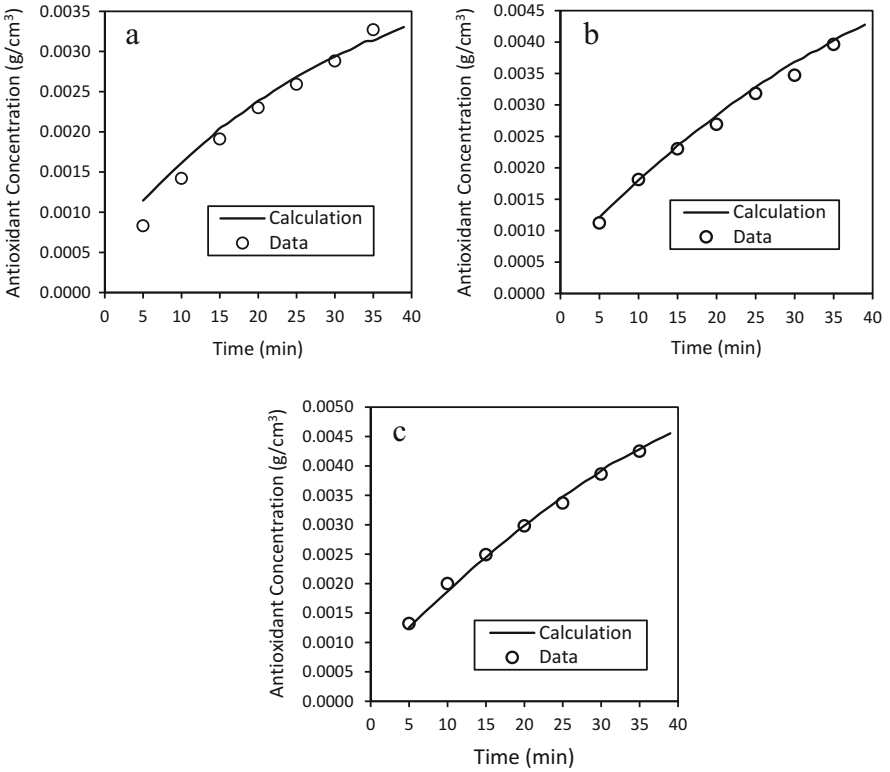


Fig. 2.6 The relationship between antioxidant concentration and extraction time with Model 1 approach on mangosteen peel extraction using MAE (**a** = 300 W, **b** = 450 W, **c** = 600 W)

2.4.2 *Mathematical model for Intra-particle Diffusion and Mass Transfer-Controlled Rate of Antioxidant Extraction of Mangosteen Peel Using MAE (Model 2)*

The extraction kinetics can be approached using solute diffusivity from inside the solid to the solid's surface and solute mass transfer from the solid's surface into solution. The solid was assumed to be the same and spherical with the radius R. During the extraction, the phenolic concentrations in mangosteen peel powder as a function of position and time ($C_A = f(r,t)$) can be derived through Eq. (2.13), with the limitation is as in Eq. (2.14). Equation (2.13) is used to calculate the phenolic concentration when $i = 1, 2, 3, \ldots$, and $N-1$. However, for $i = 0$, the phenolic concentration can be formulated using Eq. (2.21).

$$(C_A)_{0,j+1} = \frac{6(C_A)_{i,j} - (6 - M)\,(C_A)_{0,j}}{M} \tag{2.21}$$

The phenolic concentration for $i = N$ can be obtained by arranging $(C_A)_N = (C_A)_f = C_f$ as well as the mass balance of antioxidants in the solid's surface. Thus, the phenolic concentration when $i = N$, can be expressed in Eq. (2.22), with $\propto$, β, and γ in Eqs. (2.23)–(2.25), respectively.

$$(C_A)_{f,j+1} = \frac{-\alpha + \gamma.M - \frac{\beta}{H}\left[(C_A)_{f,j}\right] + \alpha.(C_A)_{f-1,j} + \beta C_f}{\gamma.M} \tag{2.22}$$

$$\left(R - \frac{\Delta r}{2}\right)^2 = \alpha \tag{2.23}$$

$$\frac{K_c.R^2.\Delta r}{D_e} = \beta \tag{2.24}$$

$$\frac{1}{2}\left(R - \frac{\Delta r}{4}\right)^2 = \gamma \tag{2.25}$$

Equations (2.13), (2.14), (2.18), (2.21)–(2.25), and total phenolic concentration data were then applied to curve-fitting method to evaluate the values of D_e, H, and K_c. For a set of values of D_e, H, and K_c the values of C_f can be calculated. The values of C_f were evaluated and the values of D_e, H, and K_c were optimized. The values chosen were the ones presenting the minimum value of the Sum of Squared Error (SSE). The SSE was defined in Eq. (2.19). Optimization is done using a solver tool of Microsoft Excel.

Calculation steps:

1. Determined C_{AO}, Δt, Δr, R, V, and Np.
2. K_c, D_e, and H values trial.
3. Calculating the value of M, α, β, and γ.

Table 2.2 Antioxidant concentration with intra-particle diffusion and mass transfer-controlled rate approach (Model 2) of mangosteen peel extraction using MAE with ethanol as solvent ($V = 400$ mL, $m = 40$ g, $N_p = 428$, $C_{AO} = 0.232$ g/cm^3, $R = 0.025$ cm)

t (min)	Antioxidant concentration (g/cm^3)					
	300 W		450 W		600 W	
	Data	Calculation	Data	Calculation	Data	Calculation
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0008	0.0009	0.0011	0.0012	0.0013	0.0014
10	0.0014	0.0014	0.0018	0.0018	0.0020	0.0020
15	0.0019	0.0019	0.0023	0.0023	0.0025	0.0024
20	0.0023	0.0023	0.0027	0.0027	0.0030	0.0029
25	0.0026	0.0026	0.0032	0.0031	0.0034	0.0034
30	0.0029	0.0030	0.0035	0.0035	0.0039	0.0039
35	0.0033	0.0033	0.0040	0.0040	0.0043	0.0044
D_e (cm^2/s)		2.81×10^{-11}		3.42×10^{-11}		3.80×10^{-11}
K_c (cm/s)		6.36×10^{-08}		8.97×10^{-08}		1.05×10^{-07}
SSE		1.99×10^{-08}		2.02×10^{-08}		3.08×0^{-08}
Average error (%)		1.82		1.89		2.028

4. Calculating the value of C_A when $j = 0$.
5. Calculating the value of C_f.
6. Repeat steps 7–10 for $j = 1$ to $j = T$.
7. $C_{f(\text{calc})}$ is compared with $C_{f(\text{data})}$ until the minimum average error value and the smallest SSE are obtained.

The value of $C_{f(\text{data})}$ and $C_{f(\text{calc})}$ on the diffusion model in solids and the mass transfer from the surface to the controlling liquid (Model 2) were obtained from the calculations presented in Table 2.2 and Fig. 2.7. Model 2 is suitable for of mangosteen peel antioxidant extraction using MAE at all powers used.

Paryanto (2017) used this model and obtained diffusion coefficients of 2.20×10^{-11}, 3.40×10^{-11}, 3.95×10^{-11} cm^2/s for 300, 450, 600 W, and Henry's constant of 0.027. Recently, each material has diffusivity varies based on the physical properties and temperature (Huang et al. 2011). In addition, it can be seen that the higher microwave power, the higher the diffusion coefficients obtained. In mangosteen peel antioxidant extraction, the effect of temperature is represented by power, the higher the microwave power, the greater the heat energy produced and the faster the solute diffusion from solids to liquids will be (Hadi 2012). On the other hand, the power also affects the mass transfer coefficient, the greater the power, and the higher the mass transfer. This is because the greater the power, the faster the solute's motion.

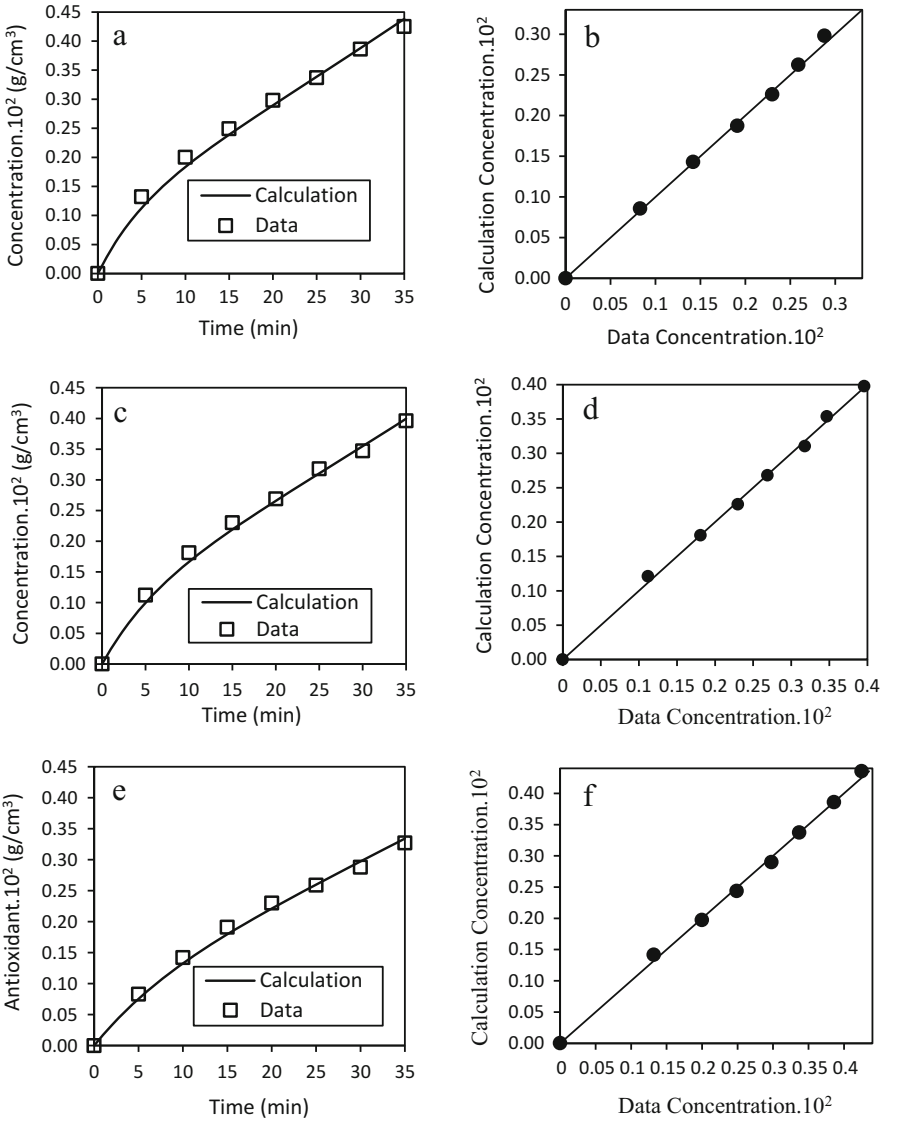


Fig. 2.7 The relationship between antioxidant concentration and extraction time with Model 2 approach on mangosteen peel extraction using MAE (V = 400 mL, m = 40 g, t = 35 menit, $N_p = 428.025$, $C_{AO} = 0.232$ g/cm^3, $R = 0.025$ cm; **a** and **b** = 300 W, **c** and **d** = 450 W, **e** and **f** = 600 W)

2.4.2.1 The Correlation Between Microwave Power (P) and Diffusion Coefficient (D_e) as Well as Microwave Power (P) and Mass Transfer Coefficient (K_c)

The correlations between microwave power and mass transfer coefficient, power, and diffusivity coefficient have not ever been analyzed. These correlations are done for scale-up calculations on an industrial scale. The equations used in these

Table 2.3 The calculation of the correlation between power (P) and diffusion coefficient (D_e) and power and mass transfer coefficient (K_c) on antioxidant extraction of mangosteen peel using MAE

P (Watt)	D_e (cm^2/s)	ln D_e	K_c (cm/s)	ln K_c
300	2.81×10^{-11}	−24.2949	6.36×10^{-08}	−16.5711
450	3.42×10^{-11}	−24.1000	8.97×10^{-08}	−16.2271
600	3.80×10^{-11}	−23.9934	1.05×10^{-07}	−16.0693

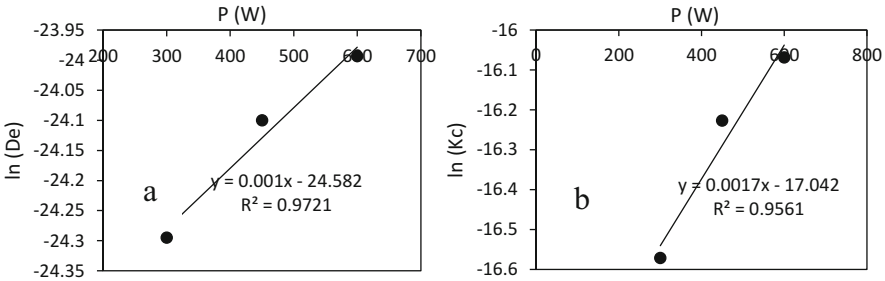


Fig. 2.8 The correlation between power (P) and D_e (**a**) and power (P) and (K_c) (**b**) on antioxidant extraction of mangosteen peel using MAE

correlations are empirical equations, such as Eqs. (2.26) and (2.27), where a, b, c, and d are constants. These constants can be calculated using linear regression and it becomes Eqs. (2.28) and (2.29), where a and c = exp. (intercept), b and d = − slope (Xin et al. 2009). The calculation results are presented in Table 2.3 and Fig. 2.8.

$$D_e = a \ \exp \ (-b.P) \tag{2.26}$$

$$K_c = c \ \exp \ (-d.P) \tag{2.27}$$

$$\text{In } D_e = \text{In } a - b.P \tag{2.28}$$

$$\ln \ (K_c) = \ \ln \ c - d.P \tag{2.29}$$

Based on Fig. 2.8, the correlation equations between P and D_e as well as P and K_c are depicted in Eqs. (2.30) and (2.31).

$$D_e = 2.109 \times 10^{-11} \ \exp\left(0.001 \ P\right) \tag{2.30}$$

$$K_c = 3.970 \times 10^{-8} \ \exp\left(0.0017 \ P\right) \tag{2.31}$$

2.4.3 *Mathematical Model for Mass Transfer-Controlled Rate of Antioxidant Extraction of Mangosteen Peel Using MAE (Model 3)*

Because the size of the mangosteen peel powder is too small, the solute diffusion from inside to solid's surface can be ignored. This mass transfer can be expressed by the homogeneous rate law. In addition, Krishnan and Rajan (2016) also did the same study on flavonoid extraction on *Terminalia bellerica* using MAE. The mass transfer of solute in the solid–liquid extraction can be expressed by the first- and second-order rate law, as described in Eqs. (2.29) and (2.30), with C_t = antioxidant concentration during the extraction (mg/mL), C_s = extraction capacity (mg/mL), t = time (min), and k_e = extraction rate constant (mL/mg/min) as well as the initial condition of $C_{t(t=0)} = 0$ and $C_{t(t=t)} = C_t$ (Krishnan and Rajan 2016).

$$-\frac{dC_t}{dt} = k_e(C_s - C_t) \tag{2.32}$$

$$-\frac{dC_t}{dt} = k_e(C_s - C_t)^2 \tag{2.33}$$

Eqs. (2.29) and (2.30) can be solved by integral method and its result is Eqs. (2.31) and (2.32) and then by using linearization method, these equations can be solved. The linear equations were expressed in Eqs. (2.33) and (2.34) and the parameters of k_e and C_s can be obtained (Fernando and Soysa 2015). The values of k_e and C_s are listed in Table 2.4 as well as the linear regression results are presented in Fig. 2.9.

$$C_t = C_s\left(1 - e^{-k.t}\right) \tag{2.34}$$

$$C = \frac{C_s^2 k_e t}{1 + C_s k_e t} \tag{2.35}$$

$$\log\ (C_s - C_t) = \log C_s - \frac{k}{2303}t \tag{2.36}$$

$$\frac{t}{C} = \frac{1}{k_e\ {C_s}^2} + \frac{t}{C_s} \tag{2.37}$$

Table 2.4 Extraction rate constant (k_e) and extraction capacity (C_s) of first-order rate law (Model 3) of mangosteen peel extraction using microwave-assisted extraction (operating condition: raw material weight of 20 g, raw material size of 500 μm, 70% ethanol volume as solvent of 260 mL)

Power (W)	Extraction capacity (C_s) (mg/L)	Extraction rate constant (k_e) (L/mg/min)
300	600	0.021
450	600	0.029
600	600	0.033

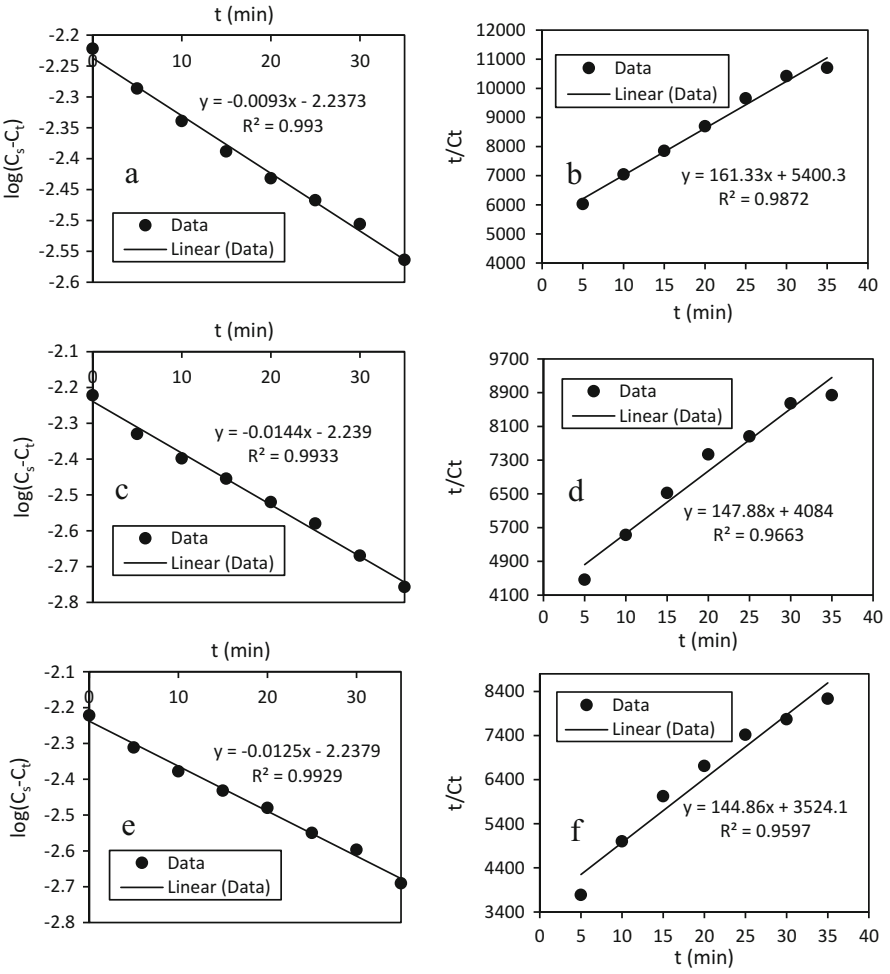


Fig. 2.9 Reaction rate law (Model 3) for mangosteen peel extraction using microwave-assisted extraction (**a**, **c**, **e** = first-order; **b**, **d**, **f** = second-order; operating condition: raw material weight of 20 g, raw material size of 500 μm, 70% ethanol volume as solvent of 260 mL)

2.5 Antioxidant Performance of Mangosteen Peel Extract on Biodiesel B20 Oxidation

Diesel fuel is very important for many aspects of daily life, especially transportation. Fossil fuels contribute 80% of the world's energy needs. Most industries use diesel engines for the production process, also in the transportation sector. This situation causes men a strong daily basis-dependence on fossil-based diesel fuel (Huang et al. 2011). To overcome this, alternative fuels, biodiesel, need to be developed. The source of biodiesel varies which generally comes from vegetable oils obtained in

nature. The properties of various fatty esters determine the properties of biodiesel fuel (Maisuthisakul et al. 2007). Biodiesel synthesis can also be done from *Chlorella* sp. oil (Widyastuti and Dewi 2015), which produces biodiesel with a density of 0.88 g/cm^3 (fulfilling one of the requirements of the Indonesian National Standard (SNI).

However, biodiesel contains unsaturated hydrocarbons which are unstable and easily oxidized to form fatty acids. Fatty acids can damage the quality of fuel which has an impact on the poor quality of fuel combustion in diesel engines. This problem can be avoided by adding antioxidants which can reduce NOx hydrocarbons, CO, particulates, polycyclic aromatic hydrocarbons, SO_2, and smoke in combustion engine exhaust emissions effectively. Antioxidants will suppress the oxidation of unsaturated fuels in their double bonds by ending the release of free radicals (Ramalingam et al. 2018). Free radicals are known as reactive and unstable molecules that contain one or more unpaired electrons in their outer orbitals. As an effort to achieve stability, free radicals will react with nearby atoms or monomers to obtain electron pairs. Meanwhile, antioxidants are compounds that can donate electrons (hydrogen atom givers) to free radicals which then can stop the chain reactions and convert free radicals into stable forms. Therefore, to reduce free radical activity, antioxidants are needed.

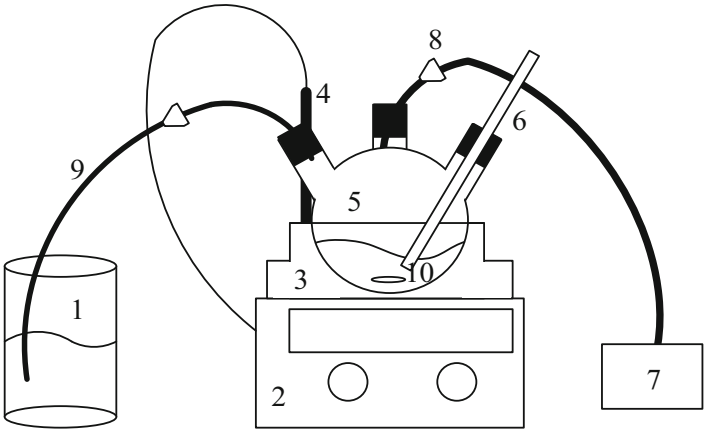
Theoretically, the oxidation reaction is divided into three stages; they are initiation, propagation, and termination. The first stage occurs when acid methyl esters (RH) release hydrogen atoms to form free radicals (R•), then it reacts with oxygen, or often called oxidized, forming peroxide radicals (ROO•), and/or hydroperoxide (ROOH). During the oxidation, peroxide radicals perpetually form new radicals (R•) to bind oxygen from the air and start chain reactions quickly (McCormick 2007).

Biodiesel oxidation occurs due to the reaction between oxygen and unsaturated fat methyl ester. Accordingly, diesel fuel is easily oxidized by oxygen, light, high temperature, and metals (Bouaid et al. 2009; Leung et al. 2006; Kivevele and Huan 2013; Park et al. 2008). This is certainly also experienced by biodiesel, because it is a mixture of biodiesel and diesel fuel in a certain ratio. In biodiesel, antioxidants function to capture free radicals formed during oxidation and stop chain reactions in fuel degradations (Spacino et al. 2016). Moreover, according to Coppo (Coppo et al. 2013) and Spacino (Spacino et al. 2016), natural antioxidants can inhibit biodiesel oxidation. Mangosteen peel extract can inhibit biodiesel oxidation with a concentration of 0.01% w/v, so the formation of free radicals can be inhibited by transferring hydrogen atoms into radical compounds or turning them into more stable forms. In the next discussion, mangosteen peel antioxidant extract used to inhibit biodiesel B20 oxidation will be explored using the oxidation kinetic. Meanwhile, the oxidation of mixture of biodiesel B20 and antioxidant obtained from mangosteen peel extraction was performed using air.

2.5.1 *Oxidation Experiment of Biodiesel B20 Using Mangosteen Peel Antioxidant Extract*

Experiments for studying biodiesel B20 oxidation using mangosteen peel extract can be carried out as follows. Before being used, biodiesel and the mixture of biodiesel and antioxidant's densities and kinematic viscosities were analyzed. The study was begun with mixing 95% biodiesel B20 and 5% antioxidant of mangosteen peel extract with a total volume of 100 mL into a three-neck volumetric flask. The mixture was then stirred at 600 rpm and heated to 100 °C. Then the air was flowed at a constant speed of 2.3 L/min. This oxidation was run for both biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidants at various temperatures of 100, 110, and 120 °C for 0–70 min. The samples were taken every 10 min and their acid numbers were analyzed. The equipment used can be seen in Fig. 2.10. Biodiesel B20 was obtained from PT Pertamina, 96% ethanol from local chemical shop, Folin–Ciocalteu reagent from Chemistry Laboratory of Universitas Diponegoro, and Na_2CO_3 (Merck 106392), methanol (Merck 106009), NaOH (Merck 106462), and distilled water from Research Laboratory of Chemical Engineering Department of Universitas Negeri Semarang.

The densities and viscosities of biodiesel B20 and the mixture of biodiesel B20 and antioxidant of mangosteen peel extract can be seen in Table 2.5. Compared to the density of biodiesel, the density of the mixture of biodiesel and antioxidant was higher. The density value still meets the predetermined standard limit of 815–860 kg/m^3. This is in line with Fattah (2014) which stated that at 40 °C, the addition of antioxidants makes the density of biodiesel B20 higher. According to



1. Beaker glass, 2. Magnetic stirrer, 3. Heating mantle, 4. Thermocouple, 5. Three-neck volumetric flask, 6. Thermometer, 7. Air pump, 8. Check valve, 9. Hose, 10. Magnetic stirring bar

Fig. 2.10 Equipment of biodiesel oxidation with air

Table 2.5 The density and viscosity of biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidant (operating conditions: temperature of 40 °C, stirrer rotation of 600 rpm, and air velocity of 2.3 L/min)

Sample	Density (kg/m^3)	Kinematic viscosity (mm^2/s)
B20	824	2.92
B20 + mangosteen peel extraction	844	2.90

Table 2.6 The conversions of biodiesel B20 and mixture of biodiesel B20 and mangosteen peel extract antioxidant during the oxidation process with air (operating conditions: antioxidant ratio of 5/95, stirrer rotation of 600 rpm, and air velocity of 2.3 L/min)

	Biodiesel B20			Mixture of biodiesel B20 and mangosteen peel extract		
Time (min)	100 °C	110 °C	120 °C	100 °C	110 °C	120 °C
0	0.000	0.000	0.000	0.000	0.000	0.000
10	0.043	0.105	0.173	0.018	0.043	0.089
20	0.106	0.179	0.298	0.061	0.100	0.139
30	0.167	0.289	0.457	0.082	0.123	0.177
40	0.267	0.394	0.516	0.101	0.169	0.211
50	0.311	0.463	0.667	0.139	0.170	0.282
60	0.418	0.540	0.730	0.172	0.230	0.376
70	0.466	0.667	0.806	0.198	0.243	0.413

Demirbas (2009) and Knothe (2007), in a fuel engine, a high viscosity will interfere with the fuel injection processes. The viscosity of the mixture of biodiesel B20 and mangosteen peel extract antioxidant was lower compared to biodiesel B20. The viscosity decreased but was still in the predetermined standard of 2–4.5 (mm^2/s). This is in accordance with a research conducted by Kivevele and Huan (2013), which stated that the addition of antioxidants could decrease the viscosity of biodiesel. Before being oxidized, the acid numbers of biodiesel B20 were 0.0881, 0.1058, and 0.1098 mg NaOH/mg at 100, 110, and 120 °C, respectively, while the acid numbers of the mixture of biodiesel B20 and mangosteen peel antioxidant were 0.2889, 0.3043, and 0.3077 mg NaOH/mg at 100, 110, and 120 °C, respectively. The addition of antioxidants increases acid numbers, but still within their limits—less than 0.5 mg KOH/mg (0.356 mg NaOH/mg) (Mahajan et al. 2006).

The effect of time and temperature on reaction conversion during the oxidation of biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidant is presented in Table 2.6. At a fixed temperature, the conversion kept increasing during the oxidation process. At 100 °C, in 70 min of biodiesel B20 oxidation, the conversion increased until 0.466. In other words, it increased 0.67%/10 min. This shows that biodiesel B20 is easily oxidized. This is in line with Bouaid (2009), who stated that acid numbers, peroxide numbers, and viscosity increased with the increase in biodiesel storage time. However, in 70 min of the mixture of biodiesel B20 and mangosteen peel extract oxidation, the conversion increased until 0.198, or 0.28%/10 min. This shows that mangosteen peel extract antioxidants could slow down the oxidation for 26.32%. At 110 and 120 °C, the antioxidant extract of

mangosteen peel could inhibit the oxidation process of biodiesel B20 for 36.84 and 51.30%. The higher the temperature, the stronger the antioxidant effect to inhibit biodiesel oxidation process. This result is in line with a research conducted by Xin (2009) and Gregorio (2017).

The effect of temperature on biodiesel B20 oxidation can be investigated in 50 min. The conversions at 100, 110, and 120 °C were 0.311, 0.463, and 0.667, respectively. Every increase of 10 °C, the conversion increased by an average of 0.178 or 47.84%. Thus, the increase in the temperature gave a sensitive effect on the biodiesel B20 oxidation (Pereira et al. 2015). However, at the same oxidation time and temperatures, the conversions of the mixture of biodiesel B20 and mangosteen peel extract antioxidants were 0.139, 0.170, and 0.282, respectively. In other words, the conversion increase was only 14%. This further strengthens that antioxidants can inhibit the oxidation of biodiesel B20.

2.5.2 *The Oxidation Kinetics of Biodiesel B20 and the Mixture of Biodiesel B20 and Mangosteen Peel Extract Antioxidant*

Gregorio (2017) has conducted a study on the performance of natural antioxidants from pepper extract, coffee leaf, bacupari leaf, and sage to inhibit biodiesel B100 oxidation. 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. Meanwhile, the performance of antioxidants obtained from mangosteen peel extraction on the oxidation kinetics will be evaluated based on the activation energy. The assumptions in the oxidation taken were: the reaction runs continuously with a constant volume (Zhou 2013); the air used is continuously flowed so that the reduction on oxygen concentration during the reaction can be ignored. The correlation between conversion and time in the first-order approach was derived into Eq. (2.38), with x_a = reaction conversion, t = time, and k = reaction rate constant. The conversion was calculated from the reduction of acid numbers during the reaction, as described in Eq. (2.39).

$$-\ln\ (1 - x_a) = k.t \tag{2.38}$$

$$x_a = \frac{AV_t - AV_0}{AV_0} \tag{2.39}$$

The rate reaction constant was influenced by temperature based on Arrhenius equation, as in Eq. (2.40) with A = frequency factor (1/min), E_a = activation energy (kJ/mol), R = universal gas constant, and T = temperature (K) (Levenspiel 1999). Parameters A and E_a were found out using curve-fitting method.

Table 2.7 Reaction rate constant (k) of biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidant (operating conditions: antioxidant ratio of 5/95, stirrer rotation of 600 rpm, and air velocity of 2.3 L/min)

	k (1/min)	
T (°C)	Biodiesel B20	The mixture of biodiesel B20 and antioxidant
100	0.0056	0.0038
110	0.0076	0.0005
120	0.0104	0.0072

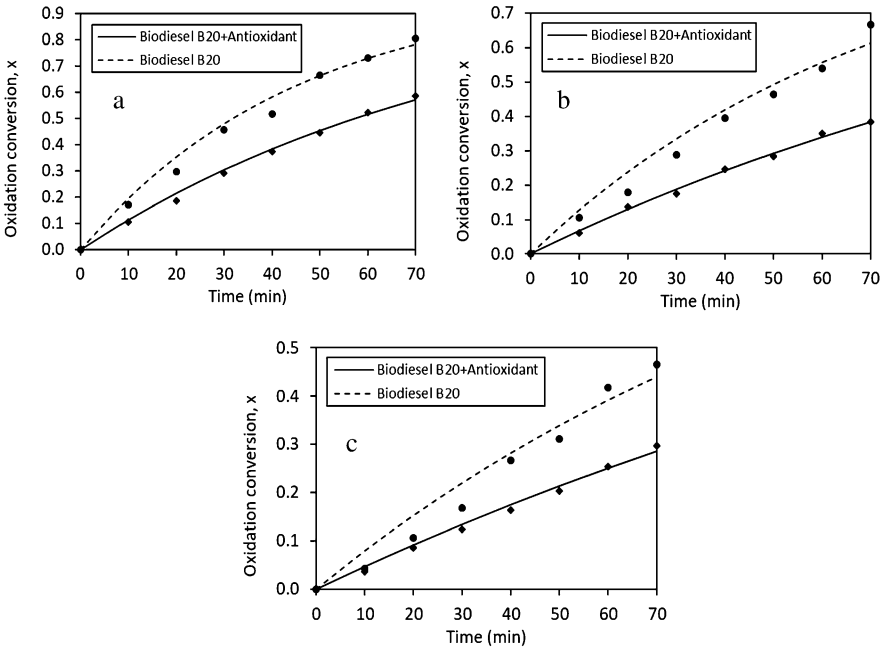


Fig. 2.11 The correlation between time (t) and conversion (x) in the mixture of biodiesel B20 and mangosteen peel extract oxidation (symbols = data; line = calculation; **a** = 100 °C, **b** = 110 °C, **c** = 120 °C, operating conditions: antioxidant ratio of 5/95, stirrer rotation of 600 rpm, and air velocity of 2.3 L/min)

$$\ln(k) = -\frac{E_a}{\mathrm{RT}} + \ln(A) \tag{2.40}$$

The conversion values obtained from biodiesel B20 oxidation were used to study the oxidation kinetics. The values of reaction rate constant (k) for biodiesel B20 and the mixture of biodiesel B20 and antioxidant oxidation, respectively, as well as are listed in Table 2.7. Fig. 2.11 shows the comparison results between the kinetics calculation using pseudo-homogeneous first-order model with experiment data. In order to check whether the values of reaction constant calculated from Table 2.7

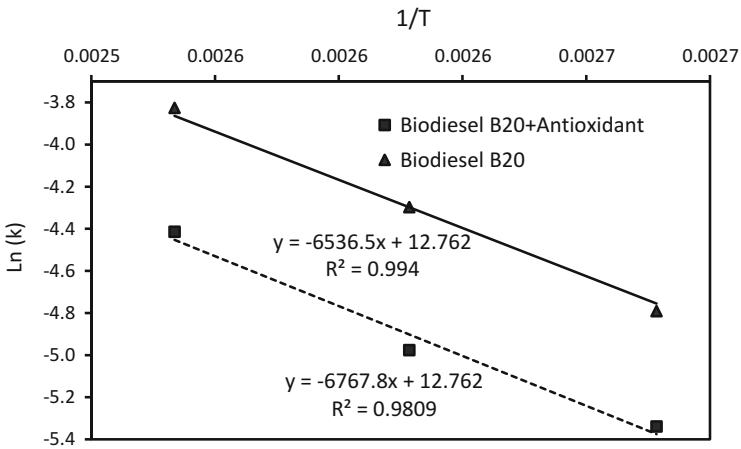


Fig. 2.12 Natural logarithm of the rate constant (ln (*k*)) versus 1/*T* for biodiesel B20 and the mixture of biodiesel B20 and mangosteen peel extract antioxidant (operating conditions: antioxidant ratio of 5/95, stirrer rotation of 600 rpm, and air velocity of 2.3 L/min)

satisfy the Arrhenius equation, the graph of ln (*k*) versus 1/*T* was made and shown in Fig. 2.12. The result shows that the data obtained from experiment agreed with Arrhenius law very well. The activation energies (E_a) for biodiesel B20 oxidation and the mixture of biodiesel B20 and mangosteen peel antioxidant calculated were 54.34 and 56.27 kJ/mol, respectively, as well as collision factors (*A*) of 348,711 and 348,711 1/min, respectively. The activation energy of the mixture of biodiesel B20 and mangosteen peel antioxidant was higher, so that the mixture of biodiesel B20 and mangosteen peel extract antioxidant is more difficult to oxidize. In a mixture of biodiesel and antioxidants of pepper extract, bacupari leaves, arabica coffee leaves, and sage leaves, when oxidized with oxygen, the activation energy was around 46.35–82.26 kJ/mol (Borsato et al. 2014; Gregorio et al. 2017).

Acknowledgments These experimental works were supported by the Ministry of Research, Technology and Higher Education of the Republic of Indonesia. We would also like to thank Arif Hidayat, Ibnu Inu Setiawan, and Viqi Akhmad Zaenuri for their assistance in collecting the data and doing the extraction and oxidation kinetics modeling.

References

Arnous A, Meyer AS (2010) Discriminated release of phenolic substances from red wine grape skins (*Vitis vinifera* L.) by multicomponent enzymes treatment discriminated release of phenolic substances from red wine grape skins (*Vitis vinifera* L.) by multicomponent enzymes treatment. Biochem Eng J 49(1):68–77. https://doi.org/10.1016/j.bej.2009.11.012

Ayala A, Muñoz MF, Argüelles S (2014) Lipid peroxidation: production, metabolism, and signaling mechanisms of malondialdehyde and 4-hydroxy-2-nonenal. Oxid Med Cell Longev 2014:1–31. https://doi.org/10.1155/2014/360438

Bagherian H, Ashtiani FZ, Fouladitajar A, Mohtashamy M (2011) Comparisons between conventional, microwave-and ultrasound-assisted methods for extraction of pectin from grapefruit. Chem Eng Process Process Intensif 50(11–12):1237–1243. https://doi.org/10.1016/j.cep.2011.08.002

Barqi WS (2015) Pengambilan minyak mikroalga chlorella sp. dengan metode microwave assisted extraction. Jurnal Bahan Alam Terbarukan:34–41. https://doi.org/10.15294/jbat.v3i1.5764

Bera D, Lahiri D, Nag A (2006) Studies on a natural antioxidant for stabilization of edible oil and comparison with synthetic antioxidants. J Food Eng 74:542–545. https://doi.org/10.1016/j.jfoodeng.2005.03.042

Borsato D, Galvan D, Pereira LL, Orives JR, Angilelli KG, Coppo R (2014) Kinetic and thermodynamic parameters of biodiesel oxidation with synthetic antioxidants: simplex centroid mixture design. J Braz Chem Soc 25(11):1984–1992. https://doi.org/10.5935/0103-5053.20140182

Bouaid A, Martinez M, Aracil J (2009) Production of biodiesel from bioethanol and *Brassica carinata* oil: oxidation stability study. Bioresour Technol 100(7):2234–2239. https://doi.org/10.1016/j.biortech.2008.10.045

BPS (2017) Produksi manggis pada tahun 2016. Badan Pusat Statistik

Buanasari, Eden WT, Solichah AI (2017) Extraction of phenolic compounds from petai leaves (Pakia speciosa Hassk) using microwave and ultrasound assisted methods. Jurnal Bahan Alam Terbarukan 6(1):25–31. https://doi.org/10.15294/jbat.v6i1.7793

Chong Y, Chang SK, Chiaw W (2015) Antioxidant efficacy of mangosteen (*Garcinia mangostana* Linn.) peel extracts in sunflower oil during accelerated storage. Food Biosci 12:18–25. https://doi.org/10.1016/j.fbio.2015.07.002

Chuyen HV, Nguyen MH, Roach PD, Golding JB, Parks SE (2017) Microwave-assisted extraction and ultrasound-assisted extraction for recovering carotenoids from Gac peel and their effects on antioxidant capacity of the extracts. Food Sci Nutr 6(1):189–196. https://doi.org/10.1002/fsn3.546

Coppo RL, Borsato D, Pereira JL, Da Silva HC (2013) FAME storage time in an optimized natural antioxidant mixture. J Renew Energy 2013:1–11. https://doi.org/10.1155/2013/497530

Dai J, Mumper RJ (2010) Plant phenolics: extraction, analysis and their antioxidant and anticancer properties. Molecules 15(10):7313–7352. https://doi.org/10.3390/molecules15107313

Damayanti A, Fitriana EA (2015) Pemungutan minyak astiri mawar (Rose oil) dengan metode maserasi. Jurnal Bahan Alam Terbarukan:14–20. https://doi.org/10.15294/jbat.v1i2.2543

Dean JR (2009) The grid: extraction techniques in analytical sciences. Wiley, West Sussex

Demirbas A (2009) Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Convers Manag 50(4):923–927. https://doi.org/10.1016/j.enconman.2008.12.023

Fattah IMR, Masjuki HH, Kalam MA, Mofijur M, Abedin MJ (2014) Effect of antioxidant on the performance and emission characteristics of a diesel engine fueled with palm biodiesel blends. Energy Convers Manag 79:265–272. https://doi.org/10.1016/j.enconman.2013.12.024

Fernando CD, Soysa P (2015) Extraction kinetics of phytochemicals and antioxidant activity during black tea (*Camellia sinensis* L) brewing. J Nutr 14(74):1–7. https://doi.org/10.1186/s12937-015-0060-x

Ghasemzadeh A, Jaafar H, Baghdadi A, Tayebi-Meigooni A (2018) Alpha-mangostin-rich extracts from mangosteen pericarp: optimization of green extraction protocol and evaluation of biological activity. Molecules 23(8):1852. https://doi.org/10.3390/molecules23081852

Gregorio APH, Borsato D, Moreira L, Silva ET, Romagnoli ES, Spacino KR (2017) Apparent activation energy and relative protection factor of natural antioxidants in mixture with biodiesel. Biofuels 8(4):1–8. https://doi.org/10.1080/17597269.2017.1332297

Guo HR, Ma SY, Wang XF, Ren EF, Li YY (2012) Microwave-assisted extraction of chlorophyll from filter mud of sugarcane mill and component analysis. Mater Res Adv 518/523:430–435. https://doi.org/10.4028/www.scientific.net/AMR.518-523.430

Gutierrez-Orozco F, Failla ML (2013) Biological activities and bioavailability of mangosteen xanthones: a critical review of the current evidence. Nutrients 5:3163–3183. https://doi.org/10.3390/nu5083163

Hadi S (2012) Pengambilan minyak astiri bunga cengkeh (Clove oil) menggunakan pelarut n-heksana dan benzena. Jurnal Bahan Alam Terbarukan 1:25–30. https://doi.org/10.15294/jbat.v1i2.2546

Handayani PA, Juniarti ER (2012) Ekstraksi minyak ketumbar (Coriander oil) dengan pelarut etanol dan n-heksana. Jurnal Bahan Alam Terbarukan 1:1–7. https://doi.org/10.15294/jbat.v1i1.2538

Handayani PA, Nurchayati H (2015) Ekstraksi minyak astiri daun zodia (Evodia suaveolens) dengan metode maserasi dan distilasi air. Jurnal Bahan Alam Terbarukan 3:1–7. https://doi.org/10.15294/jbat.v3i1.3095

Huang D, Zhou H, Lin L (2011) Biodiesel: an alternative to conventional fuel. Energy Proc C 16:1874–1885. https://doi.org/10.1016/j.egypro.2012.01.287

Jung H, Su B, Keller WJ (2006) Antioxidant xanthones from the pericarp of *Garcinia mangostana* (Mangosteen). J Agric Food Chem 54:2077–2082. https://doi.org/10.1021/jf052649z

Kapoore RV, Butler TO, Pandhal J, Vaidyanathan S (2018) Microwave-assisted extraction for microalgae: from biofuels to biorefinery. Biology 7(1):E18. https://doi.org/10.3390/biology7010018

Karami Z, Emam-Djomeh Z, Mirzaee HA, Khomeiri M, Mahoonak AS, Aydani E (2015) Optimization of microwave assisted extraction (MAE) and soxhlet extraction of phenolic compound from licorice root. J Food Sci Technol 52(6):3242–3253. https://doi.org/10.1007/s13197-014-1384-9

Kerem Z, German-Shashoua H, Yarden O (2005) Microwave-assisted extraction of bioactive saponins from chickpea (*Cicer arietinum* L.). J Sci Food Agric 85(3):406–412. https://doi.org/10.1002/jsfa.1989

Khoo HE, Azlan A, Tang ST, Lim SM (2017) Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and the potential health benefits. Food Nutr Res 61 (1):1361779. https://doi.org/10.1080/16546628.2017.1361779

Kivevele TT, Huan Z (2013) Effects of antioxidants on the cetane number, viscosity, oxidation stability, and thermal properties of biodiesel produced from nonedible oils. Energy Technol 1 (9):537–543. https://doi.org/10.1002/ente.201300072

Knothe G (2007) Some aspects of biodiesel oxidative stability. Fuel Process Technol 88 (7):669–677. https://doi.org/10.1016/j.fuproc.2007.01.005.17

Krishnan RY, Rajan KS (2016) Microwave assisted extraction of flavonoids from *Terminalia bellerica*: study of kinetics and thermodynamics. Sep Purif Technol 157:169–178. https://doi.org/10.1016/j.seppur.2015.11.035

Leung DYC, Koo BCP, Guo Y (2006) Degradation of biodiesel under different storage conditions. Bioresour Technol 97(2):250–256. https://doi.org/10.1016/j.biortech.2005.02.006

Levenspiel O (1999) Chemical reaction engineering, 3rd edn. Wiley, New York

Li H, Zeyuan D, Tao W, Rong HL, Steven LW, Rong T (2012) Microwave assisted extraction of phenolics with maximal antioxidant activities in tomatoes. J Food Chem 130:928–936. https://doi.org/10.1016/j.foodchem.2011.08.019

Li Y, Li S, Lin S, Zhang J (2017) Microwave assisted extraction of natural antioxidants from the exotic *Gordonia axillaris* fruit: optimization and identification of phenolic compounds. Molecules 22(9):1481–1497. https://doi.org/10.3390/molecules22091481

Mahajan S, Konar SK, Boocock GG (2006) Determining the acid number of biodiesel. J Am Oil Chem Soc 83(6):567–570. https://doi.org/10.1007/s11746-008-1289-8

Maisuthisakul P, Suttajit M, Pongsawatmanit R (2007) Food chemistry assessment of phenolic content and free radical-scavenging capacity of some Thai indigenous plants. Food Chem 100:1409–1418. https://doi.org/10.1016/j.foodchem.2005.11.032

McCormick RL (2007) The impact of biodiesel on pollutant emissions and public health. Inhal Toxicol 19(12):1033–1039. https://doi.org/10.1080/08958370701533509

Megawati, Kurniawan RD (2015) Ekstraksi minyak atsiri kulit jeruk manis (Citrus sinensis) dengan metode vacuum microwave assisted hydrodistillation. Jurnal Bahan Alam Terbarukan 4:61–67. https://doi.org/10.15294/jbat.v4i2.4143

Megawati, Saputra DW (2012) Minyak astiri dari kamboja kuning, putih, dan merah dari ekstraksi dengan n-heksana. Jurnal Bahan Alam Terbarukan 1:25–31. https://doi.org/10.15294/jbat.v1i1.2541

Megawati, Ulinuha AY (2015) Ekstraksi pektin kulit buah naga (Dragon fruit) dan aplikasinya sebagai edible film. Jurnal Bahan Alam Terbarukan 3:16–23. https://doi.org/10.15294/jbat.v3i1.3097

Megawati, Wulansarie R, Faiz MB, Adi S, Sammadikun W (2018) Kinetics of microwave assisted extraction of pectin from Balinese orange peel using pseudo-homogeneous model. AIP Conf Proc 1941(020016):1–7. https://doi.org/10.1063/1.5028074

Megawati, Fardhyanti DS, Sediawan WB, Hisyam A (2019) Kinetics of mace (*Myristicae arillus*) essential oil extraction using microwave assisted hydrodistillation: effect of microwave power. Ind Crops Pro 131:315–322. https://doi.org/10.1016/j.indcrop.2019.01.067

Meini M, Cabezudo I, Boschetti CE, Romanini D (2019) Recovery of phenolic antioxidants from Syrah grape pomace through the optimization of an enzymatic extraction process. Food Chem 283:257–264. https://doi.org/10.1016/j.foodchem.2019.01.037

Moraes MN, Zabot GL, Prado JM, Meireles AA (2013) Obtaining antioxidants from botanic matrices applying novel extraction techniques. J Food Public Health 3:196–214. https://doi.org/10.5923/j.fph.20130304.04

Naczk M, Towsend M, Zadernowski R, Shahidi F (2011) Protein binding and antioxidant potential of phenolics of mangosteen fruit (*Garcinia mangostana*). Food Chem 128(2):292–298. https://doi.org/10.1016/j.foodchem.2011.03.017

Nimse SB, Pal D (2015) Free radicals, natural antioxidants, and their reaction mechanisms. RSC Adv 5:27986–28006. https://doi.org/10.1039/C4RA13315C

Olalere OA, Abdurahman HN, Gan CY (2019) Microwave-enhanced extraction and mass spectrometry fingerprints of polyphenolic constituents in *Sesamun indicum* leaves. Ind Crop Prod 131:151–159. https://doi.org/10.1016/j.indcrop.2018.12.024

Palapol Y, Ketsa S, Stevenson D, Cooney JM, Allan AC, Ferguson IB (2009) Colour development and quality of mangosteen (*Garcinia mangostana* L) fruit during ripening and after harvest. Postharvest Biol Technol 51:349–353. https://doi.org/10.1016/j.postharvbio.2008.08.003

Pan X, Niu G, Liu H (2003) Microwave-assisted extraction of tea polyphenols and tea caffeine from green tea leaves. Chem Eng Process 42(2):129–133. https://doi.org/10.1016/S0255-2701(02)00037-5

Park JY, Kim DK, Lee JP, Park SC, Kim YJ, Lee JS (2008) Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresour Technol 99(5):1196–1203. https://doi.org/10.1016/j.biortech.2007.02.017

Paryanto, Suri AK, Saputro IR (2017) Difusi dan transfer massa pada ekstraksi tanin dari buah mangrove (*Rhizhopora stylosa*). Jurnal Rekayasa Bahan Alam dan Energi Berkelanjutan 1:42–48. https://doi.org/10.21776/ub.rbaet.2017.001.02.01

Pereira GG, Morales A, Marmesat S, Ruiz-Mendez MV, Barrera-Arellano D, Dobarganes MC (2015) Effect of temperature on the oxidation of soybean biodiesel. Grasas Aceites 66(2):e072. https://doi.org/10.3989/gya.0835142

Puri M, Sharma D, Barrow CJ (2012) Enzyme-assisted extraction of bioactives from plants. Trends Biotechnol 30(1):37–44. https://doi.org/10.1016/j.tibtech.2011.06.014

Ramalingam S, Rajendran S, Ganesan P, Govindasamy M (2018) Effect of operating parameters and antioxidant additives with biodiesels to improve the performance and reducing the emissions in a compression ignition engine – a review. Renew Sust Energ Rev 81:775–788. https://doi.org/10.1016/j.rser.2017.08.026

Ramaswamy HS, Marcotte M (2008) The grid: food processing: principles and applications. Taylor, Francis

Sayyar S, Abidin ZZ, Yunus R, Muhammad A (2009) Extraction of oil from jatropha seeds optimization and kinetics. Am J Appl Sci 6(7):1390–1395. https://doi.org/10.3844/ajassp.2009.1390.1395

Scott Fogler H (2016) The grid: elements of chemical reaction engineering, 5th ed. Prentice Hall

Spacino KR, Dionisio B, Gabriela MB, Leticia TC (2015) Determination of kinetic and thermodynamic parameters of the B100 biodiesel oxidation process in mixtures with natural antioxidant. J Fuel Proc Technol 137:366–370. https://doi.org/10.1016/j.fuproc.2015.05.006

Spacino KR, Silva ET, Angilelli K (2016) Relative protection factor optimisation of natural antioxidants in biodiesel B100. Ind Crop Prod 80:109–114. https://doi.org/10.1016/j.indcrop.2015.11.034

Sun J, Wang F, Sui Y, She Z, Zhai W, Wang C, Deng Y (2012) Effect of particle size on solubility, dissolution rate, and oral bioavailability: evaluation using coenzyme Q_{10} as naked nanocrystals. Int J Nanomedicine 7:5733–5744. https://doi.org/10.2147/IJN.S34365

Suttirak W, Manurakchinakorn S (2012) In vitro antioxidant properties of mangosteen peel extract. J Food Sci Technol 51(12):3546–3558. https://doi.org/10.1007/s13197-012-0887-5

Thirugnanasambandham K, Sivakumar V (2017) Microwave assisted extraction process of betalain from dragon fuit and its antioxidant activities. J Saudi Soc Agric Sci 16(1):41–48. https://doi.org/10.1016/j.jssas.2015.02.001

Tjahjani S, Widowati W, Khiong K (2014) Antioxidant properties of *Garcinia mangostana* L. (Mangosteen) rind. Proc Chem 13:198–203. https://doi.org/10.1016/j.proche.2014.12.027

Uslu N, Ozcan MM (2017) Effect of microwave heating on phenolic compounds and fatty acid compositions of cashew (*Anacardium occidentale*). J Saudi Soc Agric Sci. https://doi.org/10.1016/j.jssas.2017.10.001

Walker EB (2007) HPLC analysis of selected xanthones in mangosteen fruit. J Sep Sci 30 (9):1229–1234. https://doi.org/10.1002/jssc.200700024

Warsi Z, Sholichah AR (2017) Phytochemical screening and antioxidant activity of ethanolic extract and ethyl acetate fraction from basil leaf (*Ocimum basilicum* L) by DPPH radical scavenging method. In: IOP Conference Proceeding. IOP Conf Series: Materials Science and Engineering 259:012008. https://doi.org/10.1088/1757-899X/259/1/012008

Wibawanti J, Zulfanita Z, Runanto D (2019) The antioxidant activity of yogurt drink by mangosteen rind extract (*Garcinia mangostana* L). J Appl Food Technol 6(1):15–18. https://doi.org/10.17728/jaft.4267

Widyastuti CR, Dewi AC (2015) Sintesis biodiesel dari minyak mikroalga *Chlorella vulgaris* dengan reaksi transesterifikasi menggunakan katalis KOH. Jurnal Bahan Alam Terbarukan 4 (1):29–33. https://doi.org/10.15294/jbat.v3i1.3099

Xin J, Imahara H, Saka S (2009) Kinetics on the oxidation of biodiesel stabilized with antioxidant. J Fuel 88(2):282–286. https://doi.org/10.1016/j.fuel.2008.08.018

Zalacain A, Prodanov M, Carmona M, Alonso GL Optimisation of extraction and identification of gallotannins from sumac leaves. Biosyst Eng 84(2):211–216. https://doi.org/10.1016/S1537-5110(02)00246-5

Zarena AS, Udaya Sankar K (2009) Supercritical carbon dioxide extraction of xanthones with antioxidant activity from *Garcinia mangostana* characterization by HPLC/LC–ESI-MS. J Supercrit Fluid 49:330–337. https://doi.org/10.1016/j.supflu.2009.03.004

Zarena AS, Udaya Sankar K (2011) Xanthones enriched extracts from mangosteen pericarp obtained by supercritical carbon dioxide process. Separ Purif Technol 80:172–178. https://doi.org/10.1016/j.seppur.2011.04.027

Zhang QW, Lin LG, Ye WC (2018a) Techniques for extraction and isolation of natural products: a comprehensive review. Chin Med 13:20. https://doi.org/10.1186/s13020-018-0177-x

Zhang JJ, Li Y, Lin SJ, Li HB (2018b) Green extraction of natural antioxidants from the sterculia nobilis fruit waste and analysis of phenolic profile. Molecules 23(5):1059. https://doi.org/10.3390/molecules23051059

Zhou L (2013) The grid: reaction kinetics of biodiesel production by using low quality feedstock. Thesis, University of Regina

Ziaedini A, Jafari A, Zakeri A (2010) Extraction of antioxidants and caffeine from green tea (*Camelia sinensis*) leaves: kinetics and modeling. Food Sci Technol Int 16(6):505–510. https://doi.org/10.1177/1082013210367567

Zigoneanu IG, Williams L, Xu Z, Sabliov CM (2008) Determination of antioxidant components in rice bran oil extracted by microwave-assisted method. Bioresour Technol 99(11):4910–4918. https://doi.org/10.1016/j.biortech.2007.09.067