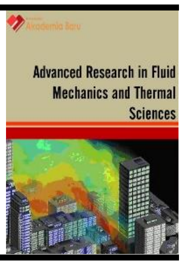
Journal of Advanced Research in Fluid Mechanics and Thermal Sciences 71, Issue 1 (2020) 39-49

Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



A Kinetic Study on *Tetraselmis chuii* Combustion: The Catalytic Impact of Nanoparticle *Titanium Dioxide* (TiO_2) Additive

Open Access

Ardianto Prasetiyo[1], Sukarni Sukarni[2,3,*], Retno Wulandari[2], Poppy Puspitasari[2]

[1] Master Program of Mechanical Engineering, Graduate School, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
[2] Center for Renewable and Sustainable Energy Engineering (CRSEE), Department of Mechanical Engineering, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
[3] Centre of Advanced Materials for Renewable Energy, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia

ARTICLE INFO

Article history:
Received 8 January 2020
Received in revised form 15 March 2020
Accepted 23 March 2020
Available online 30 April 2020

ABSTRACT

Due to the depletion of fossil fuel reserves and the increasing energy demand, biomass is a promising alternative as an alternative energy source. This study aims to investigate the catalytic effect of *Titanium dioxide* (TiO_2) nanoparticles on the thermal behavior and kinetic parameters of *Tetraselmis chuii* (*T.chuii*) microalgae during the combustion process in the thermal analyzer. TiO_2 amount of 0.05 mg was mixed with 10 mg microalgae biomass. The sample was heated up from room temperature until 900 ^{o}C with a heating rate of 15 ^{o}C/min and an atmosphere flow rate of 50 mL/min. The results indicated that the sample was decomposed into five stages throughout the escalation temperature. The addition of TiO_2 promoted each stage of decomposition toward the lower temperatures and shorter the combustion time. The activation energy value was analyzed using the *Arrhenius* method. The TiO_2 nanoparticle impacted in reducing the value of activation energy in stage II from 101.05 kJ/mol to 72.07 kJ/mol, and stage IV from 502.88 kJ/mol to 335.32 kJ/mol. The thermodynamic parameters included entropy, enthalpy and free Gibbs energy of mixed samples in stage II were -0.1396; 67.41 and 146.14 kJ/mol, respectively, and in stage IV were 0.1541; 328.31 and 203.68 kJ/mol, in that order. These results are practically proven that the addition of TiO_2 nanoparticles have been shortening the thermal process and reducing the value of activation energy.

Keywords:
Microalgae; *Tetraselmis chuii*, *Titanium dioxide*; Kinetic parameters; Thermodynamic parameters

1. Introduction

Along with the rapid expansion of the world industrialization, and the continued growth of the population, the amount of energy consumption is expected to increase quickly by 28% from 2015 until 2040 [1]. Current world energy requirements are completed by fossil fuels, specifically coal, natural gas, and crude oil [2]. The use of conventional energy sources continuously can affect the

* *Corresponding author.*
E-mail address: sukarni.ft@um.ac.id (Sukarni Sukarni)

https://doi.org/10.37934/arfmts.71.1.3949

declining amount of reserves which cannot be renewed. This problem has been attracted researchers to look for alternative energy sources that are sustainable and environmentally friendly. According to the International Energy Agency (IEA) 2018 [3], for the power generation sector, the share of renewable energy shows a positive growth rate and is prospective to increase toward 12.4% in 2023 [3]. Among these renewable energy alternatives, biomass has been becoming the most interesting choice due to it globally available. The microalgae biomass offers more beneficial compared to the terrestrial plant biomass, because of microalgae can produce 30-100 times more energy compared to the land plant [4], besides microalgae can absorb a large amount of CO_2 during the process of photosynthesis [5]. Moreover, 1% of the heat generated by a power plant boiler from microalgae biomass can reduce up to 0.48% of CO_2 emissions in the air [6]. Even though microalgae as an alternative fuel do not completely replace fossil fuels, but it can be an essential role in a global energy requirement and security [7].

Biomass thermochemical conversion processes such as torrefaction, pyrolysis, gasification, and combustion are considered as the main utilization techniques to convert biomass into biofuel with a high level of efficiency [8,9]. Direct combustion is a thermochemical technique for converting fuel to energy in the form of heat in the presence of air. This technique is more effective than the chemical extraction of biomass to be biodiesel [4], pyrolysis [10], torrefaction, and gasification [7,11]. The heat generated during the direct combustion is obtained from energy stored in biomass [12]. The direct combustion process has the advantage because it can convert solid fuel into heat directly without converting to another form. However, it has drawback regarding the lower heating value of biomass than the conventional fossil fuel, led to the same amount of energy, a greater volume of biomass will be needed, resulted in relatively high operational costs of biomass combustion [13]. Several studies have been performed for overcoming this drawback, including co-combustion of biomass with coal and utilization of additive as catalysts including zinc oxide, metal oxide, alkaline earth, and alkali metal [10,12,14]. A proper catalyst can reduce the decomposition temperature and activation energy of combustion and can increase the combustion reactivity [15-16].

The previous research by Jena, Das, and Kastner [17] revealed that utilization of Na_2CO_3, $Ca_3(PO_4)_2$ and NiO catalysts in the thermochemical liquefaction of *Spirulina platensis* microalgae could be increasing the yield of gas products. Sun, Zhao, and Su [18] studied the catalytic effect of Fe, Fe^{2+} and Fe^{3+} in the combustion of algal biomass (*Enteromorpha spp*, A*rgassum muticum* and *Chlorella sp*.). The result indicated that these additives reduce NO emissions in the combustion process, even though they play as an inhibitor. As so far, the effect of *Titanium dioxide* (TiO_2) on the combustion process of *Tetraselmis chuii* microalgae has not been explored by the researcher.

This study provides an in-depth understanding of the catalytic effects of TiO_2 nanoparticle to the combustion process of *Tetraselmis chuii* microalgae. The kinetic analysis is performed using a fitting model of the *Arrhenius* to determine kinetic parameters in the active zone of combustion, including activation energy (Ea), pre-exponential factor (A) and reaction order (*n*). In addition, the thermodynamic parameters that are enthalpies (ΔH, kJ/mol), change in free Gibbs energy (ΔG, kJ/mol) and the changes of entropy (ΔS, kJ/mol) are evaluated, as well. To understanding the catalytic impact of TiO_2 during combustion, these kinetic parameters are then compared with the kinetic parameters of pure *Tetraselmis chuii*.

2. Methodology
2.1 Raw Material

The sample (*Tetraselmis chuii* microalgae) was supplied from BBPBAP Jepara, Indonesia. This sample was cultured within eight days and then harvested by means of filtering through the siever and subsequently was deposited. The sediment sample was washing and swamping with distilled water for 6 hours in 2 times and then filtered again. Thereafter, microalgae sediments are dried in an oven at 80 ^oC for 24 hours to eliminate the water content. The microalgae hunks then were crushed with mortars and filtered in 60 mesh size to obtain the uniform sample.

2.2 TiO_2 Nanoparticle

Titanium dioxide (TiO_2) nanoparticle was used for additive in this study. TiO_2 is a transition metal oxide that has been extensively applied to various uses because it has stability and photoactivity properties [19]. This material obtains from Sigma Aldrich Singapore with a particle size of <25 nm. Around 0.05 mg of TiO_2 was mixed with 10 mg of microalgae by mechanical mixing technique in the mortar to homogenize the mixture. Finally, the sample mixture is dried in an oven at 80 ^oC for 14 hours.

2.3 Thermogravimetric Procedure

A sample of about 10.05 mg was placed in the crucible pan for thermogravimetric analysis (TGA). The experiment was carried out using the Mettler Toledo TG/DSC1. The test was carried out at a heating rate of 15 ^oC/min under an oxygen air (O_2) flowrate of 50 mL/min. The combustion experiment was performed from ambient temperature to 900 ^oC. During the experiment, the mass loss of the sample is recorded and plotted against the temperature to obtain the thermogravimetric (TG) graph. The mass-loss rate is obtained by the derivation of the mass loss to the time and resulted in the Derivative Thermogravimetric (DTG) graph. According to the TG and DTG graphs, the thermal characteristics of combustion can be determined.

2.4 Kinetic Analysis Methods

The thermal degradation of biomass during combustion can be modeled mathematically as presented in Eq. (1):

$$\frac{d\alpha}{(1-\alpha)^n} = \left(\frac{A}{\beta}\right) e^{\left(\frac{-E}{RT}\right)} dT \tag{1}$$

where $(\beta = dT/dt)$ is the heating rate. The changes in mass conversion due to the temperature escalation is expressed as the following:

$$\frac{d\alpha}{dT} = \frac{\propto_{T2} - \propto_{T1}}{T_2 - T_1} \tag{2}$$

where, α is the fractional conversion, given as:

$$\alpha = (m_i - m_t/m_i - m_\infty) \tag{3}$$

where; m_∞, m_t , m_i refer to the final residual amount at each stage, the mass at time t and the mass of biomass at the beginning, respectively. By taking the logarithm of Eq. (1) and rearranging, the final equation of the Arrhenius method is written as follows:

$$\ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (4)$$

where,
n is reaction order,
A is the frequency factor (l/min),
β is the heating rate ($^{o}C\ min^{-1}$),
E is the activation energy (kJ/mol),
R is the universal gas constant (8.314 J/mol $^{o}C^{-1}$) and
T is the absolute temperature (K).

For investigating the catalytic effects during thermal conversion process, the incremental mass loss after additive of TiO_2 (ΔM) was calculated as follow [14]:

$$\Delta m = m_c - m_w \quad (5)$$

where m_c is the mass loss of microalgae after TiO_2 addition and m_w is the mass loss of pure microalgae at uniform temperatures.

From the kinetics results, thermodynamic parameters such as enthalpies (ΔH) can be evaluated as follow [20] :

$$\Delta H = E_a - RT \quad (6)$$

In accordance with the values of activation energy (E) and the pre-exponential factors (A), the parameter of free Gibbs energy (ΔG) and entropy (ΔS) were calculated by the following Eqs. (7) and (8), respectively [21]:

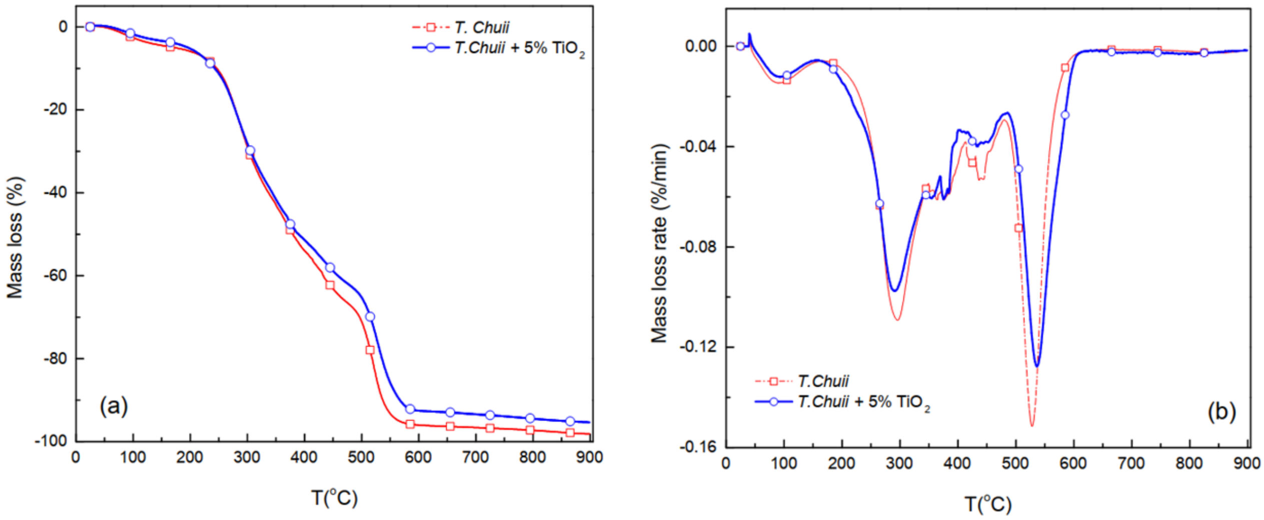
$$\Delta G = E_a + R.T_m.ln(\frac{K_B.T_m}{h.A}) \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (8)$$

where,
T_m is the maximum temperature of DTG peak (°C),
K_B is the Boltzmann constant (1.381 x 10-23 J.K^{-1}), and
h is planks constant (6.626 x 10-34 J.s).

3. Results and Discussion
3.1 Thermal Characteristic

Figure 1 shows the TG and DTG graphs of *Tetraselmis chuii* with and without TiO_2 during combustion at a heating rate of 15 °C/min. It can be seen from Figure 1 (TG and DTG graphs) that the thermal degradation of the sample has occurred in five stages. Stage I was taken place in the temperature range of 25-158 ^{o}C. In this stage, the first basin of the DTG graph was observed, indicated the release of moisture content and light volatile. Stage II was occurred in the temperature range of 158-343 ^{o}C, marked by the second basin of the DTG graph, indicated the release of volatile matter. This stage was followed by the transition of the char combustion process in stage III, at the temperature range of 343-478 ^{o}C. Stage IV was stretched at the temperature range of 478-625 ^{o}C, indicated the char combustion process and decomposition of fixed carbon. Stage V was the decomposition process of ash, appeared in the temperature range of 625-900 °C.



(a) (b)

Fig. 1. (a) TG and (b) DTG graph of *Tetraselmis chuii* with and without TiO_2

3.2 The Catalytic Effect of Tio₂ On Tetraselmis Chuii Combustion

The catalytic effect of TiO_2 on the combustion of *Tetraselmis chuii* microalgae is shown in the form of a ΔM graph in Figure 2.

It can be seen from Figure 2, the addition of TiO_2 to the *Tetraselmis chuii* microalgae shows a positive effect on the mass loss during the sample combustion. The initial influence process of TiO_2 started at a temperature range of 25 to 163 °C, in which the ΔM graph shows the upward direction, indicated that TiO_2 could promote the release of moisture content and light volatile in stage I. Then exceeding the temperature 163 °C, the graph declined up to temperature 241 °C, this indicated that the TiO_2 was played as an inhibitor for volatile matter decomposition process. This result is similar to the study of Liu *et al.,* [22], in which the addition of Al_2O_3 and CaO in the thermal process of coal showed occurrence a decrease of ΔM at the temperature range of 400-480 °C, then the additive affected the rising ΔM until to 800 °C, indicated that the additive promoted the conversion of organic matter in the thermal process by 7-11%.

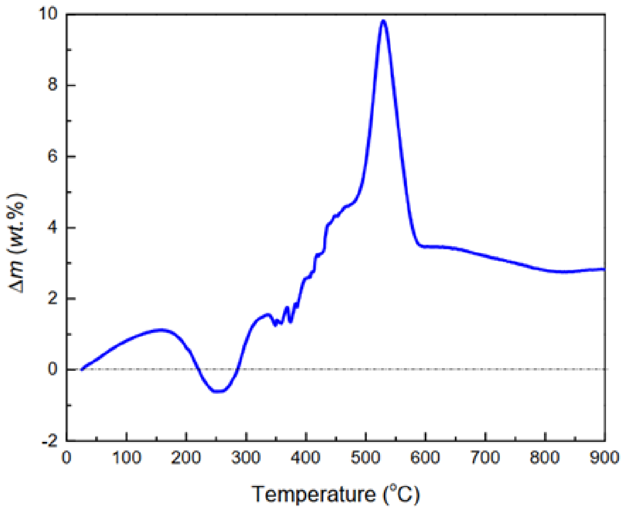


Fig. 1. The effect of TiO_2 in the combustion of microalgae

Referring back to Figure 2, it was observed that exceeding 241 °C, the ΔM value gradually increase until the temperature of 336 °C and significantly rises up until temperature 530 °C, which indicated that TiO_2 supported faster degradation of hemicellulose [23]. It means that TiO_2 to be an accelerator up to the temperature of 530 °C [24]. This overall result indicated that the addition of TiO_2 during the combustion of *Tetraselmis chuii* accelerated the decomposition process.

3.3 Kinetic Parameters

Table 1 presented the combustion parameters of *Tetraselmis chuii* with and without [25] TiO_2. It can be seen in Table 1 that the combustion of the sample with TiO_2 shifted to a lower temperature at each stage compare with the parent sample. Stage II was related to the decomposition of volatile matter, which was observed that the final combustion temperature shifted to the left (earlier) by 6 °C from 349 to 343 °C. Stage III was related to the transition process toward the char combustion, which was experiencing the shifted temperature from 480 to 478 °C. Stage IV was related to the char combustion process and fixed carbon decomposition, its final temperature shifted faster than pure microalgae by 15 °C from 640 to 625 °C.

Based on Table 1, the *Arrhenius* method was used for calculating the activation energy in this experiment. The evaluation was carried out on the active combustion zone in stages II, III and IV. Nevertheless, in stage III, the value of *n* cannot be determined, because, at every selected *n*, the value of R^2 was always rising up.

The biomass combustion can be described as a single step of the *n*th order reaction, which experiences thermal degradation in a certain temperature zone. The kinetic evaluation was performed at the conversion (α) range of 0.05-0.95. The *Arrhenius* expression was shown in Eq. (4) [26]:

$$\ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (4)$$

According to Eq. (4), plot $\ln(d\alpha/dT) - n\ln(1-\alpha)$ vs 1/T must provide a straight line for each *n* selected. To determine the appropriate *n* value in the active combustion zone (stages II and IV), several *n* values were selected, then used to determine the value of $\ln(d\alpha/dT) - n\ln(1-\alpha)$. The results were plotted with 1/T resulted in the value of the correlation coefficient (R^2). Plotted *n* vs R^2 helped to determine the most appropriate *n* value, which correlated with the highest R^2 as presented in Figure 3.

Table 1
The combustion parameters of *Tetraselmis chuii* with and without [25] TiO_2

Sample	Zone	Characteristic Temperature				
		T_s (°C)	T_p (°C)	T_f (°C)	M_{max} (°C)	Mass loss (%)
Tetraselmis chuii	II	174	296	349	-0.10923	-42.61
	III	349	375	480	-0.06116	-67.12
	IV	480	528	640	-0.15157	-96.29
Tetraselmis chuii + 5% TiO_2	II	158	291	343	-0.09753	-39.89
	III	343	375	478	-0.06099	-62.19
	IV	478	536	625	-0.12766	-92.76

T_s: Started Temperature; T_p: Maximum Peak Temperature; T_f: Ended Temperature; M_{ax} : Maximum Mass Loss Temperature

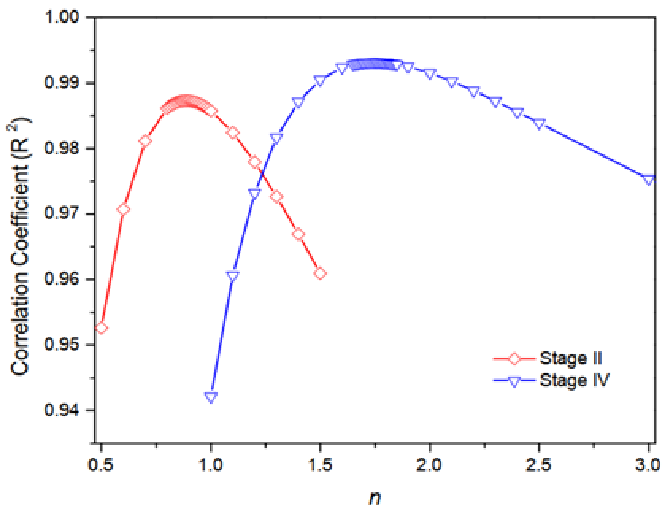


Fig. 2. The R^2-*n* curve for stage II and IV

Figure 3 indicated that the highest R^2 values in stage II and stage IV were 0.9873 and 0.9932 in correlation with the most appropriate *n* values of 0.89 and 1.75, respectively. These *n* values were subsequently used for determining the final plot of $\ln(d\alpha/dT) - n\ln(1-\alpha)$ vs 1/T, for producing a slope of $\left(\frac{-E}{R}\right)$ and intercept of $\left(\ln\left(\frac{A}{\beta}\right)\right)$ as presented in Figure 4. After obtaining slope $\left(\frac{-E}{R}\right)$ and intercept $\left(\ln\left(\frac{A}{\beta}\right)\right)$, activation energy ($E_a$) and pre-exponential factor (A) can be calculated for each stage, as presented in Table 2.

Table 2 shown the kinetics parameters of *Tetraselmis chuii* [25] and *Tetraselmis chuii* with TiO_2. The respective value of *n*, *A* and E for stage II were 0.89; 6.20/min and 72.075 kJ/mol, and for stage IV were 1.75; 21.21/min and 335.35 kJ/mol. The activation energy value in stage II that was 72,075 kJ/mol lower than *Spirulina platensis* at around 178-251 kJ/mol [27], lower than corn silk land plants that was 207.37 kJ/mol [28], but the value was greater than *Victorian brown* coal at around 30-34 kJ/mol [29], camellia shell at around 55-77 kJ/mol [30] and comparable to *T.suecica* microalgae that was at around 70.09 - 76.96 kJ/mol [29].

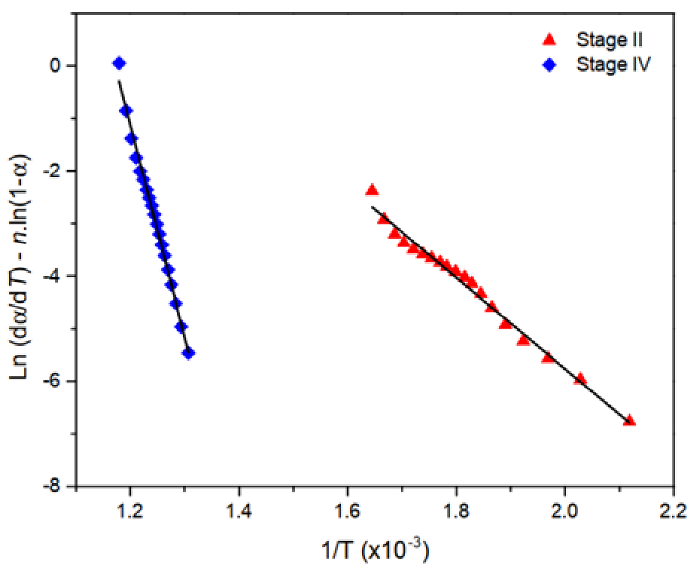


Fig. 3. The slope resulted in stage II and IV

Table 2
The kinetic parameters of *Tetraselmis chuii* with and without TiO_2

β (°C/min)	Sample	Zone	Trendline equation	R^2	Kinetics Parameters		
					E (kJ mol^{-1})	Log *A* (min^{-1})	*n*
15	*Tetraselmis chuii*	II	*y= -12155x + 18.017*	0.9819	101.05	9.00	1.24
		IV	*y= -60486x + 73.985*	0.9989	502.88	33.31	2.38
	Tetraselmis chuii + 5% TiO_2	II	*y= -8669.1x + 11.575*	0.9873	72.075	6.20	0.89
		IV	*y= -40332x + 47.272*	0.9932	335.32	21.71	1.75

The activation energy value in stage IV was 335.32 kJ/mol. This value is comparable to *C.vulgaris* microalgae that were 335.69 kJ/mol [31], but the value was greater than the sewage sludge that was 168.94 kJ/mol [32]. From the previous study observed that the value of the activation energy varied significantly in line with the different studied sample. These differences might be related to several factors including differences in various species of microalgae and biomass, culture time, harvest conditions, testing parameters such as heating rate, carrier gas flow rate, and sample weight.

For the same species and treatment, such as in this work, the addition of TiO_2 influenced the significant decreasing activation energy. In stage II, the activation energy value decreased from 101.05 kJ/mol (*Tetraselmis chuii*) to 72.075 kJ/mol (*Tetraselmis chuii* with TiO_2), decreased by 28.67 %. In stage IV, the activation energy value of *Tetraselmis chuii* was 502.88 kJ/mol declined by 33.32 % became 335.32 kJ/mol. In general, the addition of TiO_2 provides the ability to decrease the value of activation energy in the main combustion process. Thus, the smaller the value of the activation energy, the smaller the energy needed for a material to start a new reaction [27].

3.4 Thermodynamic Parameters

Table 3 presented the thermodynamic parameters of *Tetraselmis chuii* with and without TiO_2. As shown in Table 3, the entropy value ΔS stage II has a negative value of -0.1396 kJ/mol; which demonstrated that the initial substance was less organized compared to the activated complex [33]. The addition of 5% TiO_2 resulted in the positive value of ΔS in stage IV, indicated that TiO_2 promoted the initial substance more organized.

Table 3 also revealed that stage II requires enthalpy ΔH that was 67.41 kJ/mol lower than stage IV that was 328.31 kJ/mol. Stage IV that has large enthalpy value indicated more energy at each mass conversion is needed to decompose the sample [20].

Free Gibbs energy ΔG in stages II and IV were 146.15 and 203.68 kJ/mol, respectively. This value is higher than the red pepper waste that varied in the ranging of 71.77-207.03 kJ/mol [34]. The change in free Gibbs energy shows an increase in the energy of the total system in the reactants [20].

Table 3
The parameters of thermodynamic of *Tetraselmis chuii* with and without TiO_2

Sample	Zone	Ea (kJ/mol)	A (1/min)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol)
Tetraselmis chuii	II	101.05	1.00+08	96.34	175.85	-0.1397
	IV	502.88	2.03+33	496.38	610.64	-0.1426
Tetraselmis chuii + 5% TiO_2	II	72.075	1.59E+06	67.41	146.15	-0.1396
	IV	335.32	5.08E+21	328.31	203.68	0.1541

4. Conclusions

Tetraselmis chuii combustion with and without TiO_2 has been studied under the thermogravimetric analyzer. The stages of decomposition in the active combustion zone occurred in stages II, III and IV from the whole of five stages. The addition of TiO_2 influenced the significant decreasing activation energy. In stage II, TiO_2 decreased the activation energy by 28.67 %. In stage IV, TiO_2 also declined the activation energy value of *Tetraselmis chuii* by 33.32 %. The thermodynamic parameters of *Tetraselmis chuii* with TiO_2, include entropy ΔS, enthalpy ΔH and free Gibbs energy ΔG for stage II were -0.1396; 67.41 and 146.15 kJ/mol and stage IV were 0.1541; 328.31 and 203.68 kJ/mol, respectively. The overall result indicated that TiO_2 played key role in accelerating the combustion process of *Tetraselmis chuii* microalgae.

Acknowledgment
The author would like to thank the Ministry of Research, Technology and Higher Education, Indonesia, for supporting this research through the Magister Thesis Research Program with grant's number 074/SP2H/LT/DRPM/2019.

References
[1] Quah, Ray Vern, Yie Hua, N M Mubarak, Mohammad Khalid, E C Abdullah, and Cirilo Nolasco-hipolito. "An Overview of Biodiesel Production Using Recyclable Biomass and Non- Biomass Derived Magnetic Catalysts." *Journal of Environmental Chemical Engineering* 7, no. 4 (2019): 103219. https://doi.org/10.1016/j.jece.2019.103219
[2] U S, Energy Information Administration. "International Energy Outlook 2017 Overview." (2017).
[3] IEA, International Energy Agency. "Renewables 2O18 Analysis and Forecasts to 2023." (2018).
[4] Yusuf, Chisti. "Biodiesel from Microalgae." *Biotechnology Advances* 25, no. 3 (2007): 294–306. https://doi.org/10.1016/j.biotechadv.2007.02.001
[5] Demirbas, Ayhan. "Biodiesel from Oilgae , Biofixation of Carbon Dioxide by Microalgae : A Solution to Pollution Problems." *Applied Energy* 88, no. 10 (2011): 3541–3547. https://doi.org/10.1016/j.apenergy.2010.12.050
[6] Giostri, A, M Binotti, and E Macchi. "Microalgae Co Fi Ring in Coal Power Plants : Innovative System Layout and Energy Analysis." *Renewable Energy* 95 (2016): 449–464. https://doi.org/10.1016/j.renene.2016.04.033
[7] Safar, Michal, Bo-Jhih Lin, Wei-Hsin Chen, David Langauer, Jo-Shu Chang, H. Raclavska, Anélie Pétrissans, Patrick Rousset, and Mathieu Pétrissans. "Catalytic effects of potassium on biomass pyrolysis, combustion and torrefaction." *Applied Energy* 235 (2019): 346-355. https://doi.org/10.1016/j.apenergy.2018.10.065
[8] Guo, Feiqiang, Yuan Liu, Yan Wang, Xiaolei Li, Tiantao Li, and Chenglong Guo. "Pyrolysis Kinetics and Behavior of Potassium-Impregnated Pine Wood in TGA and a Fixed-Bed Reactor." *Energy Conversion and Management* 130 (2016): 184–191. https://doi.org/10.1016/j.enconman.2016.10.055
[9] Lo, Shang-lien, Yu-fong Huang, Pei-te Chiueh, and Wen-hui Kuan. "Microwave Pyrolysis of Lignocellulosic Biomass." *Energy Procedia* 105 (2017): 41–46. https://doi.org/10.1016/j.egypro.2017.03.277
[10] Zhou, Leiyu, Hongmin Yang, Hao Wu, Meng Wang, and Daqian Cheng. "Catalytic pyrolysis of rice husk by mixing with zinc oxide: Characterization of bio-oil and its rheological behavior." *Fuel processing technology* 106 (2013): 385-391. https://doi.org/10.1016/j.fuproc.2012.09.003
[11] Sanchez-Silva, L., D. López-González, A. M. Garcia-Minguillan, and J. L. Valverde. "Pyrolysis, Combustion and Gasification Characteristics of Nannochloropsis Gaditana Microalgae." *Bioresource Technology* 130 (2013): 321–331. https://doi.org/10.1016/j.biortech.2012.12.002
[12] Azizi, Kolsoom, Mostafa Keshavarz Moraveji, and Hamed Abedini Najafabadi. "A review on bio-fuel production from microalgal biomass by using pyrolysis method." *Renewable and Sustainable Energy Reviews* 82 (2018): 3046-3059.

https://doi.org/10.1016/j.rser.2017.10.033
[13] Liu, Jingyong, Limao Huang, Guang Sun, Jiacong Chen, Shengwei Zhuang, Kenlin Chang, Wuming Xie, Jiahong Kuo, Yao He, Shuiyu Sun, Musa Buyukada, and Fatih Evrendilek. " (Co-)combustion of Additives, Water Hyacinth and Sewage Sludge: Thermogravimetric, Kinetic, Gas and Thermodynamic Modeling Analyses." *Waste Management* 81 (2018): 211–219.
https://doi.org/10.1016/j.wasman.2018.09.030
[14] Xu, Qing, Xiaoqian Ma, Zhaosheng Yu, and Zilin Cai. "A Kinetic Study on the Effects of Alkaline Earth and Alkali Metal Compounds for Catalytic Pyrolysis of Microalgae Using Thermogravimetry." *Applied Thermal Engineering* 73, no. 1 (2014): 355–359.
https://doi.org/10.1016/j.applthermaleng.2014.07.068
[15] Guo, Qiang, Youzhi Liu, Guisheng Qi, and Weizhou Jiao. "Study of low temperature combustion performance for composite metal catalysts prepared via rotating packed bed." *Energy* 179 (2019): 431-441. https://doi.org/10.1016/j.energy.2019.05.033
[16] Wang, Hui, Wei Yang, Penghui Tian, Jie Zhou, Rui Tang, and Shengji Wu. "A highly active and anti-coking Pd-Pt/SiO2 catalyst for catalytic combustion of toluene at low temperature." *Applied Catalysis A: General* 529 (2017): 60-67.
https://doi.org/10.1016/j.apcata.2016.10.016
[17] Jena, Umakanta, K. C. Das, and J. R. Kastner. "Comparison of the effects of Na2CO3, Ca3 (PO4) 2, and NiO catalysts on the thermochemical liquefaction of microalga Spirulina platensis." *Applied energy* 98 (2012): 368-375.
https://doi.org/10.1016/j.apenergy.2012.03.056
[18] Sun, Jin, Bingtao Zhao, and Yaxin Su. "Advanced Control of NO Emission from Algal Biomass Combustion Using Loaded Iron-Based Additives." *Energy* 185 (2019): 229–238.
https://doi.org/10.1016/j.energy.2019.07.042
[19] Muhammad Syahizul Aidi, Berahim, Mohd Fadhil Majnis, and Taib Mustaffa Ali Azhar. "Formation of Titanium Dioxide Nanoparticles by Anodization of Valve Metals." *Progress in Energy and Environment* 7 (2019): 11–19.
[20] Kim, Yong Sang, Young Seok Kim, and Sung Hyun Kim. "Investigation of Thermodynamic Parameters in the Thermal Decomposition of Plastic Waste-Waste Lube Oil Compounds." *Environmental Science and Technology* 44, no. 13 (2010): 5313–5317.
https://doi.org/10.1021/es101163e
[21] Xu, Yiliang, and Baoliang Chen. "Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis." *Bioresource technology* 146 (2013): 485-493.
https://doi.org/10.1016/j.biortech.2013.07.086
[22] Liu, Quanrun, Haoquan Hu, Qiang Zhou, Shengwei Zhu, and Guohua Chen. "Effect of Inorganic Matter on Reactivity and Kinetics of Coal Pyrolysis." *Fuel* 83, no. 6 (2004): 713–718.
https://doi.org/10.1016/j.fuel.2003.08.017
[23] Shao, Jingai, Rong Yan, Hanping Chen, Haiping Yang, and Dong Ho Lee. "Catalytic Effect of Metal Oxides on Pyrolysis of Sewage Sludge." *Fuel Processing Technology* 91, no. 9 (2010): 1113–1118. https://doi.org/10.1016/j.fuproc.2010.03.023
[24] Ba-Abbad, Muneer M., Abdul Amir H. Kadhum, Abu Bakar Mohamad, Mohd S. Takriff, and Kamaruzzaman Sopian. "Synthesis and catalytic activity of TiO2 nanoparticles for photochemical oxidation of concentrated chlorophenols under direct solar radiation." *Int. J. Electrochem. Sci* 7, no. 6 (2012): 4871-4888.
[25] Prasetiyo, Ardianto, Sukarni Sukarni, Retno Wulandari, Heru Suryanto, and Uun Yanuhar. "Investigation on Kinetic Parameters during Combustion of Tetraselmis Chuii Microalgae under Thermogravimetric Analyzer." (2019).
[26] Acikalin, Korkut. "Pyrolytic Characteristics and Kinetics of Pistachio Shell by Thermogravimetric Analysis." *Journal of Thermal Analysis and Calorimetry* 109, no. 1 (2012): 227–235.
https://doi.org/10.1007/s10973-011-1714-3
[27] Sukarni, Sudjito, Nurkholis Hamidi, Uun Yanuhar, and I. N.G. Wardana. "Thermogravimetric Kinetic Analysis of Nannochloropsis Oculata Combustion in Air Atmosphere." *Frontiers in Energy* 9, no. 2 (2015): 125–133. https://doi.org/10.1007/s11708-015-0346-x
[28] Sumarli, Sumarli, Citrakara Upendra Sneha Bandhana Kusuma Himawan, Retno Wulandari, and Sukarni Sukarni. "Physicochemical characteristics of corn silk as biomass fuel feedstock." In *IOP Conference Series: Materials Science and Engineering*, vol. 515, no. 1, p. 012103. IOP Publishing, 2019.
https://doi.org/10.1088/1757-899X/515/1/012103
[29] Tahmasebi, Arash, Mohd Asyraf Kassim, Jianglong Yu, and Sankar Bhattacharya. "Thermogravimetric Study of the Combustion of Tetraselmis Suecica Microalgae and Its Blend with a Victorian Brown Coal in O2/N2 and O2/CO2 Atmospheres." *Bioresource Technology* 150 (2013): 15–27.
https://doi.org/10.1016/j.biortech.2013.09.113
[30] Wang, Mingfeng, Zhiwen Chen, Juan Lv, Yongzhi Ren, Yang Jiang, Enchen Jiang, and Donghai Wang. "Combustion

characteristics and kinetic analysis of heavy tar from continuous pyrolysis of camellia shell." *Fuel Processing Technology* 176 (2018): 131-137. https://doi.org/10.1016/j.fuproc.2018.03.015

[31] Chen, Chunxiang, Xiaoqian Ma, and Yao He. "Co-Pyrolysis Characteristics of Microalgae Chlorella Vulgaris and Coal through TGA." *Bioresource Technology* 117 (2012): 264–273. https://doi.org/10.1016/j.biortech.2012.04.077

[32] Lin, Yan, Yanfen Liao, Zhaosheng Yu, Shiwen Fang, and Xiaoqian Ma. "The Investigation of Co-Combustion of Sewage Sludge and Oil Shale Using Thermogravimetric Analysis." *Thermochimica Acta* 653 (2017): 71–78. https://doi.org/10.1016/j.tca.2017.04.003

[33] Xu, Feng, and Donghai Wang. "Rapid determination of sugar content in corn stover hydrolysates using near infrared spectroscopy." *Bioresource technology* 147 (2013): 293-298. https://doi.org/10.1016/j.biortech.2013.08.071

[34] Maia, Amanda Alves Domingos, and Leandro Cardoso de Morais. "Kinetic parameters of red pepper waste as biomass to solid biofuel." *Bioresource Technology* 204 (2016): 157-163. https://doi.org/10.1016/j.biortech.2015.12.055