

# Thermal Decomposition and Kinetic Study of Empty Fruit Bunch Derived Hydrochar Produced from Hydrothermal Carbonization and Washing Processes

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**Abstract**—Hydrothermal carbonization (HTC) and water washing are recognized as effective treatment processes for improving fuel properties of oil-palm empty fruit bunch (EFB). This study aims to investigate the effect of pilot-scale HTC and water washing on thermal decomposition of EFB under inert atmosphere. In experiments, Raw-EFB was hydrothermally treated at 200 °C and 2.0 MPa for 30 min. Then, water washing was performed at room temperature. The washed EFB-derived hydrochar (HTW-EFB) was evaluated in regards to its fuel properties, the results revealed that the HTC and water washing can improve fuel properties by reducing moisture and potassium contents. The thermal decomposition characteristic of the Raw-EFB and HTW-EFB were studied by the thermogravimetric analysis and kinetic study. The ignition temperature of HTW-EFB was increased from 240 to 298 °C. The burnout temperature was approximately 556-580 °C. From the two-stages kinetic study, the activation energy of HTW-EFB was higher than that of the Raw-EFB in devolatilization stage whereas exhibited the lower value in char decomposition stage. The weighted average activation energy of Raw-EFB and HTW-EFB were 55.36 and 58.60 kJ/mol, respectively.

**Keywords**—Hydrothermal carbonization, water washing, thermal decomposition, thermogravimetric analysis, kinetic study.

## I. INTRODUCTION

Nowadays, the quantity of agricultural residues has been rapidly increased due to industry expansion. Oil-palm empty fruit bunch (EFB) is one of the most agricultural wastes generated, especially in Southeast Asia [1]. In 2019, the oil palm production in Southeast Asia is accounting for 88.2%, and 1 ton of oil palm production generates approximately 20-25% of EFB. This waste may cause problems due to improper disposal. However, the utilization of EFB as fuel for energy application has been widely studied these days. The EFB has a high

potential as a carbon source, but not so efficient to be used as feedstock in combustion technologies. This is because of several poor fuel properties, such as high moisture content, low heating value, and high alkaline content [1-3]. Therefore, the pretreatment is essential to improve the fuel properties. Hydrothermal carbonization (HTC) is an effective technology that utilized subcritical water to break down the structure of biomass under a certain pressure and temperature [4,5]. In addition, water washing is a fascinating alternative process to remove alkali and alkaline earth metals (AAEMs) in EFB, such as potassium (K). Ruksathamcharoen et al. [2] reported that the HTC and water washing significantly improved the fuel properties of EFB, and also affected the combustion characteristic under the O<sub>2</sub> atmosphere. Nyakuma et al. [6] studied the thermal decomposition of EFB pellets under N<sub>2</sub> environment, and reported that the pretreatment and pelletization of EFB can potentially improve its biofuel properties for pyrolysis.

To investigate the effect of HTC and water washing on EFB fundamental thermal behavior under inert atmosphere, the comparative study on thermal decomposition characteristics of Raw-EFB and HTW-EFB was performed in this research by the thermogravimetric analysis (TGA) and kinetic study. Understanding the kinetics of thermal decomposition, such as the ignition and the burnout temperature, is useful for a handling process, co-firing, and process performance prediction, based on the estimation of reactivity parameters.

## II. MATERIAL AND METHODS

### A. Raw material

Raw-EFB was obtained from Suksomboon Palm Oil Co., Ltd. (Chonburi, Thailand). Firstly, the sample was chopped into pieces as a long fibrous form. Then, it was sun-dried for 48 h and kept for the HTC experiment. For fuel analysis, the sample was collected, dried in an electric oven at 105 °C for 12 h, grinded into powder and kept for further analysis.

### B. Hydrothermal carbonization and water washing process

A pilot-scale HTC was performed in a 1 m<sup>3</sup> cylindrical batch-type reactor, which was schematically shown in Fig. 1. In the experiments, Raw-EFB were supplied into the reactor. After the reactor was sealed, saturated steam was injected until the temperature and pressure reached about 200 °C and 2.0 MPa, respectively. The process was operated with a holding time of

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30 min. The sample was continuously mixed by a stirrer with a mixing speed of 20 rpm during the process. After finishing the process, the products were collected from the reactor through a drain valve. Finally, the solid products (hydrochar) were separated using a centrifuge.

In the pilot-scale washing experiment, HTC-EFB were mixed with distilled water by water to product ratio of 10:1. The sample was kept stirring using an automatic stirrer with a mixing speed of 400 rpm. The operating temperature was 25 °C with a holding time of 30 min. After washing, the dewatering process was carried out using the centrifuge. Finally, the obtained products were naturally dried with an average temperature of 32 °C for 24 h.

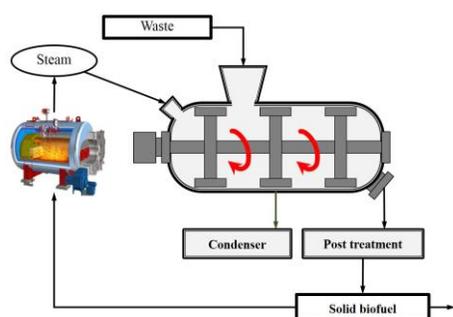


Fig. 1. Diagram of hydrothermal carbonization pilot plant

### C. Analytical techniques

HTW-EFB were dried at 105 °C for 12 h in a hot air oven and pulverized before the analysis. The proximate and ultimate analysis were analyzed on a dry basis using a thermogravimetric analyzer (Model TGA701, LECO) according to the ASTM D7582 and elemental analyzer (Model Thermo Flash 2000), respectively. The metal contents were determined by an X-ray fluorescence spectrometer (WDXRF) (Model S8 TIGER, BRUKER). The high heating value (HHV, dry basis) was measured by the Leco's AC600 Bomb Calorimeter using the ASTM D5865 Standard Test Method for Gross Calorific Value of Coal and Coke.

### D. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of Raw-EFB and HTW-EFB were performed by thermogravimetric analyzer (Netzsch, STA 449 Jupiter). At first, the samples were milled and sieved then, dried in the oven at 105 °C for 12 h to prevent the effect of inherent moisture. In each test, approximately 5 mg of sample was loaded into a crucible. To minimize the heat transfer limitation, the sample was heated from the room temperature to 800 °C at a heating rate of 10 °C/min and N<sub>2</sub> was constantly supplied at a flow rate of 40 ml/min. The sample weight loss was continuously collected as the function of time and temperature. The experiments were performed at least twice. Several repetitions were carried out when some variability occurred.

### E. Kinetic study

The activation energy ( $E$ ), the pre-exponential factor ( $A$ ), and the kinetic parameters were evaluated to study the effect of

HTC and water washing on the EFB thermal behavior. The thermal decomposition can be expressed as

$$d\alpha / dt = k(T)f(\alpha) \quad (1)$$

where  $da/dt$  is the reaction rate,  $f(\alpha)$  is a model of the reaction regarding the solid-state reaction [7],  $\alpha$  is the mass decomposition ratio of the sample at time  $t$  which is estimated by

$$\alpha = (m_i - m_t) / (m_i - m_f) \quad (2)$$

where  $m_i$  is the initial mass of the sample,  $m_t$  is the mass of the sample at time  $t$ , and  $m_f$  is the final mass of the sample.  $k(T)$  is the temperature-dependent rate constant, which generally describes through the Arrhenius equation [8,9]

$$k(T) = A \exp(-E / RT) \quad (3)$$

where  $A$  is the pre-exponential factor,  $E$  is the activation energy, and  $R$  is the universal gas constant (8.314 J/mol·K). A mathematical term of the constant heating rate ( $\beta$ ) is expressed as

$$\beta = dT / dt \quad (4)$$

Then, Equation (3) and (4) were substituted to Equation (1), rearranged in the general form, and integrated; which gives

$$g(\alpha) = \int_0^\alpha d\alpha / f(\alpha) = (A / \beta) \int_{T_0}^T \exp(-E / RT) dT \quad (5)$$

where  $g(\alpha)$  is an integral function of the reaction model. To evaluate the kinetic parameters, the temperature integral term in Equation (5) was calculated according to the Coats-Redfern approximation [10], the equation becomes:

$$\ln(g(\alpha) / T^2) = \ln(AR / \beta E)(1 - 2RT / E) - (E / RT) \quad (6)$$

Since the term  $(1 - 2RT / E)$  was approximately equal to 1. Therefore,

$$\ln(g(\alpha) / T^2) = \ln(AR / \beta E) - (E / R)(1 / T) \quad (7)$$

The plot of  $\ln(g(\alpha) / T^2)$  against  $(1 / T)$  will give a straight line whose slope equals to  $-E / R$ . Thus, the  $E$  and  $A$  can be calculated using the slope and the intercept, respectively. A suitable  $g(\alpha)$  model of each material is based on the major mechanism and the particle shape of the material. To find out the optimum  $g(\alpha)$  model, the possible reaction models applied in this study are shown in Table I, which are the first-order reaction (O1), the second-order reaction (O2), the third-order reaction (O3), and the diffusion (D1, D2, and D3) models. Under both inert and oxidizing environments, O1 is able to

investigate the thermal degradation of biomass. On the condition that the reactions go along with the reaction order model, the reaction rate is controlled by the chemical reaction. For the diffusion models, D1 is used for the concentration gradient is restricted to one dimension of mass transport while D2 and D3 demonstrate as the two-dimensional cylindrical and three-dimensional spherical diffusion mechanism, respectively.

TABLE I: THE REACTION MODELS AND THE EXPRESSION OF INTEGRAL OF REACTION MODELS USED IN THIS STUDY.

Reaction model	$g(\alpha)$
Reaction order model	
First-order reaction (O1)	$-\ln(1-\alpha)$
Second-order reaction (O2)	$[1/(1-\alpha)]-1$
Third-order reaction (O3)	$(1/2)[(1-\alpha)^{-2}-1]$
Diffusion reaction model	
One-dimensional diffusion (D1)	$-\alpha^2$
Two-dimensional diffusion (D2)	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (D3)	$[1-(1-\alpha)^{3/2}]^2$

### III. RESULT AND DISCUSSION

#### A. Effect of HTC and washing on fuel properties

As indicated in Table II, it was clearly shown that the fixed carbon (FC) and ash content of HTW-EFB were both increased whereas the volatile matter (VM) was relatively decreased. The loss of VM is mostly ascribed to the hydrolysis of organic and volatile matters during the HTC [4]. The HTC also caused an increasing of carbon content but the washing process reduced the carbon content. This due to the absorption of organic molecules during washing process [11]. Hydrogen, nitrogen, and oxygen were also decreased, the reduction in the weight ratio of oxygen can be observed and this contributed to the higher energy content in the product [12].

TABLE II: SOLID FUEL PROPERTIES OF EFB.

Items	Sample	
	Raw-EFB	HTW-EFB
Proximate analysis (%)		
Ash	2.5	7.7
Volatile matter	81.9	67.1
Fixed carbon	15.6	25.2
Ultimate analysis (%)		
Carbon	52.2	51.1
Hydrogen	7.0	6.9
Nitrogen	9.8	9.3
Oxygen	28.5	25.0
HHV(MJ/kg)	18.5	21.5

\*HHV = Higher heating value

Table II also shows the higher heating values (HHV) of Raw-EFB and HTW-EFB, which were 18.5 and 21.5 MJ/kg, respectively. The HHV of HTW-EFB was slightly increased from Raw-EFB due to the ratio of the FC, which gives considerably higher energy content compared to the VM. This

related to the improvement of the energy density of HTW-EFB.

Metal contents of Raw-EFB and HTW-EFB are summarized in Table III. The potassium (K) and chlorine (Cl) contents of HTW-EFB were decreased approximately 90% and 80% from Raw-EFB, respectively. It was noticeable that the HTC and washing process significantly reduced the metal contents especially, K. This because the water-soluble K is greatly released during the water washing process as well as the water-soluble Cl [4,13-16]. In contrast, other metal contents, such as silicon (Si), calcium (Ca), and iron (Fe) were slightly increased after treatments. This phenomenon can be also observed in previous studies [2,14,17,18]. The increase of some metal contents could be as a result of the limited of metal removal and the higher surface area of hydrochar, which is enhanced the cation reabsorption from the water during hydrothermal process [15]. It also depends on the existing linking of the metal in the structure of biomass [14]. Nevertheless, the water washing helps to relieve the ash deposition problems that caused the lower heat transfer efficiency [2,13,14,17].

#### B. Effect of HTC and washing on thermal decomposition

The weight loss and rate of weight loss of samples are shown throughout the TG and DTG profiles in Fig. 2. Thermal decomposition can be distinguished into three main stages. The first stage (S1) took place at the temperature range of 35-147 °C with approximately 8% and 5% weight loss for Raw-EFB and HTW-EFB, respectively. The weight loss in the S1 represents the loss of moisture content in the sample through evaporation as well as light volatiles. In the second stage (S2), most of the organic volatiles were lost which occurred at the temperature between 169-360 °C, caused by the decomposition of hemicellulose, cellulose, and some lignin [19]. The weight loss of Raw-EFB and HTW-EFB in S2 were approximately accounted for 64% and 47%, respectively. The lower weight loss of HTW-EFB is consistent with the decrease in VM, resulting from the HTC and washing process. During the third stage (S3), the decomposition of carbonaceous materials and inorganic compounds in char occurred at the temperature range of 360-580 °C. The weight loss of Raw-EFB was 20% while HTW-EFB was 40% at this stage. As illustrated in Fig. 2, the TG and DTG curves of both samples demonstrated a similar trend due to the slight decomposition of VM before 200 °C. Then, a shift in the DTG curves can be observed and the DTG peaks of HTW-EFB was higher and narrower than that of the Raw-EFB, resulting from the decrease in the reactivity [2]. This shift was also observed in the maximum weight loss temperature at S2 ( $T_2$ ), from 282 to 327 °C as shown in Table IV. This is because HTC and water washing are effective in removing K, which can be a catalyst to enhance the decomposition of VM at lower temperatures [16,20]. In addition, the ignition temperature ( $T_i$ ) of HTW-EFB was higher than that of the raw material, which were 298 and 240 °C, respectively, showing the improvement of fuel property.

TABLE III: THE METAL CONTENTS OF EFB.

Mineral %	Si	Ca	Fe	Mg	K	Cl	S	Al	Na	P	Ti	Zn	Cu	Mn	Cr	Sr
Raw-EFB	1.10	0.67	0.11	0.30	1.83	0.39	0.15	0.05	0.03	0.17	0.00	0.00	0.00	0.01	0.01	0.00
HTW-EFB	1.51	0.94	0.24	0.13	0.18	0.08	0.17	0.09	0.02	0.17	0.01	0.00	0.01	0.01	0.00	0.00

In S3, the DTG curve of Raw-EFB was divided into two parts, which were a shoulder and peak occurred during S3a (334-421 °C) and S3b (421-518 °C), respectively. It was found out that the maximum weight loss temperature at S3 ( $T_3$ ) of HTW-EFB was 417 °C while Raw-EFB was 457 °C. Moreover, HTW-EFB exhibited the lower volatile release temperature ( $T_v$ ) and the higher burnout temperature ( $T_b$ ) as compared to Raw-EFB. In the DTG profile of HTW-EFB, a small peak in the temperature range of 747-780 °C was detected as a result of the decomposition of inorganic carbonates, such as calcium carbonate and other minerals [21], which was increased after HTC. The enlarged retention of some cations due to the enhancement of the cation exchange capacity of hydrochar [15]. It was noted that  $T_b$  was determined regardless of the decomposition of carbonate minerals.

### C. Kinetic study

The thermal decomposition behavior of EFB and washed-hydrochar product exhibited the three main stages with different characteristics. In this kinetic study, the possible reaction models listed in Table I were applied to evaluate the activation energy ( $E$ ) and the pre-exponential factor ( $A$ ). The models that yielded the highest correlation coefficient could be the representative reaction in each stage. It was assumed that the inherent moisture evaporation and the inorganic substances decomposition, such as calcium carbonate were negligible. Therefore, only the thermal decomposition in S2 and S3 were focused.

Table V shows the evaluation temperature range of each stage chose from the DTG profiles. S2 was started from the point that the weight loss rate was higher than 0.2 %/min to the end of the peak. S3 was started at the S2 temperature ended and then terminated at  $T_b$ . The O1, O3, and D3 models yielded the highest  $R^2$ .

TABLE IV: ESSENTIAL CHARACTERISTIC PARAMETERS.

Sample	$T_v$ (°C)	$T_i$ (°C)	$T_2$ (°C)	DTG <sub>2</sub> (%/min )	$T_3$ (°C)	DTG <sub>3</sub> (%/min )	$T_b$ (°C)
Raw-EFB	173	240	282	0.7	457	0.4	556
HTW-EFB	169	298	327	0.7	417	0.3	580

The kinetic parameters were summarized in Table V. Furthermore, the plotting results of those models that gave the highest  $R^2$  are also illustrated in Fig. 3. As indicated in Table V, O1 and D3 models displayed the high correlation coefficients for S2, which was the devolatilization stage. Hence, both O1 and D3 can represent the mechanism in this stage. The  $E$  values of Raw-EFB and HTW-EFB according to O1 were 43.93 and 52.90 kJ/mol, respectively while D3 were 89.17 and 108.58 kJ/mol, respectively. It was clearly shown that the  $E$  values of HTW-EFB for both models were higher than that of Raw-EFB. This can be attributed to the effect of water washing on the release of AAEMs, and the removal of unstable volatile matters during HTC [2,22,23]. In addition to the reduction of AAEMs as the catalyst of the decomposition of volatile compounds, the thermal decomposition under the  $N_2$  atmosphere is an endothermic process which heat is required to convert the hemicellulose, cellulose, and lignin into released volatile gases.

In S3, the DTG profiles of Raw-EFB had a shoulder and peak whereas HTW-EFB presented only one peak. The reaction in S3 was distinguished into two independent ranges (S3a and S3b), where S3a indicated the shoulder while S3b represented the peak. As for the thermal decomposition of Raw-EFB, O3 and D3 models exhibited the high  $R^2$  values in S3a while O1 and D3 models presented the high  $R^2$  values in S3b. The  $E$  values were 31.34, 16.49, 45.07, and 60.00 kJ/mol for S3a-O3, S3a-D3, S3b-O1, and S3b-D3, respectively.

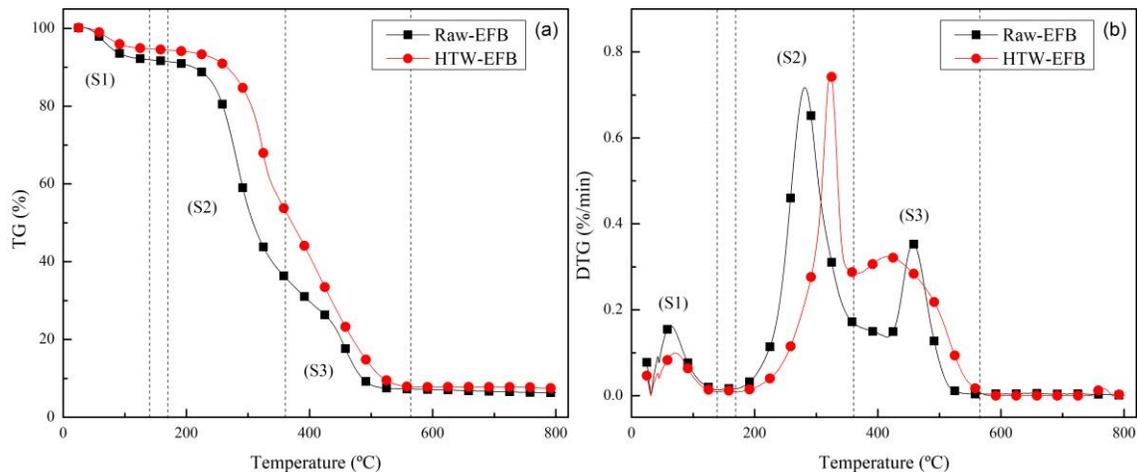


Fig. 2. TG (a) and DTG (b) profiles of Raw-EFB and HTW-EFB

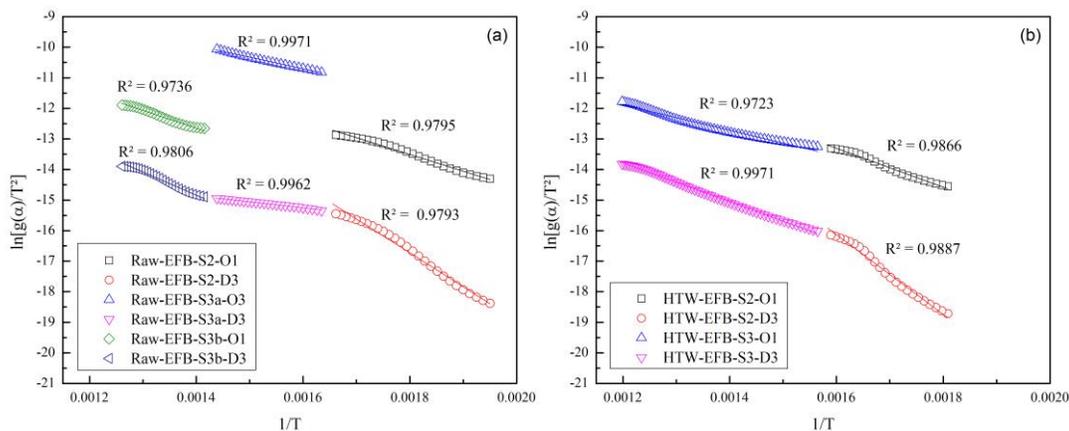
TABLE V: KINETIC PARAMETERS OF RAW-EFB AND HTW-EFB

Sample	Stage 2 (S2)				Stage 3a (S3a)				Stage 3 (S3)			
	$T$ (°C)	$E$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )	$R^2$	$T$ (°C)	$E$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )	$R^2$	$T$ (°C)	$E$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )	$R^2$
First-order reaction (O1)												
Raw-EFB	239-334	43.93	9.65E+02	0.9795	-	-	-	-	421-518	45.07	8.23E+06	0.9736
HTW-EFB	278-354	52.90	2.80E+03	0.9866	-	-	-	-	354-557	33.81	3.65E+01	0.9723
Third-order reaction (O3)												
Raw-EFB	-	-	-	-	334-421	31.34	3.52E+02	0.9971	-	-	-	-
HTW-EFB	-	-	-	-	-	-	-	-	-	-	-	-
Three-dimensional diffusion (D3)												
Raw-EFB	239-334	89.17	1.39E+06	0.9793	334-421	16.49	3.50E+09	0.9962	421-518	60.00	7.96E+06	0.9806
HTW-EFB	278-354	108.58	1.53E+07	0.9887	-	-	-	-	354-557	52.47	1.27E+02	0.9971

The high  $R^2$  valued reactions of HTW-EFB in S3 were also yielded by O1 and D3. The  $E$  value was 33.81 and 52.47 kJ/mol for O1 and D3 models, respectively. However, the decrease in  $E$  values of HTW-EFB was observed in this stage. The reduction of  $E$  can be attributed to the increase in the surface area of the sample and the amorphous carbonaceous structure, caused by HTC [9,24]. Fig. 4 shows the averaged activation energy of each stage and the weighted average value of S2 and S3. The weighted average  $E$  of HTW-EFB was approximately 58.60 kJ/mol exhibiting a slight higher value

than that of the raw material (55.36 kJ/mol), in spite of the lower char decomposition stage of Raw-EFB. This implied that the stage of volatile decomposition played an important role in the decomposition of material.

According to the highest  $R^2$  value, it can be concluded that O1 was the most effective mechanism for Raw-EFB in S2 while O3 and D3 were the best representative mechanism in S3a and S3b, respectively. Nonetheless, the most effective reaction for HTW-EFB was D3 in both stages (S2 and S3). The  $A$  value also showed the same trend with that of the  $E$  value.


 Fig. 3. Plot of  $\ln(g(\alpha)/T^2)$  vs  $1/T$  that yielded the highest  $R^2$  values for Raw-EFB (a) and HTW-EFB (b)

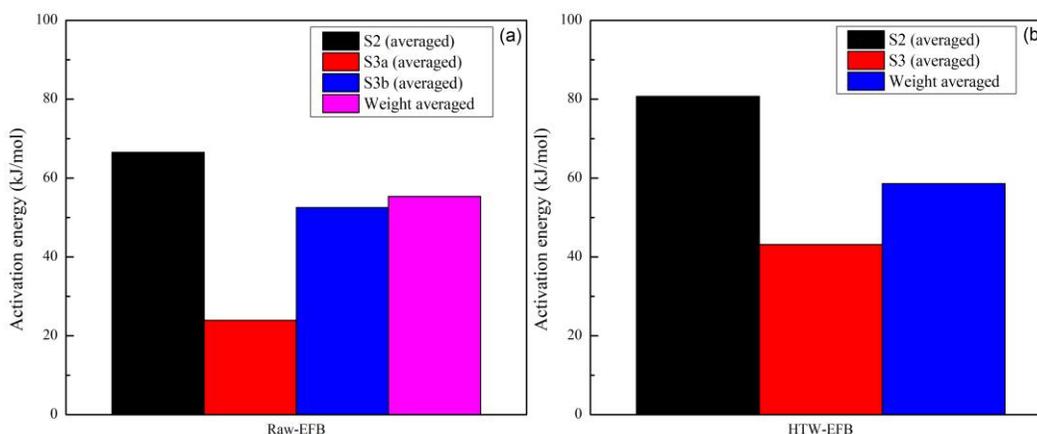


Fig. 4. The activation energy of Raw-EFB (a) and HTW-EFB (b)

#### IV. CONCLUSION

After solid fuel production from EFB by pilot-scale HTC and water washing, this study investigated the effect of treatment processes on its fuel properties, thermal decomposition behavior and kinetic parameters of samples. The HTC and water washing could remarkably elevate fuel properties of EFB. In addition, the HTW-EFB exhibited a major decrease in K content compared to the raw material. As the thermal decomposition results, DTG profiles revealed that the HTC and water washing significantly affected the thermal characteristic parameters of EFB. Consequently, the ignition temperature, the temperature of the maximum weight loss rate in the devolatilization stage, and the burnout temperature of HTW-EFB were increased due to the decrease in the reactivity. From the kinetic study, the main mechanisms in the devolatilization stage were the first-order reaction (O1) and the three-dimensional diffusion (D3). This revealed the same results in char decomposition stage of HTW-EFB. As for Raw-EFB, the third-order reaction (O3) was also assumed to be a feasible main reaction of char decomposition. The kinetic study exhibited that the weighted average activation energy of HTW-EFB was higher than that of the Raw-EFB.

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