

VALUE-CHAIN OF BIOFUELS

Fundamentals, Technology, and Standardization

Edited by
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Preface

Crude oil, coal, and natural gas are the key resources for electricity generation, heating, and transportation. Rapid depletion of these resources coupled with increasing energy demands and transition toward low carbon emissions increased the utilization of renewables in the energy mix. Biofuel is one of the renewables resources that support the sustainable energy agenda by reducing greenhouse gas emission.

The book entitled *Value-Chain of Biofuel—Fundamental, Technology, and Standardization* contains 24 chapters and comprises 3 main sections. The first section highlights the overview of biomass conversion technologies to biofuel and pretreatment methods including lignin extraction and delignification. Further, the second section (Chapters 7–15) covers various pathways of biofuel synthesis to produce biohydrogen/biogas, bio-oil, biojet, bioethanol, biobutanol, as well as value-added products. The third section covers topics related to environmental sustainability and implication of biofuels' use (Chapter 16, Experimental investigation of the characterization of emissions from waste cooking oil biodiesel), techno-economic assessment of biofuels production (Chapters 17–18), followed by a discussion on the supply chain analysis of biofuel production (Chapters 19–22). Policies related to biofuels' implementation in Malaysia and neighboring countries such as the Philippines are described in Chapter 23, Renewable Energy Transformation in Malaysia Through Bioenergy Production: Policy Insights From Spatially-explicit Modeling, and Chapter 24, Production, Regulation, and Standardization of Biofuels: A Philippine Perspective.

This book supports readership among students, researchers, scientists, practitioners, and others in the field of biomass conversion to biofuels in particular. It is expected that this book can enrich the knowledge on current and future trends of biofuel and toward future research and energy transition endeavor.

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Suzana Yusup and Nor Adilla Rashidi

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Iso-conversional kinetic and thermodynamic analysis of catalytic pyrolysis for palm oil wastes

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Abbreviations

DTG Derivative thermogravimetric
DTG_{max} Maximum derivative thermogravimetric rate
EIA Energy Information Administration
GHG Greenhouse gases
OPF Oil palm frond
OPT Oil palm trunk
TG Thermogravimetric
TGA Thermogravimetric approach

12.1 Introduction

Renewable energy is one of the important forms of energy in reducing environmental impacts such as air pollution, land pollution, water pollution, climate change, and greenhouse effect, and received great attention around the world. Air pol-

lution has contributed to the dominant part of the environmental impact. The combustion process of fossil fuels attributed to greenhouse gas (GHG) emissions to the environment. It was previously reported by the United States Energy Information Administration (EIA) in 2016 stating that activities conducted by human in the United States leads to a consumption of 301 million British thermal units of energy per person (per capita) and incremental of worldwide energy demand of 2.1% in the year of 2017 [1]. EIA had tabulated the total per capita energy consumption were based from four different major sectors namely industrial, residential, commercial and transportation with respect to the total population of the country. Hence, the highest energy consumption reported comes from the industrial sector (32%) and transportation sector (29%) from the total United States energy consumption in 2016 [1].

Among the different types of renewable energy resources, biomass energy is selected in this research as it is abundantly available, does not rely on climate change, and the topography of the country as compared to wind, solar, and hydroelectric energy. Besides that, biomass does not release carbon dioxide (CO_2) into the surroundings as it absorbed the CO_2 during the process of electricity generation. And also, biomass is considered as a clean energy and heating source. The production rate of biomass is high and can be easily obtained to form as one of the energy resources compared to other renewable energy resources.

In this research, palm oil wastes such as oil palm frond (OPF) and oil palm trunk (OPT) are selected as the biomass for the pyrolysis process because Malaysia and Indonesia have become the two largest contributors to the palm oil industry around the world. The increment of the palm oil development had increased rapidly in these two countries for both plantation and industry areas. The increment trend in the palm oil production in Indonesia has increased gradually and reached 34.5 million tons approximately in 2016 [2,3]. In Malaysia, the palm oil industry contributed 19.16 million tons of palm oil production with the increment of palm oil development. The production of palm oil has reached 90 million tons, where 43%–45% are the waste generated from the palm oil production [6].

Palm oil wastes are one of the potential biomasses used for biofuel production to replace fossil fuel production. Based on Kurnia et al. [7], palm oil is selected as the highest yield oil production with the most economical source compared to other vegetable oil. There are many industries built that use palm oil wastes as the sources for biofuel production and electricity generation [8]. In this present study, OPF and OPT are selected as the oil palm wastes for biomass pyrolysis. Pyrolysis process is a thermochemical conversion process which converts lignocellulosic biomass into solid residues, liquid fuels, and noncondensable gases [9,10]. Based on Soon et al. [11] and Khan et al. [12], it is reported that palm oil wastes such as OPF and OPT are able to achieve the preexponential factor (A) in the range of 1.2×10^{13} – $1.1 \times 10^{17} \text{ min}^{-1}$ and activation energy (E_A) in the range of 160 to 199 kJ mol^{-1} for pyrolysis process. The chemical composition for OPF in terms of hemicellulose, cellulose, and lignin content are reported to be 31.93%, 42.12%, and 26.05% respectively [13]. Meanwhile, the hemicellulose, cellulose, and lignin in OPT are 30.36%, 50.78%, and 17.87% respectively [13].

There are many studies found in the literature using palm oil wastes in the pyrolysis process in the presence of a commercial catalyst. Cheah et al. [15] had investigated the catalytic pyrolysis for OPF in the presence of commercial HZSM-5 zeolite and graphite nanofiber. Lim and Andréßen [16] had studied the catalytic effect of boric oxide on empty fruit bunches and OPF in a fixed pyrolysis bed reactor.

To our knowledge, no studies are found focusing on the kinetic (E_A and A parameters) and thermodynamic (enthalpy change (ΔH), Gibb's free energy (ΔG), and entropy change (ΔS) parameters) analyses for catalytic of OPF and OPT pyrolysis utilizing its ashes as a natural catalyst. Hence, in this work, a comparison study on the kinetic and thermodynamic analyses for pyrolysis of OPF and OPT are investigated with the absence and presence of OPF ash, OPT ash, and OPF/OPT ash using thermogravimetric approach (TGA). OPF ash, OPT ash, and OPF/OPT ash are used as natural catalysts in the pyrolysis process of palm oil wastes for further conversion of biomass to bioenergy. The experiments are conducted at various heating rates of 10–100 K min^{-1} from temperature of 323K to 1173K. Coats-Redfern, Vyazovkin, and Miura-Maki model are the selected iso-conversional kinetic models to determine the kinetic parameters.

12.2 Experiment materials and methods

12.2.1 Biomass preparation

Both OPF and OPT were obtained from a local palm oil mill in Woodman, Miri Sarawak. These biomasses were dried until the moisture content are less than 10 wt.% and ground into powder form in a particle size of less than 500 μm . The ultimate analysis for OPF are 40.5 wt.% carbon, 6.8 wt.% hydrogen, 3.5 wt.% nitrogen, 0.3 wt.% sulfur, and 48.9 wt.% oxygen. The ultimate analysis for OPT are 42.4 wt.% carbon, 7.3 wt.% hydrogen, 0.3 wt.% nitrogen, 0.7 wt.% sulfur, and 49.3 wt.% oxygen.

12.2.2 Catalyst preparation

The catalysts used for the pyrolysis process are from the ashes produced from the combustion process of OPT and OPF through a continuous heating process with a temperature of 973K for 4 h using the Laboratory Muffle Furnace, Carbolite ELF 11/14B. The ashes of OPT and OPF were ground until the particle sizes were less than 500 μm . Thereafter, the ashes were then sent to the oven for 12 h at 373K for drying purpose and left to cool down to room temperature before sending to the TGA equipment for experiments.

12.2.3 Thermogravimetric analysis

Pyrolysis experiments were conducted using a thermogravimetric analyzer (TGA-DSC 1, Mettler Toledo). An approximate of 10 mg of samples were placed in the ceramic crucible under nonisothermal condition. The samples were pyrolyzed from room temperature to 1,173K at different five heating rates of 10K.min⁻¹, 20K.min⁻¹, 30K.min⁻¹, 50K.min⁻¹, and 100K.min⁻¹. Thereafter, the temperature of 1,173K was maintained for 10 min when it reached 1173K. The biomass was mixed with the ashes in the weight ratio of 1:1, meanwhile the biomass/OPF ash/OPT ash samples were blended in the weight ratio of 1:0.05:0.05. The experiments were repeated 2–3 times to ensure the results are reproducible.

12.2.4 Kinetic theory

The kinetic principles used in pyrolysis process were based on iso-conversion principle. This principle indicates the rate of reaction can be affected by the temperature only with a basis of constant conversion rate [17]. Thus, thermal degradation of the lignocellulose component in biomass occurred simultaneously within a conversion rate of the time, with proposed reaction mechanism of the pyrolysis process as shown as below in Eq. (12.1).



where k refers to pyrolysis conversion rate constant, volatiles are in gas, and tar form and char is in solid form. According to Sadhukhan et al. [18], the conversion rate of the pyrolysis process is assumed as a single step process which follows the Arrhenius, and is as shown in Eq. (12.2) below.

$$k = Ae^{\frac{-E_a}{RT}} \quad (12.2)$$

where A represents preexponential factor (s⁻¹), E_a represents activation energy (kJ mol⁻¹), R represents the universal gas constant of 8.314 J K⁻¹.mol, and T represents the absolute temperature in Kelvin (K). The degradation rate of the reaction can be further expressed in Eq. (12.3) by showing the conversion rate of the biomass from solid to volatile state.

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (12.3)$$

The rate of degradation or conversion, $\frac{d\alpha}{dt}$ represents the conversion rate that is temperature-dependent and α is the conversion fraction degree of the sample with respect to time. The degree of conversion fraction is defined as the decomposition rate of the biomass sample at any range of the temperature in TG analysis which is expressed in Eq. (12.4) as shown below.

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (12.4)$$

where m_i represents the starting mass of biomass sample, m_t represents the sample mass at the given time, t , and m_f represents the final mass of sample. By substituting Eq. (12.2) into Eq. (12.3) hence, Eq. (12.5) is obtained as depicted below.

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha) \quad (12.5)$$

Nonisothermal method is normally applied in a solid-state kinetics where the heating rate is remained constant and defined in Eq. (12.6).

$$\beta = \frac{dT}{dt} \quad (12.6)$$

By combining both Eq. (12.5) and Eq. (12.6), which gives Eq. (12.7) as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\frac{-E_A}{RT}} \cdot f(\alpha) \quad (12.7)$$

By integrating Eq. (12.7) above with the function of $(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$, simplifies the equation for numerical approximation and gives Eq. (12.8).

$$g(\alpha) = \int_0^\alpha \left(\frac{d\alpha}{f(\alpha)} \right) = \frac{A}{\beta} \int_{T_0}^T e^{\left(\frac{-E_A}{RT} \right)} dT \quad (12.8)$$

In iso-conversional kinetics, the pyrolysis kinetic order is specified under the first order reaction, which gives Eq. (12.9) as shown below.

$$g(\alpha) = -\ln(1 - \alpha) \quad (12.9)$$

12.2.5 Kinetic models

Coats-Redfern model, Miura Maki model, and Vyazovkin model were the selected kinetic iso-conversional models to evaluate the kinetic parameters of the biomass pyrolysis in this study.

12.2.5.1 Coats-Redfern

Coats-Redfern model is the method that was used to analyze the kinetic parameters of the reaction. Eq. (12.10) to Eq. (12.14) show the temperature integral from the Arrhenius equation [Eq. (12.2)] [5].

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\frac{-E_A}{RT}} \cdot (1 - \alpha)^n \quad (12.10)$$

By rearranging,

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} e^{\left(\frac{-E_A}{RT} \right)} \cdot dT \quad (12.11)$$

Integrating Eq. (12.11) [5];

$$\frac{1 - (1 - \alpha)^{1-n}}{(1 - \alpha)^n} = \frac{A}{\beta} \int_0^T e^{\left(\frac{-E_A}{RT} \right)} \cdot dT \quad (12.12)$$

Neglecting the higher order terms, the equation is further expressed in Eq. (12.13) [5],

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1 - \alpha)} = \ln \left\{ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right\} - \frac{E_A}{RT} \quad (12.13)$$

By assuming first order reaction ($n=1$) and the term of $\frac{2RT}{E_A}$ is less than 1, the equation can be further simplified as in Eq. (12.14) [5].

$$\ln \frac{-\ln(1 - \alpha)}{T^2} = \ln \left\{ \frac{AR}{\beta E} \right\} - \frac{E_A}{RT} \quad (12.14)$$

where n represents the order of the reaction, T represents the absolute temperature (K), β represents the heating rate

(K.min⁻¹), R represents the gas constant (J.mol⁻¹. K⁻¹), A represents the preexponential factor (min.⁻¹), and E_A represents the activation energy (kJ.mol⁻¹).

12.2.5.2 Vyazovkin

The Vyazovkin (V) method is a model-free method that is used to analyze the iso-conversional kinetic analysis. Linear approximation of Vyazovkin (V) that was selected for this research is based on the Coats-Redfern basis concepts of approximation, which generates an integral of temperature equation in Eq. (12.15) [14] below.

$$g(\alpha) = \frac{A}{\beta} \frac{RT^2}{E} \exp\left(-\frac{E_A}{RT}\right) \quad (12.15)$$

By rearranging and introducing \ln to both sides of the equation, the finalized expression of the equation is presented in Eq. (12.16) [14] below.

$$\ln \frac{\beta}{T^2} = \ln \left(\frac{AR}{Eg(\alpha)} \right) - \frac{E_A}{RT} \quad (12.16)$$

Besides, it also provides an alternative method to obtain the results of apparent activation energy. From Eqs. (12.17) to (12.19) [14] below shows a nonlinear approximation of $p(x)$, which is also known as Senum–Yang approximation for obtaining the minimization of apparent activation energy $\emptyset(E_A)$.

$$\emptyset(E_A) = \sum_{i=1}^n = \sum_{j=1}^n \frac{I[E_A(\alpha), T_i] \beta_j}{I[E_A(\alpha), T_i] \beta_i} \quad (12.17)$$

$$I[E_A, T_i] = p(x) \quad (12.18)$$

where $p(x) = \int_0^\infty \frac{e^{-x}}{x^2} dx$ and $x = \frac{E_A}{RT}$

$$I[E_A(\alpha), T_j] = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(-\frac{E_A}{RT_\alpha}\right) dT \quad (12.19)$$

where n represents the number of heating rates, $I[E_A, T_i]$ represents the results of $p(x)$ exponential integral approximation from respective heating rate, β_i and $I[E_A(\alpha), T_i]$ represents exponential integral of the respective heating rate, β_j .

12.2.5.3 Miura-Maki

In Miura-Maki model, the approximation of the temperature integral is developed by combining Eq. (12.9) and Eq. (12.16) and become Eq. (12.20) [19].

$$1 - \alpha \cong \exp\left[-\frac{ART^2}{\beta E} \exp\left(-\frac{E}{RT}\right)\right] = \emptyset(E_S, T) \quad (12.20)$$

where $E=E_S$, as a step function of activation energy at respective temperature, and the equation is simplified to Eq. (12.21) [19] below.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_A}\right) - \ln[-\ln(1 - \alpha)] - \frac{E_A}{RT} \quad (12.21)$$

Since $\emptyset(E_S, T)=0.58$, the \emptyset finalized equation is expressed as Eq. (12.22) [19] as below.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_A}\right) + 0.6075 - \frac{E_A}{RT} \quad (12.22)$$

12.2.5.4 Kinetic analysis

The equations of the models were linearized and plotted in a linear graph to verify the values of preexponential and the activation energy of the reaction. Fig. 12.1 shows the linear expression of each models with the respective x-axis, y-axis, y-intercept, and slope. By plotting y-axis vs x-axis of each model, the activation energy can be obtained from the slope of the graph while the preexponential can be obtained from the y-intercept of the graph. Hence, there were three sets of activation energies and preexponential values obtained from three different models and the best model that fits the pyrolysis process in this research was evaluated.

12.2.6 Thermodynamic analysis

The thermodynamic parameters [Enthalpy (ΔH), Gibbs free energies (ΔG), and Entropies (ΔS)] were determined by Eqs. (12.23) to (12.25) [4].

$$\Delta H = E_A - RT \quad (12.23)$$

$$\Delta G = E_A + R \cdot T_m \cdot \ln \left(\frac{K_B \cdot T_m}{h \cdot A} \right) \quad (12.24)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (12.25)$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), h is the Planck's constant ($6.626 \times 10^{-34} \text{ Js}$), and T_m is the average DTG peak temperature in Kelvin (K).

12.3 Results and discussions

12.3.1 Thermal degradation behavior of oil palm frond and oil palm trunk in pyrolysis process

In the present study, the thermal degradation effect of the OPF and OPT with or without the presence of catalyst was analyzed via TGA equipment. Fig. 12.2 shows the curves of the thermogravimetric (TG) and derivative thermogravimetric (DTG) of OPF and OPT in noncatalytic and catalytic pyrolysis reaction, with five different types of heating rates 10 to 100K.min⁻¹. The TG curve is used to determine the weight loss of the sample in weight percentage with the increased of temperature, meanwhile the DTG curve is used to analyze the initial, maximum, and final biomass degradation temperature. Based on this figure, the trend of the curves can be categorized into three main stages of thermal degradation. The Stage I, Stage II, and Stage III are known as dehydration stage, main devolatilization stage, and decomposition of carbonaceous components stage, respectively.

Stage I of thermal degradation for OPF and OPT pyrolysis started from room temperature to 495K and 500K respectively with a slight reduction of weight fraction of OPF and OPT. This is where the dehydration process takes place to reduce the moisture content and light volatiles of the component [11]. The surface tension tends to cause evaporation to both moisture content and the water bounded of the OPF and OPT biomass surface. When the temperature reached the end of Stage I decomposition, the internal forces such as intermolecular and intramolecular forces start to break the hydrogen bond in lignocellulose component and form water molecules to generate the char. When most of the moisture content in the OPF and OPT have been evaporated, the weight of the OPF and OPT decreases dramatically in all five differ-

Model	Equation	y-axis	x-axis	Eq.
Coats-Redfern	$\ln \left(\frac{-\ln(1-\alpha)}{T^2} \right) = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT}$	$\ln \left(\frac{-\ln(1-\alpha)}{T^2} \right)$	$\frac{1}{T}$	(8.14)
Vyazoykin	$\ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{AR}{Eg(\alpha)} \right) - \frac{E}{RT}$	$\ln \left(\frac{\beta}{T^2} \right)$	$\frac{1}{T}$	(8.16)
Miura-Maki	$\ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{AR}{E} \right) + 0.6075 - \frac{E}{RT}$	$\ln \left(\frac{\beta}{T^2} \right)$	$\frac{1}{T}$	(8.22)

FIGURE 12.1 Linear expression of three different models.

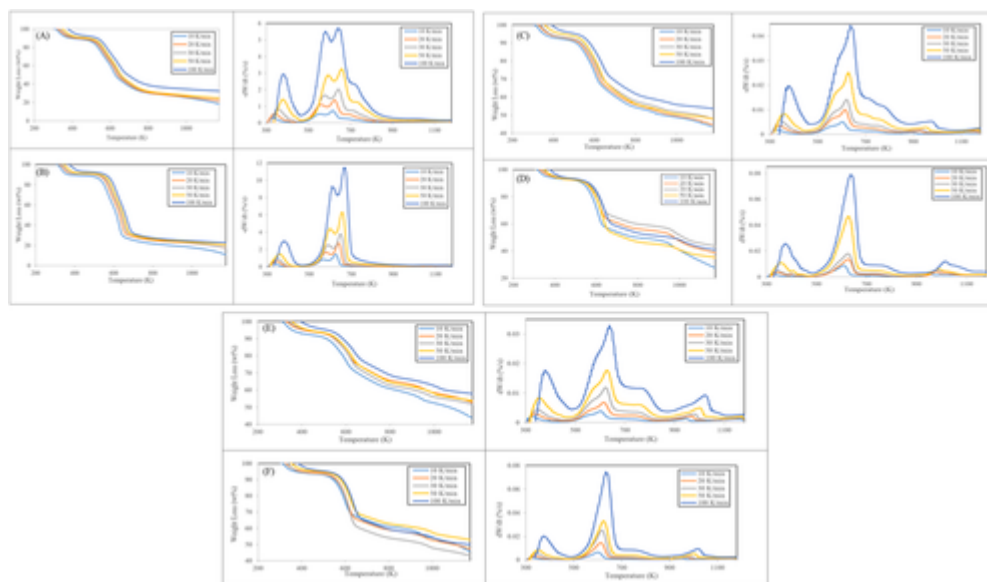


FIGURE 12.2 TG and DTG graphs of (A) noncatalytic pyrolysis of OPF, (B) noncatalytic pyrolysis of OPT, (C) pyrolysis of OPF using OPF ash catalyst, (D) pyrolysis of OPT using OPT ash catalyst, (E) pyrolysis of OPF using OPF/OPT ash catalysts (F) pyrolysis of OPT using OPF/OPT ash catalysts.

ent heating rates. This indicated that the biomass had experienced Stage II decomposition in temperature range from 495K–750K and 500K–710K for OPF and OPT, respectively. This is the phase where the organic compound of OPF and OPT is undergoing main devolatilization process for carbon and volatile component extraction. In this stage, transglucosidation process happened, where the intermediate cellulose component starts to degrade to levoglucosan and oligosaccharides [20]. In stage III, a slight weight loss of OPF and OPT with the temperature range from 750K–1173K and 500K–1173K, respectively due to occurrence of passive devolatilization process. Passive devolatilization process is where the carbonaceous component started to decompose and both carbon monoxide and CO_2 started to form by vaporization of nonvolatile carbon compounds that contained in the solid residue of the biomass [21]. Besides, aromatization and bond cracking happen to convert the cellulose and carbonaceous material to char and volatile matter.

Fig. 12.2 shows that there are two exothermic peaks in between the temperature range from 500K to 820K for both OPF and OPT with and without ash catalyst occurred in this curve for the five different heating rates. The first peak occurred due to the thermal decomposition of protein and carbohydrates component while the decomposition of lignin happened in the second peak. The second peak for both OPF and OPT are relatively higher than the first peak due to high content of lignin content in oil palm wastes. It is where the main decomposition stage happened in the second decomposition stage as mentioned in the description for the TG curve. At the last stage (stage III), a small endothermic peak indicated that the remaining residue undergoes final decomposition stage after the temperature reached 820K. Based on Fig. 12.2, the optimum mass loss was observed to be at stage II where the temperature ranged from 495K to 750K. The mass loss was observed in the average range of the residues weight (%) from the initial temperature, T_{initial} until the final temperature of stage II, T_{final} for the main pyrolysis stage (stage II). The results of different sets of samples based on heating rates of 10 to 100K min^{-1} were tabulated in Table 12.1.

The mass loss for pure OPF in stage II was estimated in the range of 64.55% to 69.02%. With the presence of OPF and OPF/ OPT ash catalyst, the mass loss was observed in the range of 74.55% to 82.93% and 77.43% and 82.99%. While for pure OPT pyrolysis, the mass loss was observed from the range of 57.38% to 67.75%. With the presence of OPT and OPF/ OPT ash catalyst in OPT pyrolysis, the mass loss was estimated from 69.70% to 76.77% and 73.63% to 78.87%. Similar observation found in TG and DTG curves for both OPF and OPT pyrolysis process from literature [11,12].

12.3.2 Effect of heating rates on oil palm frond and oil palm trunk thermal decomposition

Devolatilization is the process where the feedstock started to decompose. In this stage, the degradation of the biomass is highly depended on the heating rate of the samples. The relationship of time and temperature can be known as heating rate. High heating rate of the process favors the depolymerization of hemicellulose and cellulose and volatile cracking in

TABLE 12.1 Mass loss of thermal decomposition of pyrolysis for oil palm frond (OPF) and oil palm trunk (OPT) with the presence of OPF ash, OPT ash, and OPF/OPT ash catalyst in stage II.

Stage II	Heating rate	T _{initial}	T _{final}	T _m	Mass loss (%)	DTG _{max}
	(β , K min ⁻¹)	(K)	(K)	(K)		(% min ⁻¹)
OPF	10	445.97	670.57	613.28	65.32	0.73
	20	446.98	685.7	624.78	65.51	1.38
	30	454.61	713.64	630.67	64.55	2.04
	50	463.78	715.8	636.48	65.08	3.27
	100	479.04	723.53	640.86	69.02	5.74
OPF—OPF ash	10	468.53	739.33	611.57	74.55	4.51×10 ⁻³
	20	471.71	741.87	613.76	82.93	1.00×10 ⁻²
	30	479.39	743.91	618.66	76.84	1.41×10 ⁻²
	50	484.67	744.64	628.74	77.07	2.52×10 ⁻²
	100	495.68	750.05	636.38	80.29	4.43×10 ⁻²
OPF—OPF/OPT ash catalyst	10	469.46	747.54	602.54	77.43	3.87×10 ⁻³
	20	473	759	613.1	80.57	6.76×10 ⁻³
	30	483.63	761.25	622.44	79.37	1.19×10 ⁻²
	50	487.47	761.93	624.73	80.32	1.77×10 ⁻¹
	100	495.8	771.5	636.88	82.99	3.30×10 ⁻¹
OPT	10	450.26	687.42	626.58	57.38	1.47
	20	455.73	693.58	638.24	59.89	2.76
	30	467.08	706.22	649.67	60.43	3.8
	50	468.91	716.56	656.52	67.75	6.42
	100	469.36	722.11	664.93	61.68	11.49
OPT—OPT ash	10	464.3	781.08	599.78	71.53	8.85×10 ⁻³
	20	469.87	787.39	613.53	74.80	1.36×10 ⁻²
	30	477.29	793.58	616.82	76.77	1.80×10 ⁻²
	50	480.91	797.41	624.54	69.70	4.69×10 ⁻²
	100	487.81	794.69	633.27	73.37	7.90×10 ⁻²
OPT—OPT/OPFash catalyst	10	499.68	773.44	599.78	77.35	6.94×10 ⁻³
	20	506	782.44	613.53	76.72	1.45×10 ⁻²
	30	507.37	791.96	616.82	73.63	2.53×10 ⁻²
	50	509.28	793.82	624.54	78.87	3.30×10 ⁻²
	100	515.34	797.16	633.27	77.27	7.48×10 ⁻²

the secondary reactions. Besides that, the composition of the volatile compound in biomass decreased, as the compounds such as aldehydes, alcohols, acetone, and paraffin reduced due to generation of polyhydroxy aromatics component increased [22]. Fast pyrolysis usually uses high temperature for the process in order to generate high yield of bio-char, oil, and noncondensable gases. From Fig. 12.2, it is observed that both TG and DTG curves increased with heating rates. The trend is in similar behavior as reported by Soon et al. [11], Khan et al. [12], and Fong et al. [14].

Besides that, it is important for the reaction to take account the residence time of the volatile component. The effect of the residence time is corresponding to the carrier gas flow such as nitrogen gas, as high flow of carrier gas enhances the solid entrainment and reduces the efficiency of the biomass conversion inside the reactor. From Table 12.1, the maximum degradation rate, DTG_{max} for pure OPF pyrolysis can be found to increase from 0.73 to 5.74% min^{-1} with the increment of heating rate from 10 to 100K. min^{-1} as for reference. This is because the residence time of the degradation decreased as the heating rate increased. The efficiency of the heat transfer can be increased at the same time as the heating rate increased and produced higher yield production [23].

12.3.3 Effect of catalyst on oil palm frond and oil palm trunk thermal decomposition

The addition of the catalyst to the process is to lower down the E_A pathway and improve the secondary devolatilization reaction of the pyrolysis of oil palm wastes samples. In this study, the catalyst plays an important role in upgrading the bio-fuel by increasing the efficiency of the devolatilization reaction. Commercial catalyst such as zeolites are widely used in catalytic pyrolysis process, with an overview of different zeolites catalyst such as HZSM-5, USY, and zeolite- β . Apart from that, this study promotes the importance of catalytic pyrolysis process using renewable resources such as OPF and OPT ash catalyst. Chen et al. [20] reported that the E_A of the palm oil pyrolysis decreased significantly using rice husk ash as the natural catalyst in representing CaO catalyst. The main purpose of the study is to enhance the reusability of the oil palm wastes and improved the bio-fuel production [7].

In this present study, the E_A of OPF was reduced from 28.49 kJ mol^{-1} to 23.66 kJ mol^{-1} with the addition of OPF/OPT ash. Furthermore, the DTG_{max} reduced significantly from 5.74 to $4.43 \times 10^{-2}\%$ min^{-1} at heating rate of 100K. min^{-1} . A similar behavior is observed for OPT pyrolysis when comparing with literature findings by Chen et al. [20] and Liu et al. [21].

12.3.4 Kinetic analysis and thermodynamic study

Three iso-conversional kinetic models such as Coats-Redfern, Vyazovkin, and Miura-Maki were selected to identify the kinetic mechanism of the OPF and OPT pyrolysis with the presence of OPF ash and OPT ash in this study. Fig. 12.3 shows the kinetic plots of OPF pyrolysis using three models where Coats-Redfern is identified by the effect of the heating rate, and Vyazovkin and Miura-Maki are identified based on the biomass weight fraction. Based on the TG curve, the main devolatilization stage (Stage II) was selected as the main pyrolysis stage for both OPF and OPT at five different heating rates respectively. These three kinetic models were applied to determine the kinetic parameters such as E_A and A for the pyrolysis of OPF and OPT in the absence and presence of catalyst. The role of E_A determines the amount of energy that reactants need to overcome the pathway before the chemical reaction, meanwhile A represents the frequency of the collisions of the chemical reactants molecules during the pyrolysis reaction [24]. The values of E_A and A were calculated based on the slope and intercept point of the kinetic plot. It was found that the average of E_A and A for pure OPF were 28.49 kJ mol^{-1} and $1.12 \times 10^6 \text{ min}^{-1}$. With the presence of OPF ash, the values of E_A and A are slightly reduced to 28.02 kJ mol^{-1} and $1.15 \times 10^6 \text{ min}^{-1}$. With the presence of OPF/OPT ash catalyst, the values of E_A and A are reduced even more significantly to 23.66 kJ mol^{-1} and $1.11 \times 10^6 \text{ min}^{-1}$ respectively when compared without catalyst. On the other hand, the average of E_A and A for pure OPT were 44 kJ mol^{-1} and $5.78 \times 10^6 \text{ min}^{-1}$ respectively. With the presence of OPT and OPF/OPT ash, the values of E_A and A reduced to the range of 36.86–38.86 kJ mol^{-1} and 1.14×10^6 – $1.16 \times 10^6 \text{ min}^{-1}$. Based on Xu et al. [25], a good catalytic effect reduces the E_A with the increment of rate of reaction for providing an efficient bio-fuel production rate in catalytic pyrolysis process.

Table 12.2 shows the average correlation coefficients (R^2) values for Coats-Redfern model are in the range from 0.9579 to 0.9951 for catalytic and noncatalytic of OPF and OPT for the five different heating rates. This indicated that a good linear curve was plotted between $\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$ and at $\frac{1}{T}$ different heating rates from 10 to 100K. min^{-1} as shown in Fig. 12.3. It was observed that the regression coefficient values were above 95% for all heating rates, and showed that this model was suitable for kinetic analysis with high accuracy of the results. The observation of the results found in this study is in agreement with the literature as reported by Gan et al. [26], where the A were range from $1.1 \times 10^6 \text{ min}^{-1}$ to $189.4 \times 10^9 \text{ min}^{-1}$ using the Coats-Redfern model. It was observed that the pyrolysis of OPF with OPF/OPT ash catalyst gave the lowest E_A and A for all samples using the Coats-Redfern model.

For Vyazovkin and Miura-Maki models, the kinetic parameters were determined by using a linear plot between $\ln\left(\frac{\beta}{T^2}\right)$ and $\frac{1}{T}$ at various weight fraction of the residues, ranging from 0.2 to 0.6. The kinetic mechanism of main devolatilization (Stage II) can be observed from $\alpha = 0.2$ – 0.6 based on the temperature range from 500 to 690K. From Table

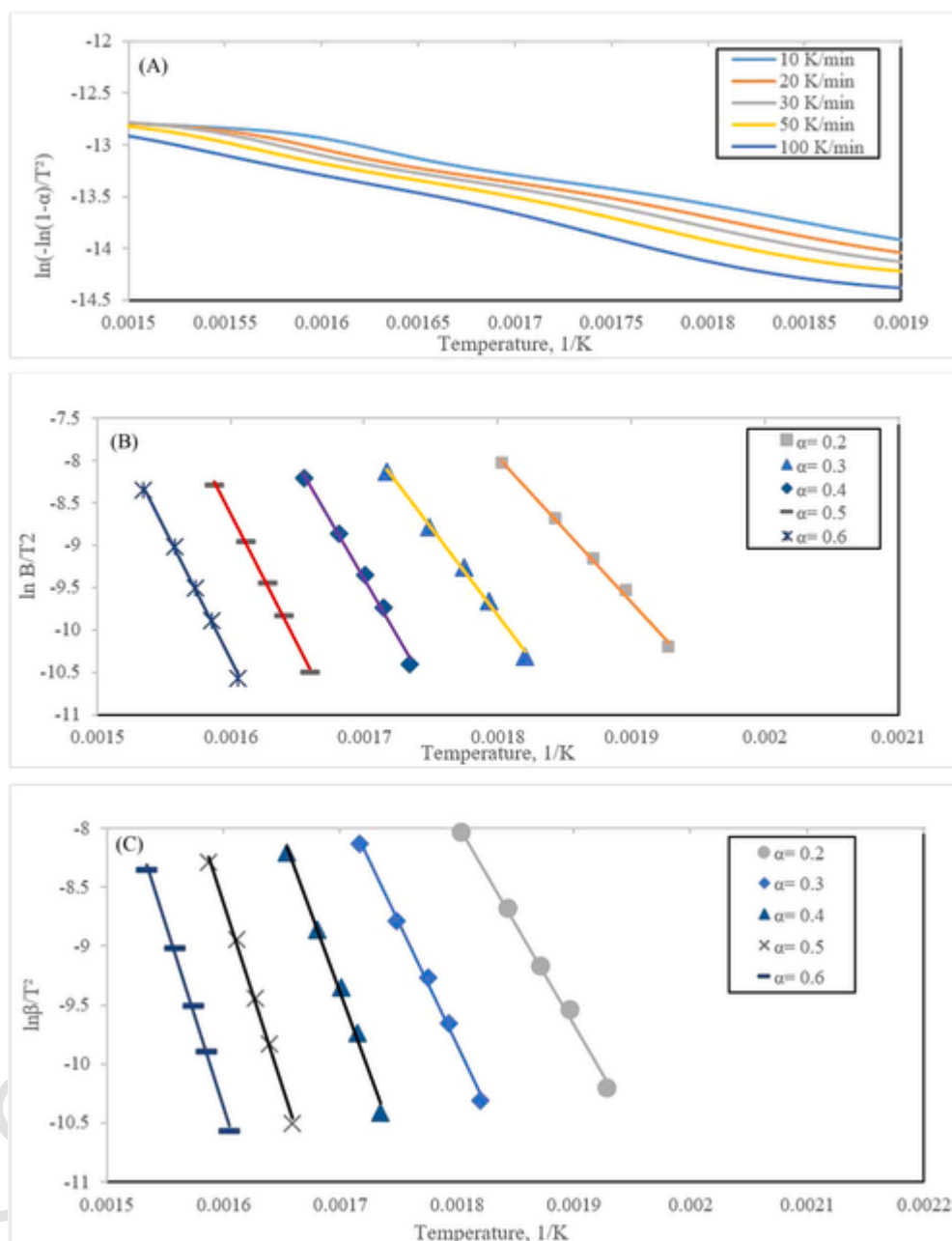


FIGURE 12.3 Kinetic plots of pyrolysis of OPF using (A) Coats-Redfern, (B) Vyazovkin, and (C) Miura-Maki method.

12.3, the average values of the E_A for noncatalytic and catalytic pyrolysis of OPF can be observed from 133.26 to 211.69 kJ mol⁻¹ respectively while A were observed to be 2.08×10^{19} – 2.14×10^{21} min⁻¹. Besides that, the average values of the E_A for noncatalytic and catalytic of OPT were 168.06–269.67 kJ mol⁻¹ respectively while A were observed to be 1.65×10^{16} – 1.04×10^{26} min⁻¹. The average values of the E_A and A that were determined by Miura-Maki method can be observed from Table 12.4. The values of A were observed to be 1.22×10^{16} – 2.21×10^{21} min⁻¹. On the other hand, the average values of the E_A for noncatalytic and catalytic of OPT pyrolysis were within the range of 168.06–269.67 kJ mol⁻¹ meanwhile A were in the range of 1.19×10^{16} – 1.04×10^{26} min⁻¹.

In addition, thermodynamic behavior of the OPF and OPT were studied by calculating the thermodynamic parameters such as the enthalpy change (ΔH), Gibb's free energy change (ΔG), and entropy change (ΔS). The calculated thermodynamic parameters were tabulated in Tables 12.2, 12.3 and 12.4, according to the respective kinetic models. The positive values of ΔH indicates that the pyrolysis reaction undergoes endothermic reaction, where the heat is absorbed from the

TABLE 12.2 Kinetic and thermodynamic parameters of catalytic and noncatalytic pyrolysis of oil palm frond and oil palm trunk using Coats-Redfern model.

Sample	Kinetic analysis				Thermodynamic analysis		
	β	E_A	A	R^2	ΔH	ΔG	ΔS
	$(^{\circ}\text{C}.\text{min}^{-1})$	$(\text{kJ}.\text{mol}^{-1})$	(min^{-1})		$(\text{J}.\text{mol}^{-1})$	$(\text{J}.\text{mol}^{-1})$	$(\text{J}.\text{mol}^{-1}.\text{K})$
OPF	10	24.27	2.43×10^5	0.9881	1.81×10^4	1.03×10^5	-158.17
	20	26.79	5.09×10^5	0.9955	2.06×10^4	1.02×10^5	-152.12
	30	28.81	7.85×10^5	0.9976	2.25×10^4	1.02×10^5	-148.61
	50	30.22	1.34×10^6	0.998	2.39×10^4	1.01×10^5	-144.34
	100	32.36	2.74×10^6	0.9961	2.57×10^4	1.00×10^5	-138.65
	Average	28.49	1.12×10^6	0.9951	2.22×10^4	—	—
OPF—OPF ash	10	24.27	2.24×10^5	0.995	1.81×10^4	1.16×10^5	-158.5
	20	28.14	5.26×10^5	0.9936	2.09×10^4	1.16×10^5	-151.53
	30	26.77	7.84×10^5	0.9901	2.05×10^4	1.12×10^5	-148.28
	50	31.06	1.38×10^6	0.992	2.47×10^4	1.14×10^5	-143.75
	100	29.89	2.82×10^6	0.9792	2.33×10^4	1.09×10^5	-138.08
	Average	28.02	1.15×10^6	0.97	2.17×10^4	—	—
OPF—OPF/OPT ash	10	18.66	2.19×10^5	0.9672	1.25×10^4	1.11×10^5	-158.71
	20	22.13	4.87×10^5	0.9871	1.59×10^4	1.11×10^5	-152.18
	30	26.05	7.88×10^5	0.9911	1.98×10^4	1.12×10^5	-148.27
	50	24.44	1.29×10^6	0.9906	1.81×10^4	1.08×10^5	-144.3
	100	27.02	2.75×10^6	0.9887	2.05×10^4	1.07×10^5	-138.31
	Average	23.66	1.11×10^6	0.9849	1.73×10^4	—	—
OPT	10	41.42	2.44×10^5	0.9878	3.52×10^4	1.37×10^5	-157.76
	20	46.10	4.57×10^5	0.9871	3.99×10^4	1.39×10^5	-152.63
	30	43.97	7.48×10^5	0.9762	3.77×10^4	1.34×10^5	-148.56
	50	44.48	1.26×10^6	0.9636	3.82×10^4	1.32×10^5	-144.32
	100	44	2.67×10^6	0.9504	3.75×10^4	1.27×10^5	-138.34
	Average	44	5.78×10^6	0.973	3.77×10^4	—	—
OPT—OPT ash	10	38.89	2.68×10^5	0.9795	3.27×10^4	1.31×10^5	-157.03
	20	34.6	5.42×10^5	0.9715	2.84×10^4	1.23×10^5	-151.28
	30	33.61	8.64×10^5	0.9612	2.73×10^4	1.19×10^5	-147.66
	50	43.45	1.29×10^6	0.9614	3.71×10^4	1.27×10^5	-144.27
	100	33.73	2.87×10^6	0.916	2.72×10^4	1.13×10^5	-137.83
	Average	36.86	1.16×10^6	0.9579	3.05×10^4	—	—

Sample	Kinetic analysis				Thermodynamic analysis		
	β	E_A	A	R^2	ΔH	ΔG	ΔS
	($^{\circ}\text{C}.\text{min}^{-1}$)	($\text{kJ}.\text{mol}^{-1}$)	(min^{-1})		($\text{J}.\text{mol}^{-1}$)	($\text{J}.\text{mol}^{-1}$)	($\text{J}.\text{mol}^{-1}.\text{K}$)
OPT—OPT/OPF ash	10	31.77	2.72×10^5	0.943	2.56×10^4	1.23×10^5	-156.93
	20	39.71	5.34×10^5	0.9664	3.35×10^4	1.27×10^5	-151.42
	30	40.77	7.89×10^5	0.9976	3.45×10^4	1.26×10^5	-148.22
	50	40.13	1.37×10^6	0.959	3.38×10^4	1.23×10^5	-143.8
	100	41.92	2.76×10^6	0.9417	3.54×10^4	1.24×10^5	-138.21
	Average	38.86	1.14×10^6	0.9615	3.26×10^4	—	—

surrounding to the system and formed chemical bonding. In the Coats-Redfern model, the calculated average for noncatalytic and catalytic of OPF pyrolysis were $2.22 \times 10^4 \text{ J mol}^{-1}$, $2.17 \times 10^4 \text{ J mol}^{-1}$, and $1.73 \times 10^4 \text{ J mol}^{-1}$, while the calculated average for noncatalytic and catalytic of OPT pyrolysis were observed to be $3.77 \times 10^4 \text{ J mol}^{-1}$, $3.05 \times 10^4 \text{ J mol}^{-1}$, and $3.26 \times 10^4 \text{ J mol}^{-1}$ respectively. The calculated average using Vyazovkin and Miura-Maki were $2.07 \times 10^5 \text{ J mol}^{-1}$, $1.68 \times 10^5 \text{ J mol}^{-1}$, $1.78 \times 10^5 \text{ J mol}^{-1}$, $1.63 \times 10^5 \text{ J mol}^{-1}$, $2.64 \times 10^5 \text{ J mol}^{-1}$, and $2.02 \times 10^5 \text{ J mol}^{-1}$ accordingly, for noncatalytic and catalytic pyrolysis of both OPF and OPT. The ΔG represents the change of the energy within the thermodynamic system via and based temperature changed during product-reactant approach in activated complex. Meanwhile, the ΔS indicates the disorder of the closed system. The results for both and observed from Table 12.2 showed the best prediction for OPF and OPT system disorder as majority values were in the negative values which can be categorized as in high degree of arrangement, resulting high reactivity of reactant and high product formation in a short residence time. Based on studies by Fong et al. [14], Gan et al. [26], and Wu et al. [27], the calculated ΔS was reported in a similar trend for different types of biomass pyrolysis process when compared to the present study.

Among the three iso-conversional kinetic models, Coats-Redfern gave the best prediction for both kinetic and thermodynamics analysis of OPF and OPT pyrolysis with the presence of OPF and OPT ash catalysts. The catalytic pyrolysis also shows good catalytic effect by reducing the E_A values for both OPF and OPT samples. For OPF pyrolysis, the E_A and ΔH reduced from $28.49 \text{ kJ mol}^{-1}$ to $23.66 \text{ kJ mol}^{-1}$ and $2.22 \times 10^4 \text{ J mol}^{-1}$ to $1.73 \times 10^4 \text{ J mol}^{-1}$ with the presence of OPF/OPT ash catalyst. While for OPT pyrolysis, the E_A and ΔH were observed to be reduced from 44 kJ mol^{-1} to $36.86 \text{ kJ mol}^{-1}$ and $3.77 \times 10^4 \text{ J mol}^{-1}$ to $3.05 \times 10^4 \text{ J mol}^{-1}$ respectively. In overall, the E_A of noncatalytic and catalytic pyrolysis of OPF give lower values compared to noncatalytic and catalytic pyrolysis of OPF which shows that the pyrolysis of OPF requires lower energy for thermochemical reaction for pyrolysis reaction.

12.4 Conclusions

The kinetic and thermodynamic analysis for the pyrolysis of OPF and OPT were successfully investigated with the absence and presence of OPF ash, OPT ash, and OPF/OPT ash using TGA. It is found that the Coats-Redfern model gave the best prediction (regression coefficient >95%) for the noncatalytic and catalytic pyrolysis process using OPT and OPF, compared to Vyazovkin and Miura-Maki models. Based on E_A calculated, the degradation results were found with the following conclusion: OPF-OPF/OPT ash > OPF-OPF ash > OPF > OPT-OPF ash > OPT-OPF/OPT ash > OPT. It is proven that OPF/OPT ash was suitable for OPF pyrolysis and OPT ash was suitable for OPT pyrolysis process for an effective energy-efficient bioenergy production.

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TABLE 12.3 Kinetic and thermodynamic parameters of oil palm frond pyrolysis and oil palm trunk pyrolysis with and without different catalysts using Vyazovkin model

Sample	α	Kinetic analysis			Thermodynamic analysis		
		E_A	A	R^2	ΔH	ΔG	ΔS
		$(kJ.mol^{-1})$	(s^{-1})		$(J.mol^{-1})$	$(J.mol^{-1})$	$(J.mol^{-1}.K)$
OPF	0.2	142.34	5.21×10^{13}	0.9974	1.38×10^5	1.39×10^5	-2.34
	0.3	173.29	4.73×10^{15}	0.9968	1.68×10^5	1.44×10^5	45.47
	0.4	226.64	3.24×10^{13}	0.994	2.22×10^5	2.20×10^5	2.13
	0.5	256.59	2.57×10^{22}	0.998	2.51×10^5	1.64×10^5	162.12
	0.6	259.57	9.45×10^{21}	0.9975	2.54×10^5	1.71×10^5	154.59
	Average	211.69	2.14×10^{21}	0.9967	2.07×10^5	—	—
OPF—OPF ash	0.2	109.79	7.49×10^9	0.9829	1.05×10^5	1.25×10^5	-69.62
	0.3	148.15	1.45×10^{13}	0.9938	1.43×10^5	1.48×10^5	-7.08
	0.4	177.75	2.28×10^{15}	0.9965	1.73×10^5	1.48×10^5	34.66
	0.5	185.95	4.48×10^{15}	0.9934	1.81×10^5	1.51×10^5	39.97
	0.6	245.48	1.04×10^{20}	0.9459	2.40×10^5	1.56×10^5	123.23
	Average	133.26	2.08×10^{19}	0.9825	1.68×10^5	—	—
OPF—OPF/OPT ash	0.2	123.22	1.44×10^{11}	0.9618	1.18×10^5	1.47×10^5	-45.02
	0.3	169.96	9.76×10^{14}	0.973	1.65×10^5	1.48×10^5	27.83
	0.4	201.04	1.32×10^{17}	0.9671	1.53×10^5	1.53×10^5	68.28
	0.5	246.36	1.99×10^{20}	0.8944	1.96×10^5	1.61×10^5	128.77
	0.6	173.94	4.27×10^{12}	0.9203	2.41×10^5	1.48×10^5	-18.71
	Average	182.91	3.98×10^{19}	0.9919	1.78×10^5	—	—
OPT	0.2	127.45	1.41×10^{11}	0.9948	1.23×10^5	1.52×10^5	-45.48
	0.3	147.69	8.31×10^{12}	0.9939	1.43×10^5	1.50×10^5	-11.83
	0.4	169.17	3.90×10^{14}	0.9945	1.64×10^5	1.51×10^5	19.97
	0.5	197.76	5.31×10^{16}	0.9901	1.92×10^5	1.53×10^5	60.6
	0.6	198.25	2.90×10^{16}	0.9864	1.93×10^5	1.57×10^5	55.38
	Average	168.06	1.65×10^{16}	0.9919	1.63×10^5	—	—
OPT—OPT ash	0.2	293.62	5.00×10^{26}	0.9759	2.89×10^5	1.31×10^5	252.33
	0.3	283.36	7.50×10^{24}	0.9501	2.78×10^5	1.43×10^5	217.04
	0.4	268.67	8.67×10^{22}	0.9625	2.63×10^5	1.52×10^5	179.72
	0.5	297.98	1.04×10^{25}	0.9535	2.93×10^5	1.56×10^5	219.36
	0.6	204.71	1.65×10^{16}	0.9765	2.00×10^5	1.68×10^5	50.7
	Average	269.67	1.04×10^{26}	0.9637	2.64×10^5	—	—

Sample	α	Kinetic analysis			Thermodynamic analysis		
		E_A	A	R^2	ΔH	ΔG	ΔS
		$(kJ.mol^{-1})$	(s^{-1})		$(J mol^{-1})$	$(J mol^{-1})$	$(J mol^{-1}.K)$
OPT—OPF/OPTash	0.2	157.72	8.88×10^{13}	0.9794	1.53×10^5	1.48×10^5	8.13
	0.3	193.77	8.38×10^{16}	0.9842	1.89×10^5	1.49×10^5	64.78
	0.4	217.4	4.47×10^{18}	0.9854	2.12×10^5	1.52×10^5	97.63
	0.5	235.01	8.46×10^{19}	0.998	2.30×10^5	1.54×10^5	121.91
	0.6	233.88	3.13×10^{19}	0.9468	2.28×10^5	1.58×10^5	113.46
	Average	207.56	2.41×10^{19}	0.9788	2.02×10^5	—	—

TABLE 12.4 Kinetic and thermodynamic parameters of OPF pyrolysis and OPT pyrolysis with and without different catalysts using Miura-Maki method.

Sample	α	Kinetic analysis			Thermodynamic analysis		
		E_A	A	R^2	ΔH	ΔG	ΔS
		$(kJ.mol^{-1})$	(s^{-1})		$(J mol^{-1})$	$(J mol^{-1})$	$(J mol^{-1}.K)$
OPF	0.2	142.34	7.96×10^{13}	0.9974	1.38×10^5	1.34×10^5	7.72
	0.3	173.29	1.20×10^{16}	0.9968	1.68×10^5	1.42×10^5	48.99
	0.4	226.64	4.75×10^{13}	0.994	2.22×10^5	2.20×10^5	2.66
	0.5	256.59	8.36×10^{21}	0.998	2.51×10^5	1.65×10^5	160.11
	0.6	259.57	2.66×10^{21}	0.9975	2.54×10^5	1.74×10^5	150.27
	Average	211.69	2.21×10^{21}	0.9967	2.07×10^5	—	—
OPF—OPF ash	0.2	109.79	4.07×10^{11}	0.9829	1.05×10^5	1.28×10^5	−36.4
	0.3	148.15	1.27×10^{13}	0.9938	1.43×10^5	1.48×10^5	−8.18
	0.4	177.75	4.37×10^{14}	0.9965	1.73×10^5	1.60×10^5	20.92
	0.5	185.95	3.92×10^{16}	0.9934	1.81×10^5	1.45×10^5	58.01
	0.6	245.48	2.14×10^{16}	0.9459	2.40×10^5	2.07×10^5	52.64
	Average	173.42	1.22×10^{16}	0.9825	1.68×10^5	—	—
OPF—OPF/OPT ash	0.2	123.22	4.84×10^{11}	0.9618	1.18×10^5	1.40×10^5	−34.97
	0.3	169.96	1.49×10^{15}	0.973	1.65×10^5	1.45×10^5	31.35
	0.4	201.04	1.41×10^{17}	0.9671	1.53×10^5	1.53×10^5	68.81
	0.5	246.36	1.56×10^{20}	0.8944	1.96×10^5	1.62×10^5	126.77
	0.6	173.94	2.54×10^{12}	0.9203	2.41×10^5	1.82×10^5	−23.05
	Average	182.91	3.13×10^{19}	0.9919	1.78×10^5	—	—
OPT	0.2	127.45	4.73×10^{11}	0.9948	1.23×10^5	1.46×10^5	−35.42
	0.3	147.69	1.26×10^{13}	0.9939	1.43×10^5	1.48×10^5	−8.36
	0.4	169.17	4.16×10^{14}	0.9945	1.64×10^5	1.51×10^5	20.5
	0.5	197.76	4.17×10^{16}	0.9901	1.92×10^5	1.54×10^5	58.6
	0.6	198.25	1.73×10^{16}	0.9864	1.93×10^5	1.60×10^5	51.05
	Average	168.06	1.19×10^{16}	0.9919	1.63×10^5	—	—
OPT—OPT ash	0.2	293.62	1.67×10^{27}	0.9759	2.89×10^5	1.25×10^5	262.38
	0.3	283.36	1.14×10^{25}	0.9501	2.78×10^5	1.41×10^5	220.56
	0.4	268.67	9.24×10^{22}	0.9625	2.63×10^5	1.51×10^5	180.25
	0.5	297.98	8.19×10^{24}	0.9535	2.93×10^5	1.57×10^5	217.36
	0.6	204.71	9.81×10^{15}	0.9765	2.00×10^5	1.70×10^5	46.37
	Average	269.67	1.04×10^{26}	0.9637	2.64×10^5	—	—

Sample	α	Kinetic analysis			Thermodynamic analysis		
		E_A	A	R^2	ΔH	ΔG	ΔS
		($kJ.mol^{-1}$)	(s^{-1})		($J.mol^{-1}$)	($J.mol^{-1}$)	($J.mol^{-1}.K$)
OPT—OPF/OPT ash	0.2	157.72	2.98×10^{14}	0.9794	1.53×10^5	1.42×10^5	18.19
	0.3	193.77	1.28×10^{17}	0.9842	1.89×10^5	1.46×10^5	68.3
	0.4	217.4	4.76×10^{18}	0.9854	2.12×10^5	1.52×10^5	98.17
	0.5	235.01	6.64×10^{19}	0.998	2.30×10^5	1.56×10^5	119.91
	0.6	233.88	1.86×10^{19}	0.9468	2.28×10^5	1.61×10^5	109.13
	Average	207.56	1.80×10^{19}	0.9788	2.02×10^5	—	—

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