

# 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.

We thank contributing authors for their valuable contributions and cooperation throughout various stages of the publications. Finally, we extend our heartfelt appreciation to Dr. Peter W. Adamson, Acquisitions Editor for *Renewable Energy*; Leticia Lima, the Project Manager; and the entire team at Elsevier for their support and timely effort in publishing this book.

**Suzana Yusup and Nor Adilla Rashidi**

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# Thermal degradation behavior and kinetic modeling of green solvents-delignified biomass: a sustainable biomass-to-energy approach

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## Abbreviations

AIL Acid insoluble lignin  
ASL Acid soluble lignin  
DTG Differential thermogravimetric  
EFB Empty fruit bunch  
KAS Kissinger-Akahira-Sunose  
LTTMs Low-transition-temperature-mixtures  
MSW Malic acid-sucrose-water  
TG Thermogravimetric  
TGA Thermogravimetric analysis

## 4.1 Introduction

The depletion of fossil fuels has resulted in an inadequate amount of fossil fuels left to support the ever-growing demand for energy and further leads to the surge in global dependency on the nonrenewable fossil fuels to sustain the current energy demand. Thus, it is necessary for mankind to have an alternative source of energy, which is renewable and sustainable [1]. In this sense, the conversion of lignocellulosic biomass to value-added products such as biofuels and biochemicals has gained its popularity as lignocellulosic biomass resources are readily available, cheap, and renewable [2]. Lignocellulosic biomass consists of three main components, namely cellulose, hemicellulose, and lignin. The content of these components varies according to the type of lignocellulosic biomass whereby oil palm biomass is one of the most abundant biomass. As the second largest palm oil producer in the world, Malaysia has a tremendous amount of agricultural residual generated from the palm oil industries in line with the huge production of crude palm oil. The residues from the palm oil

mills such as palm kernel shell, empty fruit bunch (EFB), and mesocarp fiber are considered as the sources of lignocellulosic biomass. At the plantation area, some other biomass are also being generated such as oil palm trunk and oil palm frond [3]. The complex structures of lignocellulosic biomass and its recalcitrant nature need to be overcome through the introduction of pretreatment processes before conversion to value-added products [1].

Lignocellulosic biomass has the recalcitrant nature, which is resistance to breakdown through chemical and biological methods due to the complex hierarchical structures formed by the three main components of lignocellulosic biomass. Pretreatment processes come in handy where they help to disrupt the recalcitrant structure of lignocellulosic biomass through breaking of lignin sheath for the efficacious utilization of the lignocellulosic biomass [1]. Pretreatment also eases the accessibility of enzymes to hydrolyze both cellulose and hemicellulose [2]. The removal of lignin causes the transformation of cellulose crystalline to amorphous structure which ameliorates the biodegradability of biomass and enhances the yield of pyrolysis oil [4,5]. Various pretreatment technologies are available nowadays which consist of physical, chemical, biological, and green solvents pretreatment [6–10], as shown in Table 4.1.

According to Kandaneli et al. [11], four major bonds exist in the complex structure of lignocellulosic biomass namely ester, ether, carbon-carbon, and hydrogen bonds. The recalcitrance nature of lignocellulosic biomass is mainly due to the presence of hydrogen bonds. A study conducted by Kandaneli et al. [11] showed an increment in the percentage of delignification for rice husk using the mixture of deep eutectic solvent and alcohol from 9% to 48% when the pretreatment

**TABLE 4.1 Summary of mechanism of actions, advantages and disadvantages of multiple pretreatment methods.**

Pretreatment category	Methods	Mechanism of actions	Advantages	Disadvantages	References
Physical	Steam explosion	Reduce the size of biomass fiber, enzymatic hydrolysis	Low energy consumption, low capital investment, low impact on the environment	Formations of fermentation inhibitors, condensation and precipitations of lignin leads to lower digestibility	[6]
	Mechanical comminution	Reduce the size of particles	No fermentation inhibitors produced	High energy consumption, no delignification effect	[6]
Chemical	Concentrated acid	Turn lignocellulose into fermentable sugars	No enzymes required	High equipment cost due to corrosiveness, high energy consumption	[7]
	Dilute acid	Hydrolysis of lignocellulose, improve the digestibility by enzymes	Effective solubilization and hydrolyzation of hemicellulose, increased cellulose hydrolysis yield	High equipment cost due to corrosiveness, formation of gypsum and fermentation inhibitors	[7]
	Alkaline	Modify structure of lignin and saponification of hemicellulose	Low operating conditions, low corrosiveness, produced substrate high in xylan and cellulose	Long reaction time	[8]
Biological	Fungi	Cellulose, hemicellulose and lignin decomposition	Low cost, low demand of energy, no chemicals required	Long residence time, huge space required, carbohydrate loss	[6]
Green solvents	Ionic liquids	Breakdown complex structure of lignocellulose	High recyclability, high thermal stability	High cost, low toxicological data	[6,9]
	Deep eutectic solvents	Destroy complex structure, intra and intermolecular interaction of polymers	Highly biodegradable, easy to prepare, low in cost, low level of toxicity	High viscosity, high hygroscopicity	[9]
	LTTMs	Selective delignification	Low cost, environmentally friendly solvent, high delignification selectivity, enhanced enzymatic hydrolysis and thermal degradation	High viscosity for amino acid based LTTMs	[10]

temperature is increasing from 50°C to 120°C. This is mainly due to the breaking of hydrogen bonds caused by high temperature, which enhanced the interactions between biomass and solvent resulted in better lignin dislocation. The enhancement of delignification process is also proven in other studies conducted using different types of biomass and solvents [12,13].

The performance of pyrolysis, a complex thermal degradation of materials in a low oxygen environment, is influenced by the heating rates. Based on the study conducted by Alias et al. [14], higher heating rates lead to an increase of degradation peak for cellulose and hemicellulose. This may be due to the fast endothermic decomposition of biomass caused by the fast heating pace which resulted in the abundance of volatile. This research is the first attempt to conduct the analysis on the thermal degradation behavior of green solvents-delignified biomass using sucrose-based LTTMs for pretreatment at different temperatures. This research aims to discover the ideal pretreatment temperature for delignification and heating rates for pyrolysis using oil palm EFBS as feedstocks. The kinetic analysis for the pyrolysis process of delignified biomass was carried out by utilizing thermogravimetric analysis (TGA). According to Soria-Verdugo et al. [15], TGA is able to identify the kinetic parameters of the biomass pyrolysis processes, which provides information to clarify the process of thermal decomposition and to apprehend the formation of products through the reactions of pyrolysis. The parameters and reaction mechanism of the pyrolysis processes were estimated based on the TGA data. In this sense, optimum conditions are required in order to enhance the pyrolysis yield. The kinetic parameters are also important for the optimization and design of the pyrolysis process.

## 4.2 Methodology

### 4.2.1 Materials

EFBs used in this project were obtained from Sarawak Oil Palm Lambir Palm Oil Mill. Distilled water was used to wash the EFBS, and completely dried in an oven at temperature of 100°C for 3 days. The EFBS were then cut into smaller pieces before being grounded using rotor mill (Fritsch Pulverisette 14) and sieved to the desired particle size of <500 µm [16].

### 4.2.2 Synthesis of low-transition-temperature-mixtures

The chemicals required for the synthesis of LTTMs, such as 99+% malic acid and sucrose were ordered from Borneo Indah Sdn Bhd. The LTTMs were synthesized by mixing malic acid-sucrose-water (MSW) in a ratio of 2:4:2 [16]. The mixture was stirred and mixed thoroughly using a magnetic stirrer to stimulate the contact between the solid crystals. The mixture was then being heated up slowly in an oil bath to the temperature of 80 to 90°C until all the solid crystals were melted, forming transparent liquid mixtures. The heating process was extended to 15 min to ensure a complete formation of hydrogen bonding in the mixtures.

### 4.2.3 Pretreatment of empty fruit bunches

The LTTMs were used to pretreat the EFBS sample in a ratio of 20:1 (w/w) at 80°C, 90°C, 100°C, 110°C, and 120°C for 6 h. The pretreatment was conducted using an oil bath with magnetic stirring. After the pretreatment process, distilled water was used to wash the mixtures for lignin precipitation. The supernatant was removed and left the delignified biomass behind. The delignified biomass was washed with distilled water to remove the remaining solvent and dried at 80°C for 12 h [16,17].

### 4.2.4 Determination of lignin content

Klason method was used to determine lignin content in both the untreated and delignified EFBS [18]. 72% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was used to treat the samples at room temperature for 2 h. This step was followed by dilution of the hydrolyzed sample to 3% H<sub>2</sub>SO<sub>4</sub> using distilled water and boiled under a reflux condition for 4 h. The acid insoluble lignin (AIL) was then removed from the solution and dried at 50°C. The content of the acid soluble lignin (ASL) left in the 3% H<sub>2</sub>SO<sub>4</sub> solution was analyzed using UV/Vis spectrophotometer (Perkin Elmer Lambda 35) and calculated based on Eq. (4.1) be-

low:

$$\text{Acid soluble lignin} = \frac{\text{Absorbance at 205 nm}}{\text{Cell path length} \times \text{Absorptivity} \times \text{Dilution factor}} \quad (4.1)$$

The value of ASL was calculated based on a reference blank of 3% H<sub>2</sub>SO<sub>4</sub>, standard dilution factor of 20, cell path length of 1 cm, and lignin absorptivity of 110 L gcm<sup>-1</sup> at 205 nm [19].

#### 4.2.5 Thermogravimetric analysis of untreated and delignified empty fruit bunches

The thermal degradation behaviors of the untreated and delignified EFBs were determined using a simultaneous thermal analyzer (Perkin Elmer STA8000). The analysis was carried out in an inert nitrogen atmosphere with a flowrate of 30 mL min<sup>-1</sup>. 5 mg of samples was loaded into the STA sample pan and heated from 40°C to 1000°C at different heating rates of 10, 30, 50, and 70°C min<sup>-1</sup> [20].

#### 4.2.6 Kinetic modeling

The differential thermogravimetric (DTG) and thermogravimetric (TG) data obtained from the TGA of untreated and delignified EFBs were applied to demonstrate the pyrolysis kinetic model by the iso-conversional, Kissinger-Akahira-Sunose (KAS) integral method, which does not require the exact thermal degradation mechanism [21]. The non-isothermal thermal reaction rate equation according to the Arrhenius law can be represented as below:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (4.2)$$

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (4.3)$$

where  $\alpha$  is the process conversion,  $t$  is the time,  $f(\alpha)$  is the reaction model,  $m_i$  is the initial sample weight in mg,  $m_t$  is the sample weight at the time  $t$  in mg,  $m_f$  is the final sample weight after pyrolysis in mg,  $A$  is the frequency factor in 1 min<sup>-1</sup>,  $E_a$  is the activation energy for the degradation reaction in kJ mol<sup>-1</sup>,  $T$  is the temperature in K, and  $R$  is the universal gas constant in kJ mol<sup>-1</sup>.K.

The heating rate,  $\beta$  for non-isothermal experiment is defined as Eq. (4.4) by substituting Eq. (4.3) into Eq. (4.2):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (4.4)$$

The expression of KAS model is shown as Eq. (4.5) below:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a(1-\alpha)}\right) - \frac{E_a}{RT} \quad (4.5)$$

The activation energies were obtained from the linear plots of  $\ln(\beta/T^2)$  versus  $1/T$  for each conversion rate. The slope and intercept were  $(-E_a/R)$  and  $\ln(AR/(E_a(1-\alpha)))$ , respectively.

### 4.3 Results and discussion

#### 4.3.1 Effects of pretreatment temperature on delignification process

The lignin content of samples and delignification efficiency at different temperatures are tabulated in Table 4.2. The lignin content in the untreated EFBs was determined to be 21.89 wt.%. The extent of delignification was increased initially and decreased towards the end with the increasing of pretreatment temperature. The highest delignification efficiency was obtained at the pretreatment temperature of 90°C with a delignification efficiency of 31.23%. Nonetheless, the delignification efficiency at 100°C, 110°C and 120°C of pretreatment temperature was lower compared to 90°C, with 11.47%, 13.48%, and 3.99%, respectively. The lowest delignification efficiency was achieved at the pretreatment temper-

**TABLE 4.2 Lignin content in untreated and delignified EFBs at different temperatures.**

Type of sample	Untreated	80°C	90°C	100°C	110°C	120°C
AIL (wt.%)	13.94	11.69	11.26	12.21	12.50	14.00
ASL (wt.%)	7.95	5.20	3.79	7.17	6.43	7.01
Total (wt.%)	21.89	16.90	15.05	19.38	18.94	21.01
Delignification efficiency (%)	–	22.80	31.23	11.47	13.48	3.99

ature of 120°C with 21.01 wt.% of lignin remained in the delignified sample. The highest delignification efficiency achieved in this study was 31.23% at 90°C which is lower compared to the works reported by Yiin et al. [19], whereby 50.14% lignin removal was achieved when using LTTMs synthesized from MSW in a ratio of 2:4:2. This phenomenon might be due to the chemical composition of lignocellulosic biomass differs accordingly based on the origin and types [22]. The EFBs used in the research of Yiin et al. [19] were obtained from Kilang Sawit FELCRA Berhad Nasaruddin, KM 37, Jalan Tronoh, 32600 Bota, Perak, Malaysia. In this context, Abdul Khalil et al. [23] reported that the composition of EFBs varies depending on the plant age, soil condition, weather effect, and environment. Higher lignin extraction rate can be achieved when greater proportion of non-structural low molecular constituents exist in the lignocellulosic biomass, due to better accessibility of the LTTMs to the lignin during pretreatment [24]. Thus, the chemical composition of the EFBs used in both studies was different which relatively might affect the delignification efficiency.

The pretreatment temperature of delignification process using LTTMs is limited by the degradation temperature of the solvent. The upper limit of pretreatment temperature in this study was set at 120°C as Yiin et al. [17] reported that the degradation temperature of LTTMs synthesized from MSW was 127°C. The solvents started to caramelize with reduced viscosity and turned darker in color at higher temperature. This might be the factor which contributes to the decreased in the delignification efficiency at higher pretreatment temperature that was exceeding the optimal temperature. Reaction temperature was known to be the factor that intensify the reaction kinetics, therefore, explains that higher pretreatment temperature can improve the breaking process of hydrogen bonds and disrupt the recalcitrant nature of lignocellulosic biomass. This theory was proven by the increment in extent of delignification efficiency when the pretreatment temperature increased, with a certain limit based on the degradation temperature of the solvents.

#### 4.3.2 Thermogravimetric analysis

The curves of mass loss for the TG and DTG of raw and delignified EFBs with varying heating rates are displayed in Figs. 4.1 and 4.2. The pyrolysis of EFBs have three distinct stages of thermal degradation based on the TG and DTG curves. Stage 1 usually refers to the elimination of light volatile compounds and moisture that are bound by surface tension which occurred at lower temperature (30°C to 200°C). This was followed by Stage 2, where the removal of volatile components of hemicellulose and cellulose was occurred between the temperature of around 200°C–450°C. Stage 2 contributed to the significant mass loss and higher degradation peaks as observed in TG and DTG curves, respectively. Stage 3 was the last stage where the slow degradation of lignin occurred at the temperature of above 450°C. Several works have also reported on the temperature ranges at different stages for the thermal degradation of lignocellulosic biomass in pyrolysis condition, which have close agreement to the ranges of temperature determined in this research. Lee et al. [25] reported that the mass reduction starting from ambient temperature to 200°C was attributed to Stage 1. Stage 2 happened around 200°C to 500°C where heavy organic compounds were devolatilized, and followed by Stage 3, where slow mass loss had happened at the temperature of above 500°C. Hussain et al. [26] also reported the ranges of temperature at different stages whereby Stage 1 occurred between 25°C and 180°C, Stage 2 at around 180°C–380°C, and Stage 3 at about 500°C.

Fig. 4.1 shows that the trend of the weight loss profiles at different heating rates are almost similar to each other, but somehow slightly skewed towards higher temperature with increasing heating rate for both the untreated and delignified EFBs. This phenomenon might be due to the low heat transfer efficiency with increasing heating rate, which shorten the time for the pyrolysis process to take place [25]. Rapid heating of biomass at higher heating rate resulted in the poor flow of heat into the interior of the solid, which explains the trend of the weight loss profiles [27]. Based on the DTG profiles shown in Fig. 4.2, there are three obvious peaks which can be clearly seen at different temperatures when varying the heating rate. The first peak indicates the release of moisture and light volatile. The second peak was due to the decomposition of hemicellulose while the third peak was due to the degradation of cellulose. This is consistent with the fact that



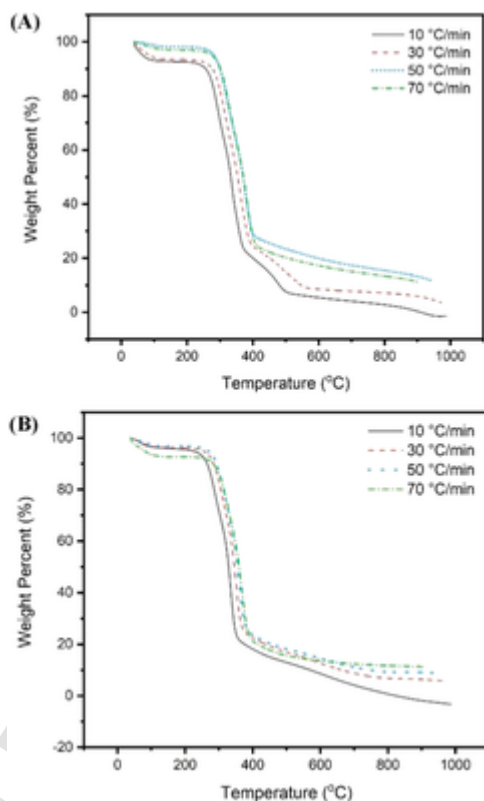


FIGURE 4.1 TG profiles of (A) raw EFBs and (B) delignified EFBs.

cellulose with the unbranched crystalline structure linked by glycosidic bonds tends to be more stable than hemicellulose, as the degradation of cellulose occurred at higher temperature [28]. It was observed in the DTG curves that the peaks for the maximum degradation were moved to higher temperature with increasing heating rate. The temperatures at which the peaks occurred at different heating rates were tabulated in Table 4.3. Besides, the height of the peaks for the maximum degradation also decreased with increasing heating rate. These observations were contributed by the combined effects of heat and mass transfer which resulted in a process taking place under non-negligible effects of internal heat transfer, whereby the same trends were reported in the works of Hu et al. [29] and Lee et al. [25].

Fig. 4.2 also shows that the shoulders associated with the degradation of hemicellulose and cellulose in Stage 2 are more obvious after the delignification process as lignin plays the role of hindering the decomposition of hemicellulose and cellulose, which induce the shoulder to appear less obvious with lower degradation peaks. The maximum degradation rates of delignified EFBs are noticeably higher than the untreated sample, due to enhanced cellulose content after removing lignin from the lignocellulosic biomass structure [30]. Thus, the delignified EFBs showed observable differences in their thermal degradation behavior during pyrolysis such as much obvious shoulders in the DTG curves for cellulose degradation. When comparison was made between the pyrolysis behavior of the untreated and the delignified EFBs, remarkable difference and improvement can be observed. One of the observations made based on DTG curves shown in was that the shoulders associated with the degradation of hemicellulose and cellulose in Stage 2 was more obvious after the delignification process. This is because lignin plays the role of hindering the decomposition of hemicellulose and cellulose, which makes the shoulder to appear less obvious with lower degradation peaks. The maximum degradation rates based on DTG curves in Fig. 4.2 for delignified EFBs were noticeably higher than that for the untreated sample. The increased in the maximum degradation rate resulted from the enhanced cellulose content when lignin were removed from the lignocellulosic biomass structure. Thus, the delignified EFBs showed observable differences in their thermal degradation behavior during pyrolysis such as much obvious shoulders in the DTG curves for cellulose degradation.

### 4.3.3 Pyrolysis kinetic

The activation energy ( $E_a$ ) of untreated and delignified EFBs were determined through the plotting of iso-conversional KAS model as shown in Fig. 4.3. The linear regression fitted lines were presented with the value of conversion within

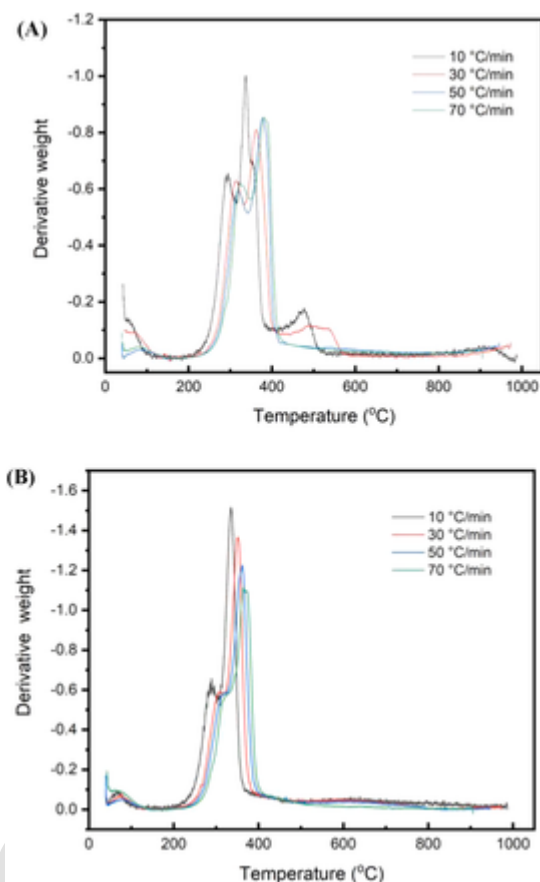


FIGURE 4.2 DTG profiles of (A) raw EFBs and (B) delignified EFBs.

TABLE 4.3 The temperature at which the peaks occur at different heating rates.

Type of EFBs	Heating rates ( $^{\circ}\text{C min}^{-1}$ )	Temperature at peak ( $^{\circ}\text{C}$ )		
		Peak 1	Peak 2	Peak 3
Untreated	10	54.9	292.9	336.7
	30	72.5	312.9	362.1
	50	80.1	318.5	376.9
	70	83.1	324.8	381.1
Delignified	10	67.9	289.4	335.1
	30	75.9	306.9	350.9
	50	79.5	320.8	362.3
	70	65.4	322.3	365.4

0.1–0.9. The  $E_a$  which indicates the amount of energy needed for the pyrolysis reaction to occur was estimated from the slopes of the linear plots at a given conversion. The  $E_a$  value estimated for the untreated EFBs varied within 42.27–254.16  $\text{kJ mol}^{-1}$ , while for delignified EFBs were within the range of 57.73–262.12  $\text{kJ mol}^{-1}$ . This shows an increment in the  $E_a$  after the EFBs were pretreated using the sucrose-based LTTMs. This might be due to the changes in the composition of EFBs after the degradation of hemicellulose or depolymerization of cellulose and lignin. Zhang et al. [31] reported that the pretreated samples have higher activation energies compared to the untreated or raw samples. Another work also reported that the activation of EFB was increased after the process of pretreatment [20].

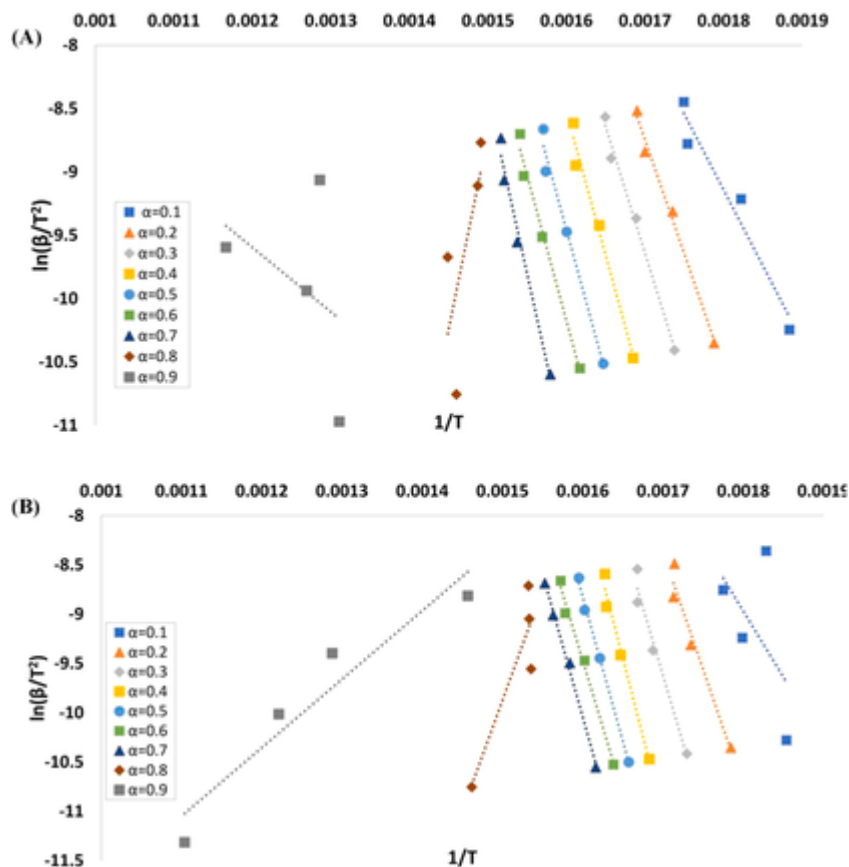


FIGURE 4.3 Kinetic plots for (A) untreated and (B) delignified EFBs using KAS method.

#### 4.4 Conclusions

The results showed that the pretreatment temperature of 90°C had the highest delignification efficiency for the 6 h pretreatment. The delignification efficiency increased along with the increase in pretreatment temperature, which was limited by the degradation temperature of the LTTMs. Along with the increase in heating rates, the peaks of the maximum degradation were shifted to higher temperature with a reduction in the height of the peaks. Kinetic parameters of the pyrolysis of EFBs were determined through the linear plots of the iso-conversional KAS model. The results of the kinetic modeling showed that the estimated  $E_a$  for the untreated EFBs varied within 42.27–254.16 kJ mol<sup>-1</sup> while that for delignified EFBs were within the range of 57.73–262.12 kJ mol<sup>-1</sup>. The activation energies of the delignified EFBs increased after the pretreatment process using LTTMs. These results are critical as they provide information for the design and optimization of the pretreatment for lignocellulosic biomass as well as the pyrolysis of the biomass.

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