Reaction kinetics for catalytic pyrolysis of empty fruit bunch (EFB) with silica-alumina (SiO_2-Al_2O_3) catalyst: Kissinger and Ozawa methods

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ABSTRACT: In this study, EFB components such as hemicellulose, cellulose and lignin were analyzed and it was determined that the hemicellulose, cellulose and lignin content were 53.03, 30.24 and 16.71 % respectively. The dynamic catalytic pyrolysis of EFB with silica-alumina (SiO_2-Al_2O_3) at several heating rates in the range of 10-40 $Kmin^{-1}$ were performed in a thermogravimetric analyzer (TGA) under nitrogen atmosphere. The reaction kinetics were calculated using Kissinger and Ozawa methods. The values of activation energy are 231. 28 and 241.03 kJ/mol by Kissinger and Ozawa methods respectively. Meanwhile, the values of pre-exponential factor are 47.72 and 47.39 by Kissinger and Ozawa methods respectively.

Keywords: *Empty fruit bunch; Catalytic pyrolysis; Kinetics*

1. INTRODUCTION

In Malaysia, crude palm oil processing industry creates biomass waste such as palm kernel shell (PKS) and empty fruit bunch (EFB) [1]. Approximately 6.7 million metric tonnes per year of EFB was produced [2]. However, this amount has increased to about 15.8 -17.0 million tonnes of empty fruit bunch (EFB) was generated in 2018 [3]. It is apparent that abundant quantities of EFB waste produced. Catalytic pyrolysis of biomass with certain types of catalysts have been reported [4-5]. However, the kinetics for catalytic pyrolysis of EFB with SiO_2-Al_2O_3 using Kissinger and Ozawa methods have not reported yet. Therefore, this paper reports about the kinetics for catalytic pyrolysis of EFB with SiO_2-Al_2O_3 using Kissinger and Ozawa methods.

2. METHODOLOGY

2.1 EFB Pretreatment

Treated EFB was collected from North Star Palm Oil Mills, which was located in Kuala Ketil, Kedah, Malaysia. It was sieved to several particle sizes and stored in separate containers. The sieved EFB with particle of size 125-250 µm was chosen to be mixed with the catalyst for the catalytic pyrolysis process. EFB with particle size less than 125 µm was used for component analysis.

2.2 Catalyst preparation

Approximately 10 g silica-alumina (SiO_2-Al_2O_3) catalyst support was calcined at 923 K for 5 hours at a ramp rate 3 $Kmin^{-1}$ under static atmosphere and the catalyst was placed in desiccators before use.

2.3 Component analysis

The composition of EFB fiber obtained was determined by measuring the acetone extractable material, the hemicellulose and cellulose. All remaining material was taken to be lignin [6].

2.4 Thermogravimetric (TG) catalytic EFB pyrolysis at a linear heating rate

The catalytic pyrolysis of EFB with SiO_2-Al_2O_3 was conducted using thermogravimetric analyzer. Initially, 10.0 mg of EFB was located into the alumina crucible and followed by about 1.0 mg of SiO_2-Al_2O_3 catalyst to yield the catalyst to biomass ratio of 9.09 wt% . The nitrogen gas was used as the carrier gas at the constant flow rate of 100 $mlmin^{-1}$ under dynamic conditions from 301 K towards final pyrolysis temperature of 1,273 K at a linear heating rate of 10, 15, 20, 25, 30 and 40 $Kmin^{-1}$. Each heating rate produced experimental data and transferred to Excel spreadsheet [7]. Analysis was performed using Excel software with Kissinger and Ozawa methods.

The Kissinger (5) and Ozawa (6) equations are as shown below:

$$\ln(\frac{\beta}{T_p^2}) = -\frac{E_a}{RT_p} + \ln(\frac{AR}{E_a}) \quad (1)$$

$$\ln(\beta) = \ln(\frac{AE_a}{Rg(a)}) - 5.331 - 1.052\frac{E_a}{RT} \quad (2)$$

g(a) was the integral form of the kinetics mechanism function in Equation (2). The equation is applicable when the reaction order (n) equals to 1.

3. RESULTS AND DISCUSSION

3.1 Component analysis

The EFB sample comprised of 19.02 % acetone extractives, 53.03 % hemicellulose, 30.24 % cellulose and 16.71 % lignin.

3.2 Kinetic analysis of catalytic pyrolysis of EFB using TGA.

For Kissinger and Ozawa methods, the graph of Ln (β/T_p^2) versus on $1/T_P$ and Ln β against $1/T_P$ were plotted for catalytic pyrolysis of EFB with SiO_2-Al_2O_3 as shown in Figures 3 and 4 respectively. The linear equations from both figures are shown in Table 1, with the values of E_a and Ln A. All the R^2 values are > 0.94. Therefore, the non-dependable parameter has strong correlation with dependable parameter.

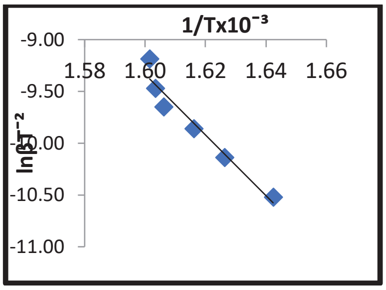

Figure 3 Kissinger plot for EFB pyrolysis with SiO_2-Al_2O_3

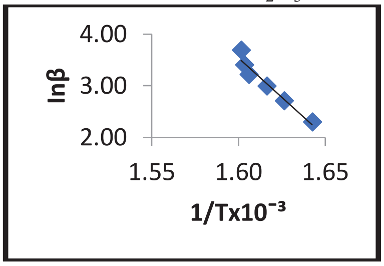

Figure 4 Ozawa plot for EFB pyrolysis with SiO_2-Al_2O_3

Table 1 The kinetic parameters (E_a and Ln A) for catalytic pyrolysis of EFB with SiO_2-Al_2O_3

Method	Equation	R^2	E_a(kJmol^{-1})	Ln A
Kissinger	y = -29.2649 x 10^3 x + 37.4881	0.944	231.28	47.72
Ozawa	y = -30.4986 x 10^3 x + 52.3373	0.948	241.03	47.39

Table 2 shows the values of activation energy and pre-exponential factor for the catalytic pyrolysis of EFB with SiO_2-Al_2O_3.

Table 2 The kinetics parameters for **c**atalytic EFB pyrolysis with SiO_2-Al_2O_3 .

Method	E_a(kJmol^{-1})	Ln A
Kissinger	231.282	47.7216
Ozawa	241.032	47.3936

4. CONCLUSION

As a conclusion, the thermochemical profiles of catalytic EFB pyrolysis with SiO_2-Al_2O_3 catalyst can be divided into three stages. The kinetics parameters which are the activation energy, Ea for the catalytic pyrolysis of EFB with SiO_2-Al_2O_3 by Kissinger and Ozawa methods are 231. 28 and 241.03 kJ/mol respectively.

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