Thermogravimetric kinetic analysis of powdered and pelletized sawdust under oxidative environment

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ABSTRACT: A thermal degradation behavior of powdered and pelletized sawdust is evaluated employed thermogravimetric analyzer using selected non-isothermal methods to assess the solid-state kinetics data. TGA in an oxidative atmosphere was used to determine the weight loss. The samples were heated at four different heating rates of 5, 10, 15, and 20 K/min over a temperature range of 30°C to 950°C. The results of the thermal decomposition process indicate that there are four main process. Meanwhile, the temperature peaks at maximum weight loss rate in the DTG thermograms altered with increasing heating rate. The activation energy and pre-exponential factor obtained by Kissinger approach are (189.72 kJ/mol, 7.61 x 10^{13} min^{-1}) for SD and (163.43 kJ/mol, 1.15 x 10^{11} min^{-1}) for SDP. Meanwhile, the same average parameters calculated from FWO and DAEM methods for SD are (149.08 kJ/mol, 5.49 x10^{18} min^{-1}) and (150.32 kJ/mol, 1.53 x10^{13} min^{-1}), respectively. For SDP, the average parameter are (120.75 kJ/mol, 5.16 x10^{15} min^{-1}) determined for FWO, and (116.92 kJ/mol, 5.90 x10^9 min^{-1}) for DAEM. Experimental results reveal that values of kinetic parameters obtained from three distinct methods agree well, although the FWO and DAEM methods are more reliable in describing the degradation mechanism for biomass fuels.

Keywords: *Biomass; Thermogravimetric analysis; Kinetic*

1. INTRODUCTION

Thermochemical processes can have highly efficient conversion of biomass to gaseous, liquid and solid products. In-depth understanding of the reaction kinetics in thermochemical conversion of the biomass for energy production are necessary for industrial scale implementation. Numerous studies have applied the TGA technique to investigate thermal decomposition profiles and kinetic parameters of biomass fuels in nitrogen and air atmospheres[1], [2]. However, this study intended to focus on the air atmosphere as there is a lack of adoption of the kinetic model in the air environment. The reaction in air environment are much more complex as in the combustible atmosphere the pyrolytic and combustion reactions simultaneously takes place making it difficult to distinguish adding together the sample tend to self-ignite resulting in unrealistics behaviour in measured graph [3]. In addition, there were limited studies have compared the thermokinetics of raw and pelletized biomass.

The non-isothermal kinetic assessment in the air environment is particularly complex since it involves various phases reacting concurrently or simultaneously. Thus, the kinetic model can be classified as model fitting or model-free, with the latter allowing the activation energies to be determined independently on the specific mechanism that governs the transformation [4].Thus, in this paper, the thermal conversion characteristics of powdered and pelletized sawdust were investigated employed macro-TGA under oxidative atmosphere. Three model –free (Kissinger, Flynn-Wall-Ozawa and and Distribution Activation Energy Model) methods were adopted to measure the kinetic parameter and to gain an insight on the comprehensive findings of thermal behavior between SD and SDP.

2. METHODOLOGY

In order to evaluate the thermal decomposition of materials corresponding to time as a result of chemical reactions, the thermogravimetric analysis was performed using thermogravimetric analyser modelled Rigaku Thermo plus EVO II. Sawdust (SD) in the powdered form. and pelletized sawdust (sawdust pellet, SDP) were weighing approximately 10 mg and filled in an alumina crucible. During the experiment the furnace of TGA is flushed with air under dynamic conditions with the temperature ranging from 30°C to 950°C to maintain an oxidative atmosphere during thermal decomposition. The experiment was run as a batch-type process at different heating rates, β set at 5, 10, 15, and 20 K/min. The heating rate was varied from 0.1 to 0.9 for the purpose of calculating the kinetic parameter based on the approach method. Data were then continuously record by the TGA software in order to create and analyse the TG and DTG curves (the first derivatives of the TG curves). To achieve repeatability, duplicate analysis of each sample was conducted. Three model –free (Kissinger, Flynn-Wall-Ozawa and and Distribution Activation Energy Model) methods were adopted to measure the kinetic parameter

3. RESULT AND DISCUSSION

The apparent E_a obtained from the slope; the A was calculated from the interception of the regression lines, are presented in Table 1. It was apparent that SD at α of 0.1 from the FWO and DAEM methods deviated from 1.0 calculated at R^2 as 0.39 and 0.70, respectively. Despite this, the E_a value was in-parallel with those obtained by Mishra and Mohanty [5], which were in the range of 146.44 to 157.01 kJ/mol for sawdust by applying the DAEM method. Thus, it is best to consider the conversion of SD using a range of 0.2 to 0.9. Subsequently, for both the degradation model approaches, it can be seen that as the conversion value goes beyond 0.7, the E_a is significantly lower and it fluctuates as the conversion value reaches 0.9. Fan et al. [6] revealed that the E_a changes markedly when the α value is at 0.8 to 0.9, which is probably due to heat and mass transfer in the reaction that causes complications in the reaction and the sudden increase of E_a at the end of the reaction process. Wang et al., [7] stated that considering the DAEM method that corresponds to the whole thermal reaction process, it is suggested that further decomposition could decrease the threshold energy that converts the reactant into a product, resulting from the gradual decrease of E_a until the end of the reaction. It is crucial to note that SDP possesses the lowest E_a compared to SD due to the softened lignin during palletisation, making it more reactive [8]. Furthermore, A follows the same pattern as E_a for all models with the lowest A calculated by employing the DAEM method. A, or the pre-exponential factor, signifies the collision of activated molecules corresponding to a substantial A, denoting a high reaction rate. Thus, lowering the reaction rate provides the least A, which induces a higher E_a and this is referred to as the compensation effect in kinetic studies [9].

Table 1. E_a and A values for SD and SDP by calculated using the Kissinger, FWO and DAEM methods.

Sample	α	Kissinger		FWO			DAEM		
		E_a (kJ/mol)	A (s⁻¹)	E_a (kJ/mol)	A (s⁻¹)	R^2	E_a (kJ/mol)	A (s⁻¹)	R^2
SD	0.1			-7.05	-3.65×10	0.39	14.27	8.07×10^5	0.70
	0.2			181.03	4.63×10^{19}	0.98	181.47	1.34×10^{14}	0.90
	0.3			162.94	3.66×10^{17}	0.99	162.16	5.37×10^{11}	0.99
	0.4			166.90	4.99×10^{17}	1.00	165.11	5.51×10^{11}	0.99
	0.5	189.72	7.61×10^{13}	175.52	1.74×10^{18}	1.00	174.96	1.63×10^{12}	1.00
	0.6			173.14	5.55×10^{17}	1.00	172.24	4.02×10^{11}	1.00
	0.7			163.12	1.81×10^{16}	1.00	161.26	9.07×10^9	0.99
	0.8			152.63	3.56×10^{14}	0.99	149.52	1.19×10^8	0.99
	0.9			173.46	3.89×10^{14}	0.99	170.89	1.36×10^9	0.99
Average				149.08	5.49×10^{18}		150.32	1.53×10^{13}	
SDP	0.1			122.42	8.47×10^{13}	0.95	120.07	2.34×10^8	0.95
	0.2			147.06	8.12×10^{13}	0.99	145.48	1.46×10^{10}	0.99
	0.3			153.23	1.56×10^{16}	0.97	151.66	1.91×10^{10}	0.96
	0.4			156.20	1.83×10^{16}	0.95	154.56	1.65×10^{10}	0.94
	0.5	163.43	1.15×10^{11}	150.47	4.31×10^{15}	0.92	148.36	2.78×10^9	0.91
	0.6			119.04	5.43×10^{12}	0.86	115.11	1.73×10^6	0.84
	0.7			54.32	1.24×10^7	0.55	46.56	5.72×10^{-1}	0.45
	0.8			89.06	2.60×10^9	0.78	82.39	2.66×10^2	0.73
	0.9			94.97	4.01×10^9	0.50	88.05	3.78×10^2	0.44
Average				120.75	5.16×10^{15}		116.92	5.90×10^9	

4. CONCLUSION

In this study, an experimental kinetic study of SD and SDP is presented where kinetic constants were determined and compared through three different methods. Overall, the maximum activation energy of SDP was significantly greater than that of SD while their average activation energies were 163.04 ± 23.11 kJ/mol for SD, and 133.1 ± 25.82 kJ/mol for SDP denoting an effective reaction of thermochemical conversion process with pre-treatment biomass.

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