THERMOKINETICS OF CATALYTIC PYROLYSIS OF BIOMASS FOR PRODUCTION OF SUSTAINABLE ENERGY

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Abstract

Pyrolysis can be described as the thermal decomposition of the organic matrix in the absence of oxygen. Currently, the pyrolysis of biomass is paid much attention for the production of sustainable energy. In this study, the catalytic effect on kinetic behavior of biomass pyrolysis has been examined thermogravimetrically. The biomass used here is the sugarcane bagasse, a readily available agricultural waste in Perlis region of Malaysia. The sugarcane bagasse was characterized in terms of its composition and heating value. The thermogravimetric analyses were conducted during heating the bagasse from room temperature to 800 ^{o}C. The kinetic parameters for the pyrolysis were determined by analyzing the weight loss curves at three different heating rates (5°C/min, 15°C/min and 20 ^{o}C/min). Dolomite as a catalyst and/or promoter for the bagasse pyrolysis was also studied and the kinetics with and without using the dolomite were compared. Results showed that the rate of pyrolysis in the presence of dolomite is higher than that without it. Thus it is obvious that the catalytic effect plays an important role in the pyrolysis of biomass.

Keywords: Biomass pyrolysis, Kinetics of pyrolysis, Dolomite, Thermogravimetry, Sustainable energy

Introduction

There is a great potential for biomass to be converted into commercial fuels, suitable to substitute for fossil fuels for various applications. The most common technique of conversion of biomass to commercial fuels is the pyrolysis [1]. Pyrolysis can be described as the thermal decomposition of the organic matrix in the absence of oxygen. Currently, the pyrolysis of biomass is paid much attention for the production of sustainable energy. The rationale is that the thermal utilisation of biomass can contribute to the reduction of CO_2 emissions as the same amount of CO_2 is extracted from the atmosphere during the growth period of the plants as is released by combustion [2]. In this study, the catalytic and/or promoter effect of calcined dolomite on kinetic behavior of biomass pyrolysis has been examined thermogravimetrically.

Experimental

Material

The biomass used here is the sugarcane bagasse, a readily available agricultural waste in Perlis region of Malaysia. It was dried under the sun. The dried sugarcane bagasses were ground and seived to 300 µm size. The sugarcane bagasse was characterized in terms of its composition and heating value. Calcined dolomite was used as catalyst in this study. The dolomite obtained from the Perlis area was ground and sieved to 300 µm and then calcined up to 900°C.

Apparatus and Procedures

The thermogravimetric analyses were conducted during heating the bagasse from room temperature to 800 ^{o}C. Approximately 5 mg each of the sample (bagasse only or 10% dolomite+90% bagasse) was heated at the rate of 20 degree/min up to 800°C under the nitrogen flow of 50 ml/min. The kinetic parameters for the pyrolysis were determined by analyzing the weight loss curves using the integral Coats-Redfern method with the reaction order model of the conversion function. The catalytic and/or promoter effect of calcined dolomite on the bagasse pyrolysis was studied by comparing the kinetic behavior of the two TG curves.

Kinetic Analysis

The global kinetics of decomposition with nth reaction order is given by

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

where $k = A\exp(-E/RT),\quad \frac{d\alpha}{dt} = \left(\frac{d\alpha}{dT}\right)\left(\frac{dT}{dt}\right) = \left(\frac{d\alpha}{dT}\right)\beta$

Thus, $\dfrac{d\alpha}{dT} = \dfrac{A}{\beta}\exp(-E/RT)(1-\alpha)^n$

To determine the kinetic parameters E and A for a given n, the above equation is integrated with experimental TG data. The classical Coats-Redfern method [3] uses the following approximated solution:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E} - \frac{E}{RT} \qquad \text{where } g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n}$$

The slope of the linear regression line of $\ln\dfrac{g(\alpha)}{T^2}$ vs $\dfrac{1}{T}$ gives the apparent activation energy E and the y-intercept gives the pre-exponential factor A.

Results and Discussions

The mass loss curves on dolomite-free basis of the two samples are comparatively shown in Figure 1. It is observed that the presence of 10% calcined dolomite increases the rate of decomposition of biomass, especially at high temperatures.
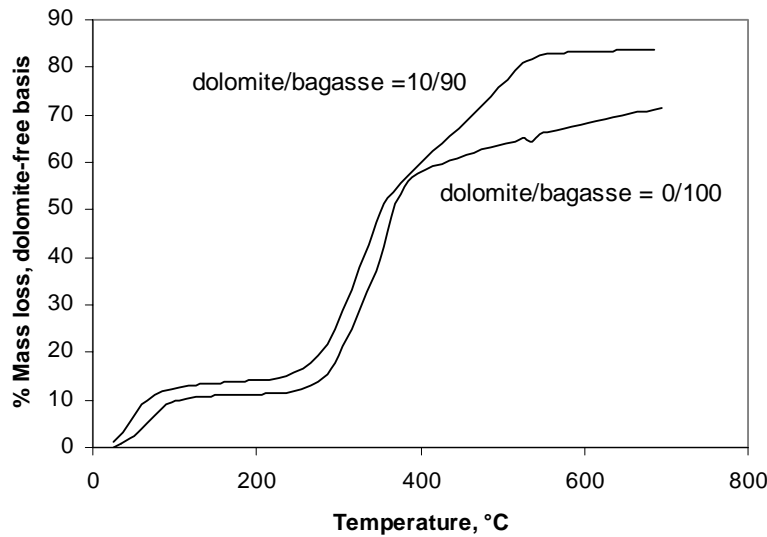

Figure 1: Percentage mass loss curves (dolomite-free basis) of thermal decomposition of bagasse

The reaction orders considered for the conversion function and their degrees of fitness in terms of the regression coefficients, obtained by the Coats-Redfern method, are given in Table 1. Thus the order of reaction that gives the highest regression coefficient for pyrolysis of both samples are O-3.

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Table 1: Reaction orders and their regression coefficients for thermal decomposition of bagasse[1]

Reaction order	Wt% dolomite / wt% baggase	
	0/100	10/90
O-0	0.3934	0.4739
O-1	0.6229	0.7683
O-2	0.7393	0.8452
O-3	0.7957	0.859

[1]Dolomite-free basis

The corresponding kinetic parameters for O-3 decomposition model of the two samples are given in Table 2. It is observed from Table 2 that the presence of 10% dolomite increases both the apparent activation energy (E) and the pre-exponential factor (A). The ten-fold increase in the pre-exponential factor more than offsets the slight increase in the activation energy so that the reaction rate constant increases in net, especially at high temperatures in consistence with figure 1.

Table 2: Kinetic parameters of thermal decomposition of bagasse using O-3 kinetic model[1]

Sample	E, kJ/mol	A, min^{-1}
Wt% dolomite/wt% baggase = 0/100	17.29	1.33
Wt% dolomite/wt% baggase = 10/90	25.25	15.62

[1]Dolomite-free basis

Conclusion
Results showed that the rate of pyrolysis of biomass in the presence of 10% calcined dolomite is higher than that without it, especially at high temperatures. In light of increased activation energy and even higher pre-exponential factor in the presence of dolomite, it can be concluded that the calcined dolomite acted as a promoter rather than as a catalyst.

References

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