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THERMAL DECOMPOSITION KINETICS OF TORREFIED OIL PALM EMPTY FRUIT BUNCH BRIQUETTES

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Abstract. The study is aimed at investigating the thermal behavior and decomposition kinetics of torrefied oil palm empty fruit bunches (OPEFB) briquettes using a thermogravimetric (TG) analysis and the Coats-Redfern model. The results revealed that thermal decomposition kinetics of OPEFB and torrefied OPEFB briquettes is significantly influenced by the severity of torrefaction temperature. Furthermore, the temperature profile characteristics; T_{onset} , T_{peak} , and T_{end} increased consistently due to the thermal lag observed during TG analysis. In addition, the torrefied OPEFB briquettes were observed to possess superior thermal and kinetic properties over the untorrefied OPEFB briquettes. It can be inferred that torrefaction improves the fuel properties of pelletized OPEFB for potential utilization in bioenergy conversion systems.

Keywords: thermal analysis, kinetics, torrefaction, oil palm, empty fruit bunches briquettes.

1. Introduction

The thermochemical and physical properties of biomass species can be considerably enhanced by pretreatment techniques such as pelletization and torrefaction [1-3]. Torrefaction is a low temperature, mild pyrolysis aimed at improving the energy density, hygroscopicity and grindability of biomass [4-7]. Pelletization is the process of compacting or densifying pulverized biomass into a uniform solid form to improve moisture content, energy density and handling [8-11]. Consequently, pelletization and torrefaction can be utilized for the pretreatment and valorization of biomass wastes from agriculture, forestry, and municipal sources.

The cultivation of oil palm (*Elaeis guineensis*) and crude palm oil (CPO) produced in Malaysia generates vast quantities of oil palm waste (OPW) annually. Over the years, the accumulation of OPW has resulted in significant waste disposal challenges thereby exacerbating greenhouse gas (GHG) emissions and environmental pollution in Malaysia. However, pelletization and torrefaction have been proposed as cheap, sustainable and efficient technologies for the sustainable management and utilization of OPW. Consequently, numerous studies have examined and highlighted the prospects of OPW torrefaction [12-16]. However, there have been no studies on the torrefaction of pelletized OPW or pelletization of torrefied OPW despite the effects of the respective technologies on the biomass properties.

To the best of authors' knowledge, there has been no research on the torrefaction of pelletized oil palm waste (OPW) such as oil palm empty fruit bunches (OPEFB) in literature. Hence, there is an urgent need to examine the thermochemical and physical properties as well as the thermal decomposition kinetics of torrefied empty fruit bunches (OPEFB) briquettes for bioenergy utilization in future biomass conversion systems (BCS). The study will also examine the thermal behavior, temperature profile characteristics and compute the kinetic parameters; activation energy (E_a) and frequency factor (A) of torrefied OPEFB briquettes under pyrolysis conditions using the Coats-Redfern model.

2. Experimental

The oil palm empty fruit bunch (OPEFB) briquettes were acquired from Felda Semenu Oil Palm Mill, Johor, Malaysia. The detailed procedure for the pre-

treatment and physicochemical characterization of the OPEFB briquettes is described in previous studies [8, 17]. The torrefaction of the OPEFB briquettes was carried out at 523, 548 and 573 K with the following labels: *Torr 250*, *Torr 275* and *Torr 300*, according to the procedures described in scientific literature [18].

The thermal decomposition behavior of torrefied OPEFB briquettes was examined using the high precision thermal microbalance Thermogravimetric (TG) analyzer (Netzsch 209 F3, Germany) by heating approximately 10 mg of the pulverized samples within 303–1273 K. Thermal analysis was performed at a heating rate of 20 K·min⁻¹ under inert atmosphere using nitrogen as a purge gas at 50 ml/min. The resulting TG-DTG data were analyzed using Netzsch Proteus™ software to investigate the thermal decomposition kinetics of the OPEFB and the torrefied OPEFB briquettes.

Consequently, the comparative kinetic analysis of the OPEFB briquettes and torrefied OPEFB fuels was evaluated using the modified Coats-Redfern method (CRM). This “model fitting” method has been widely applied in analyzing the complex reaction mechanism and kinetics of biomass conversion processes such as pyrolysis [19]. The model is widely used for the determining the solid rate reactions kinetic parameters of biomass particularly when a single heating rate is applied in the thermal analysis [20].

Biomass pyrolysis is typically described as a single or first order reaction [21, 22]. Hence, the simple expression in Eq. (1) can be used to describe the process.



The volatiles fraction is the sum total of all liquid and gaseous products of pyrolytic decomposition. The rate of biomass conversion during this pyrolysis process depends on the rate of conversion, residual mass, and temperature as described by the modified Arrhenius relation in Eq. (2) [23]:

$$\frac{da}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(a) \quad (2)$$

where A – the pre-exponential or frequency factor, s⁻¹; E_a – activation energy, kJ·mol⁻¹; R – molar or Moore’s gas constant, J·mol⁻¹·K⁻¹; $f(a)$ – reaction model which depends on the reaction mechanism of the pyrolysis process.

Consequently, an expression to describe the rate of biomass pyrolysis at a constant heating rate β (where $\beta = dT/dt$) can be deduced by rearranging Eq. (2) as presented in Eq. (3):

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (3)$$

By plotting $\ln[-\ln(1-a)/T^2]$ against $1/T$, a straight line can be obtained from which the activation energy, E_a , and frequency factor, A , can be deduced from the slope – E_a/R and $\ln[AR/\beta E_a]$, respectively.

3. Results and Discussion

3.1. Thermal Analysis

The TG curves for OPEFB briquettes and the torrefied OPEFB are presented in Fig. 1. The results displayed the typical reverse S-shaped curves generally observed during the thermal decomposition of biomass [24, 25]. Furthermore, the thermal decomposition of the torrefied products in Fig. 1 noticeably occurred at higher temperatures compared to the original untorrefied OPEFB briquettes.

The results in Fig. 1 also indicate that the TG curves clearly shifted to higher temperatures with the increase in severity of torrefaction temperature. The shifts to higher temperatures can be attributed to the removal of hemicellulose and volatile compounds during torrefaction. Similar observation has been reported in literature [16, 26].

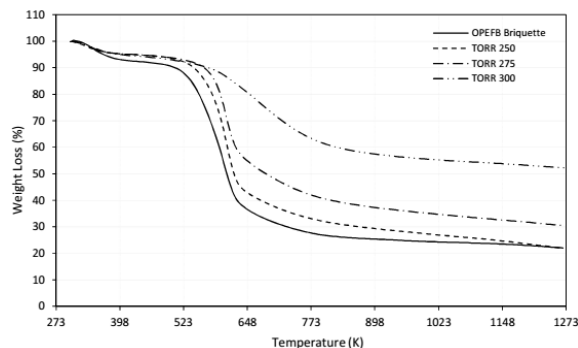


Fig. 1. TG curves for OPEFB briquettes and torrefied OPEFB

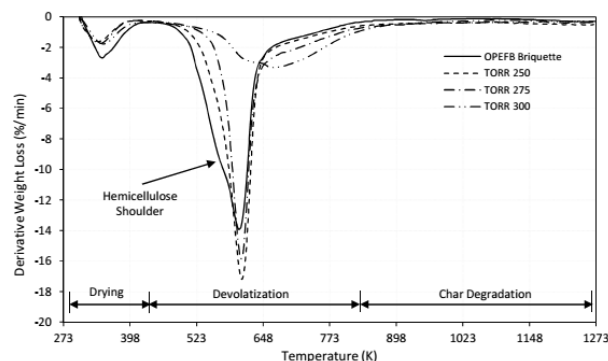


Fig. 2. DTG curves of OPEFB briquettes and torrefied OPEFB

Conversely, the severity of torrefaction temperature on OPEFB briquettes can also be evaluated from the DTG curves of the torrefied products presented in Fig. 2. The DTG curve of the OPEFB briquettes and the torrefied ones showed the typical DTG curves observed for the thermal decomposition of biomass materials. As can be observed in Fig. 2, the decomposition of the OPEFB fuels occurred in three (3) stages namely; drying, partial

devolatilization (active pyrolysis) and char decomposition (passive pyrolysis) as observed by other research groups [20, 27]. From Fig. 2 it was observed that the DTG curve of *Torr 300* fuel is smaller and asymmetrically shaped compared to the *Torr 250* and *Torr 275* which are symmetrically shaped and larger than the untorrefied OPEFB briquettes. This observation deviates markedly from DTG curves of other torrefied biomass reported by other groups [24]. However, the results suggest that torrefaction of OPEFB briquettes may have also resulted in the partial degradation of cellulose. Since hemicelluloses and cellulose decompose rapidly from 541 to 628 K [28, 29], the degradation of hemicellulose and possibly cellulose may explain the significant deviation from a probable trend.

Furthermore, the “hemicellulose shoulder” typically observed for biomass fuels at 573–583 K was non-existent in DTG profiles of the torrefied products, signifying the complete removal during torrefaction. For the untorrefied OPEFB briquettes in this study, the hemicellulose shoulder was observed at 581 K. The results confirm that hemicellulose was eliminated during the torrefaction of OPEFB briquettes from 523 to 573 K.

The characteristic temperature profiles of the torrefied OPEFB fuels are presented in Table 1. As can be observed, torrefaction significantly modified the characteristic temperature profiles; T_{onset} , T_{peak} , and T_{end} of the OPEFB fuels. The onset temperature (T_{onset}) is the temperature in which weight loss of the sample begins during thermal degradation. The peak temperature T_{peak} is the temperature in which maximum thermal conversion of the fuel occurs while T_{end} represents the end of the active pyrolysis during thermal analysis of the fuel.

The T_{onset} in the untorrefied OPEFB briquette increased from 546 to 578 K after torrefaction at 573 K. Furthermore, the values of T_{peak} increased with increasing severity of the torrefaction process from 609 K for the original untorrefied OPEFB briquettes to 663 K after torrefaction at 573 K. The difference in T_{onset} , T_{peak} and T_{end} values between the untorrefied OPEFB briquettes and the *Torr 300* fuel are 309, 334 and 419 K, respectively. For each parameter, the values increased by a factor of 2 which may be partly due to the change in fuel properties such as volatile matter and moisture content.

Furthermore, the yield of biochar, deduced from the residual mass after TGA was 21.89 % for torrefaction at 523 K; 30.49 % at 548 K and 52.26 % at 573 K. Consequently, this indicates that the devolatilization of biomass component results in an increase in biochar yield as observed during thermal analysis. The increase in char yield may be due to the effect of increased thermal resistance encountered by the evolved gas species during thermal analysis.

Consequently, slow rate of degradation shifts the peak decomposition temperatures to higher values as observed in Table 1. Comparable results have been reported in [24], which are in good agreement with experimental findings reported in literature [26, 30].

3.2. Kinetic Analysis using Coats-Redfern Model

By plotting $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$, a straight line can be obtained from which the activation energy and frequency factor can be deduced from the slope $-E_a/R$ and $\ln[AR/\beta E_a]$, respectively. The kinetic plots for the OPEFB fuels using the Coats-Redfern kinetic method are presented in Fig. 3.

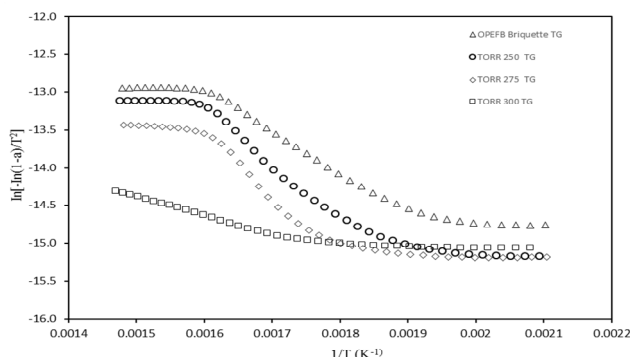


Fig. 3. Kinetic plots for OPEFB briquettes and torrefied OPEFB

It is important to state that the plots represent only the decomposition of the OPEFB fuels in the temperature region of 473–673 K which is frequently denoted as the region of active pyrolysis. Therefore, the calculated kinetic parameters in Table 3 represent only the reactions taking place within this region.

The results in Table 2 indicate that the activation energy (E_a) of the OPEFB fuels decreased progressively with the increase in the degree of severity of the torrefaction temperature. Similar results have been reported for the torrefaction of Douglas fir wood in literature [24]. The observed trend in Table 1 may be due to the increase in the density of highly reactive species such as carbon and fixed carbon in the fuels, which increase with temperature during torrefaction. In addition, the lower values of E_a and A for the torrefied OPEFB briquettes indicate a higher reactivity and improved thermal properties compared to the original untorrefied OPEFB briquettes.

4. Conclusions

The thermal decomposition kinetics of torrefied oil palm empty fruit bunch (OPEFB) briquettes was investigated using the Coats-Redfern model. The findings indicate that severity of torrefaction temperature significantly influenced the thermal behavior and kinetic decomposition of OPEFB briquettes. Furthermore, a linear relationship was observed between the severity of torrefaction and temperature profile characteristics; T_{onset} , T_{peak} , T_{end} and residual mass (biochar yield) for the OPEFB fuels. In addition, the kinetic analysis showed that the torrefied OPEFB torrefaction possesses superior thermo-

Table 1

Temperature profile of OPEFB briquette and torrefied OPEFB

| Fuel | T_{onset} , K | T_{peak} , K | T_{end} , K | Residual mass, % |
|----------|-----------------|----------------|---------------|------------------|
| OPEFB-B | 546.45 | 602.75 | 643.85 | 22.05 |
| Torr 250 | 569.05 | 607.15 | 638.65 | 21.89 |
| Torr 275 | 578.05 | 606.35 | 644.65 | 30.49 |
| Torr 300 | 579.05 | 663.85 | 789.65 | 52.26 |

Table 2

Kinetic parameters of OPEFB briquettes and torrefied OPEFB

| Biomass fuel | E_a , kJ·mol ⁻¹ | A, min ⁻¹ | Correlation coefficient R^2 |
|-----------------|------------------------------|----------------------|-------------------------------|
| OPEFB briquette | 31.80 | 65.07 | 0.9530 |
| Torr 250 | 36.54 | 138.30 | 0.9302 |
| Torr 275 | 19.52 | 1.49 | 0.5767 |
| Torr 300 | 10.79 | 0.09 | 0.8498 |

chemical properties compared to the original untorrefied OPEFB briquettes. Hence, it can be inferred that torrefied oil palm waste (OPW) such as OPEFB briquettes can potentially be utilized for efficient energy conversion in future biomass conversion systems.

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КІНЕТИКА ТЕРМІЧНОГО РОЗКЛАДУ ВИСУШЕНИХ БРИКЕТІВ ПОРОЖНІХ ФРУКТОВИХ ПУЧКІВ ОЛІЙНОЇ ПАЛЬМИ

Анотація. З використанням термогравіметричного аналізу (ТГА) і моделі Коатс-Редферна вивчено термічну поведінку і кінетику розкладу висушених брикетів порожніх фруктових пучків олійної пальми (ОРЕФВ). Показано, що кінетика термічного розкладу ОРЕФВ і висушених брикетів ОРЕФВ в значній мірі залежить від температури висушування. За результатами ТГА доведено, що температурний профіль постійно збільшується внаслідок теплової інерції. Окрім того, висушені брикети ОРЕФВ мають чудові термічні і кінетичні властивості в порівнянні з невисушеними брикетами. Встановлено, що висушування покращує паливні властивості гранульованих ОРЕФВ для потенційного використання в системах перетворення біоенергії.

Ключові слова: термічний аналіз, кінетика, висушування, олійна пальма, брикети порожніх фруктових пучків.