



Enhancement of Energy Properties of *Leucaena Leucocephala* Pellets via Torrefaction and its Non-Isothermal Decomposition Kinetics

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Abstract

The quality of raw woody biomass as biofuels can be greatly improved by applying a suitable pre-treatment either by thermochemical or biochemical conversions. The aim of this work is to investigate the impact of torrefaction parameters i.e. torrefaction temperature and holding time, on short-rotation energy crop pellet, *Leucaena Leucocephala* (LL) under inert atmosphere. Torrefaction temperature range under study was set between 200 to 300°C with holding times of 30 and 60 minutes. Torrefied biomass pellet was compared to its raw pellet form in terms of mass-energy properties, hardness quality, and their respective kinetic parameters via Kissinger's method. Results of the study revealed that temperature has a more significant impact on mass-energy index with holding times influence becoming more apparent at higher torrefaction temperature above 250°C. Energy properties were improved significantly in terms of calorific value and energy density. Increasing the torrefaction parameters also resulted in the decrease of pellet's hardness due to increase in brittleness. Under pyrolysis conditions, the activation energy of raw LL was lower at 186 kJ/mol than torrefied samples (200- 272 kJ/mol). The understanding of the torrefied biomass properties and its weight loss kinetics will give better prediction of product quality by varying torrefaction conditions.

Keywords: Energy properties; kinetic analysis; *Leucaena Leucocephala*; pellet hardness; torrefaction

1. Introduction

Biomass as a source of bioenergy feedstock has been gaining global recognition in the past decades where its energy application has been researched extensively as one of the promising renewable sources. During plant photosynthesis, solar energy is captured and stored, thus bioenergy can be produced directly from biomass, for example, direct biomass combustion in a boiler or gaseous combustion from biomass gasification. Thermochemical conversion technologies are generally preferred due to their simplicity and consistency in producing value-added products for energy generation purpose. Both non-woody/herbaceous and woody biomass can be utilised for power generation or liquid biofuels production. However, utilization of raw biomass as bioenergy feedstock has its own share of challenges. Among the problems associated with raw biomass are its high moisture content, proneness to biological attack during storage, relatively low bulk and energy density as well as inhomogeneous [1]. One approach is to pretreat raw biomass via torrefaction i.e. slow pyrolysis, in which during torrefaction, the removal of water and part of volatile matters would occur, thus yielding carbon-rich, brittle and near-hydrophobic biochars [2], [3].

Torrefaction is described as a thermochemical conversion treatment in an air-free or oxygen-free environment under atmospheric pressure and its main purpose is to produce the highest possible amount of biochar whilst maintaining high mass and energy values [4]. Typically, 60-95% energy value and 50-90wt% mass yield of biomass are retained in the bio-char [5], [6].

The torrefaction process is normally performed between low temperature range of 200 to 300°C with short residence time of less than an hour [7]. Combining torrefied biomass with densification such as pelletization increases the energy density thus biomass is converted into a high-value bioenergy feedstock in terms of easier storage and handling, good biological stability, better grindability and comparable to fossil solid fuels such as coal.

In this research study, common short rotation tree species of choice for energy crop is *Leucaena Leucocephala* (LL). It is a leguminous tree i.e. it is adjusted to harbouring nitrogen-fixing bacteria in its root nodules, has an easy adaptability to tropical ecological conditions [8]. In the context of LL as bioenergy crop, it is considered as underutilized by many researchers although our neighbouring countries i.e. Thailand and Philippines are actively researching this potential energy crop for dendrothermal energy plant. Considerably high heating value, high yield, high specific gravity, steady burning characteristics with little/ no sparking are favourable criteria of LL as energy crop [9], [10]. Its physical and chemical characteristics are of importance and should be researched in detail in order to use LL as energy source whether as substitute or stand-alone source.

The quality of torrefied biomass pellets is normally assessed based on its mass and energy values, durability and its reaction kinetic analysis. High mass-energy density of pellet denotes high energy per unit mass volume of material. Durability is an important criterion during storage and handling where it measures the endurance of pellets to withstand shear and impact forces during

handling and transportation. Low durability, particularly pellet's hardness will create safety problems such as dust emissions which may lead to self-ignition risk and disturbance during pellet feeding systems [11], [12]. Thermal degradation kinetics of biomass during torrefaction/pyrolysis is another significant area to be studied where reaction kinetic parameters evaluation related to the conversion of raw into torrefied biomass needs to be well understood. The information regarding reaction kinetics is necessary in order to transform raw biomass into valuable form of energy through the torrefaction process. Furthermore, reaction kinetic study is equally important in an optimized design of a torrefaction furnace/reactor.

In consideration of the above criteria, the aim of this study is to investigate the effects of temperature and holding times during torrefaction, specifically on mass-energy properties, durability of raw/torrefied pellets and non-isothermal kinetic behaviour of raw/torrefied biomass using thermogravimetric analyser under inert atmospheric condition. Kinetic analysis calculations were accomplished by using the Kissinger method with various heating rates. An in-depth investigation of torrefied *Leucaena Leucocephala* pellets pertaining to its energy properties, mechanistic behaviour upon compression corresponding to pellet's stability and non-isothermal kinetic study is important in order to transform Malaysia's potential energy crop into a valuable form of bioenergy feedstock.

2. Materials and Methods

2.1. Material Preparation

Leucaena Leucocephala, (LL), a fast-growing tree species were collected from open areas in Shah Alam province, Selangor, Malaysia. Bulky LL stem samples were cut, chipped and ground into small particle sizes of approximately 5 mm. The samples were then dried to achieve moisture content less than 15wt% prior to densification. Pelletization was done in Forest Research Institute of Malaysia (FRIM) using a pellet machine with a cylindrical die opening of 6 mm in diameter and the length of produced pellets ranged from 1 to 6 cm.

2.2. Torrefaction Experiments

Approximately 10-15g of raw LL pellets were initially placed in a crucible and positioned in the middle of a double-zone horizontal tube furnace OTF-1200X (MTI Corporation, USA). Nitrogen gas (purity 99.9%) was then purged through the reactor for 15 minutes at a rate of 1 L/min prior to the start of the torrefaction experiments in order to provide an inert condition within the furnace. Torrefaction experiments commenced at continuous nitrogen flow rate of 100 mL/min with a heating rate of 10°C/min. The LL pellets were torrefied at 200, 225, 250, 275 and 300°C and upon reaching target temperatures, samples were held for continuous torrefaction with holding times of 30 and 60 minutes. After torrefaction experiments were completed, the furnace was turned off, and left to cool down to ambient temperature where the samples were taken out, weighed and stored in air-tight containers.

2.3. Mass and Energy Yields

The previously published paper presenting the results of proximate, and elemental analyses of *Leucaena Leucocephala* were referred [13]. Mass and energy yields, energy density and torrefaction energy index (TEI) were calculated according to the following equations [13], [14]:

$$\text{Mass Yield, } M_Y (\text{wt}\%) = (\text{Torrefied mass / Raw biomass mass}) * 100 \quad (1)$$

$$\text{Energy Yield, } E_Y (\text{wt}\%) = M_Y \times (\text{HHV}_{\text{torr}} / \text{HHV}_{\text{raw}}) \quad (2)$$

where HHV_{torr} and HHV_{raw} are high heating values of torrefied and raw pellets, respectively, in MJ/kg.

$$\text{Energy Density} = E_Y / M_Y \quad (3)$$

$$\text{Torrefaction Energy Index (TEI)} \\ = (\text{HHV increase} \times 10) / (100 - E_Y (\%)) \quad (4)$$

2.4. Meyer Hardness Index

Hardness test, or also known as the crushing resistance is defined as the maximum compressive load a pellet may withstand before breakage [15]. In this study, the Meyer hardness of pellets was analysed in a single pellet press unit, Tinius Olsen Universal Testing Machine, with a hemispherical end rod of 10-mm diameter. Compressive force was exerted on the centre of a single pellet placed horizontally on a steel plate. The tester was run at a speed of 2 mm/min and stopped after the pellet fractured where the maximum load (F in N) applied was recorded. Three pellets were tested to obtain representative data. The Meyer hardness, H_M (in N/mm²), defined as the applied force divided by the projected indentation area, was calculated by the following equation [16]:

$$H_M = F / [\pi(Dh - h^2)] \quad (5)$$

where D is the probe diameter (mm) and h is the indentation length (mm).

2.5. Non-isothermal decomposition kinetics study

The Kissinger method applied in this study is used to determine kinetic parameters, which are the activation energy (E_a) and pre-exponential factor (A). This method is a model-free method although not isoconversional as it assumed constant activation energy with progress of conversion [17]. Kinetic data were obtained using a thermogravimetric analyser Mettler Toledo/TGA/SDRA51° in a nitrogen atmosphere where samples were subjected to dynamic heating from ambient temperature up to 800°C at four heating rates of 5, 10, 15 and 20°C/min. Upon reaching 105°C, heating was held for 5 minutes for complete surface moisture removal. The Kissinger equation is based on assumption of first order reaction and is expressed as:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m} \quad (6)$$

where β is the linear heating rate (°C/min), T_m is the peak temperature (in Kelvin), A is the pre-exponential factor (min⁻¹) and R is the universal gas constant (kJ/mol·K). The slope of the linear equation (6) is given by $-E_a/R$, thus the apparent activation energy, E_a can be calculated while pre-exponential factor, A , can be obtained from its intercept of the integral function of conversion [18]. It should also be noted that in this study, only the kinetic study on raw/torrefied LL HT60min will be reported.

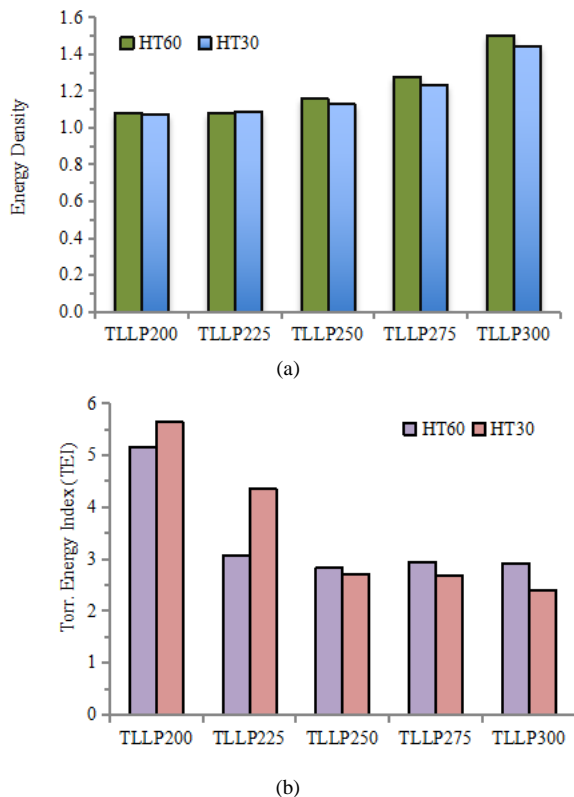
Table 1: Mass yield (M_Y), energy yield (E_Y), energy density and torrefaction energy index (TEI) of raw and torrefied LL at different holding times (HT).

Sample	HT	HHV (MJ/kg)	M_Y (wt %)	E_Y (wt %)	Energy	TEI
	(min)				Density	
Raw LLP	-	18.16	-	-	-	-
TLLP200	60	19.60	90.05	97.20	1.079	5.15
TLLP225		19.64	88.00	95.18	1.082	3.07
TLLP250		21.04	77.50	89.81	1.159	2.83
TLLP275		23.23	68.16	87.18	1.279	2.95
TLLP300		27.26	45.77	68.71	1.501	2.91
TLLP200	30	19.53	90.74	97.57	1.075	5.64
TLLP225		19.74	88.63	96.36	1.087	4.35
TLLP250		20.54	80.63	90.18	1.131	2.70
TLLP275		22.36	68.47	84.32	1.232	2.68
TLLP300		26.17	46.22	66.61	1.441	2.40

3. Results and Discussions

3.1 Energy Enhancement

Table 1 displays the high heating values (HHVs), mass yield (M_Y), energy yield (E_Y), energy density and torrefaction energy index (TEI) of raw and torrefied LL pellets (TLLP) whereas Fig. 1 shows the graphical presentations of (a) energy density and (b) TEI. As shown in Table 1, as torrefaction temperature increased, the heating values improved significantly up to 50% increment while the mass yield decreased to 46% at maximum torrefaction temperature. During torrefaction heating process, moisture removal and light volatiles from hemicellulose fraction as well as limited cellulose and lignin fractions were also removed via decarbonisation and devolatilisation, which is particularly noticeable when the torrefaction temperature was increased above 275°C. As for energy yield, by referring to Equation (2), energy yield is dependent on mass yield which consequently decreased as mass yield decreased [19].

**Fig. 1:** (a) Energy density of torrefied LL and (b) Torrefaction Energy Index (TEI) of torrefied LL

Energy density, a significant factor for energy evaluation in biomass feedstock, indicates the amount of chemical energy

retained in fuel per unit volume. According to Cellatoğlu and İlkan [20], a value greater than unity is desirable as the energy gain is higher due to enhanced heating values as shown in Table 1 and Fig. 1(a) whereby samples subjected to higher torrefaction temperature and holding time reached up to a factor of 1.5 that implies 50% rise in energy stored. According to Bergman [21], mass and energy balances on biomass torrefaction generally obtained energy densification factor typically at 1.3. In comparison with torrefied biomass pellets in literatures of various biomass categories, energy densities obtained in this study are relatively higher (*Leucaena* bark -1.21; larch wood -1.03-1.20; willow wood - 1.12-1.18; beech wood - 1.12-1.19; straw -1.15; rice husk - 1.24; sawdust - 1.35-1.37; peanut husks - 1.31-1.32) [22]–[24].

Through heating, light volatiles which have weaker C-H and C-O chemical bonds are removed, leaving behind stronger C-C bonds with higher energy content [25]. Furthermore, as mentioned in previous paper [13], atomic H/C and O/C ratios decreased considerably as torrefaction temperature rose above 250°C, which is agreeable to the findings of several researchers on lignocellulosic biomass [20], [26]. Consequently, a better property of biochar pellet i.e. higher reactivity due to lower moisture, better hydrophobicity and higher energy content were produced.

Another substantial term in energy evaluation is the torrefaction energy index (TEI), which according to Benavente and Fullana [14], TEI may indicate at which temperature should be carried out in order to obtain high energy value while maintaining sufficiently high mass yield. The higher the index, the more torrefaction of biomass will compensate, since a higher value of TEI indicates higher HHV rise or energy densification improvement and lower energy losses. In other words, targeted TEI should be of a good balance between high heating value and high-energy yield. With reference to Fig. 1(b), generally TEI decreased as torrefaction temperature was increased, but distinctly of consistent value when torrefaction temperature was above 225°C in the case of HT60. As compared to torrefaction HT of 30min, TEI decrease was more apparent which was unfavourable. However, from energy recovery point of view, there should be a compromise between high TEI that is achievable at lower torrefaction temperature region and its corresponding energy content. At lower torrefaction temperature i.e. <250°C, light volatiles and internal capillary moisture in woody fibres still existed, thus leading to environmental problems such as smoke formation during combustion and uncontrolled water vapour release [27].

3.2 Hardness Test

In order to study the effect of torrefaction on the hardness for both raw and torrefied LL pellets, maximum compressive force was recorded and Meyer Hardness index (H_M) was calculated. As shown in Fig. 2, both compressive force and Meyer hardness for raw LL pellets were significantly higher than its torrefied pellets

Maximum compressive force and Meyer Hardness for raw LL was 264 N and 4.16 N/mm², respectively.

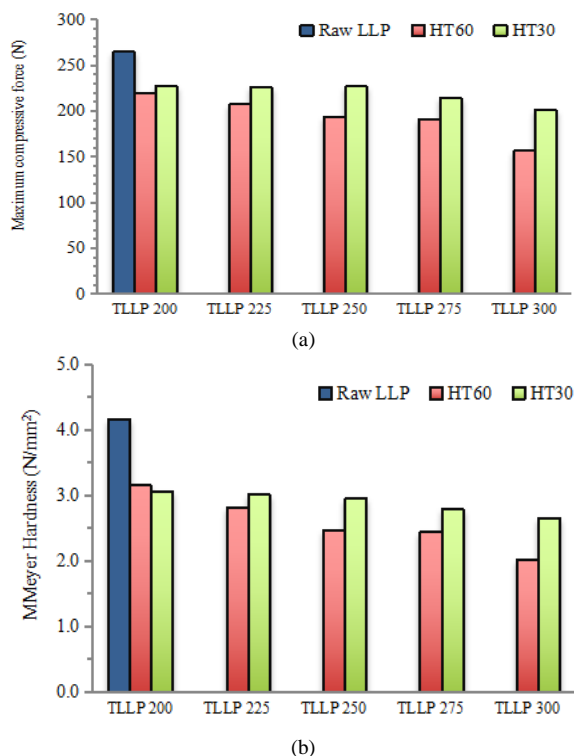


Fig. 2: (a) Maximum compressive force and (b) Meyer Hardness Index of raw and torrefied LL

The increase in brittleness caused by torrefaction heating process has resulted to the breakage tendency in torrefied pellets. According to Cao et al. [28], the brittleness in torrefied pellets was caused by the lack of binders and solid bridges between torrefied particles. The loss of natural binders from hemicellulose/lignin components, increased voids and spaces in pellet matrices, moisture loss and improved grindability property of pellets are among the factors to brittleness increment [16], [28]. However, as shown in Fig. 2(a) and (b), it can be noted that torrefied samples at HT30 min gave better resistance towards compression thus better Meyer hardness. This phenomenon is due to less devolatilisation and moisture removal during this shorter heating time. Therefore, it is suggested that relation between heating time with strength of pellets should be further studied to produce adequately strong pellets.

3.2 Kinetics analysis

Using the model-free method of Kissinger's, the kinetic parameters i.e. activation energies (E_a) and pre-exponential factor (A) of raw and torrefied LL pellets under pyrolysis non-isothermal conditions (temperature range of 105-800°C) were calculated and presented in Table 2 and Fig. 3. The Kissinger's plot obtained sufficiently high coefficient of correlations, R^2 at values more than 90%. The activation energy of the raw sample was lower than the torrefied samples, at 186 kJ/mol, indicating the pyrolysis of raw LL progresses faster. This is due to higher volatile matter content in raw LL, which contributed to its higher reactivity [29].

Table 2: Kinetic parameters via Kissinger method for raw/torrefied *Leucaena Leucocephala* at holding time 60 min

Sample	E_a (kJ/mol)	A (min ⁻¹)	R^2
RAW LLP	185.89	3.21E+13	0.953
TLLP 200	200.29	5.73E+14	0.959
TLLP 225	205.89	1.68E+15	0.990
TLLP 250	206.60	1.89E+15	0.996
TLLP 275	209.79	4.33E+15	0.917
TLLP 300	271.62	8.88E+18	0.932

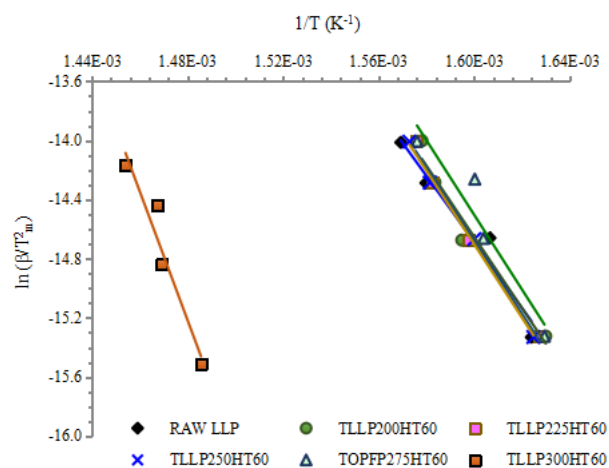


Fig. 3: Kissinger plot of raw and torrefied LL at HT60 min

As torrefaction temperature increased, activation energies of torrefied samples also increased and E_a value was predominantly highest (272 kJ/mol) at maximum torrefaction temperature of 300°C. In Kissinger plot (Fig. 3), the coordinate points of TLLP300HT60 were observed to be in the most left region as compared to torrefied samples produced at lower temperatures. This can be explained by a reduction in volatility caused by the loss of hemicellulose composition in biomass as reported in our previous study [13]. Hemicellulose is known to undergo decomposition in the temperature range of 220-315°C [30]. Since activation energy is the minimum amount of energy for a reaction to commence i.e. energy barrier, it also acted as an indicator to thermal decomposition stability of certain material [31]. Thus, in this present study, torrefied LL can be regarded as more thermally stable (as compared to its raw form) when subjected to heating at higher temperature and this is crucial in relation to auto ignition temperature during storage and transportation. Furthermore, information regarding biomass torrefaction kinetics is needed to accurately predict reactions behaviour, as well as to optimize and control the process of conversion toward products during the thermal degradation [32].

4. Conclusions

Leucaena Leucocephala solid biochar pellets produced from torrefaction in this study has been examined in terms of bioenergy potential together with other characterizations of hardness and kinetic study during thermal decomposition via Kissinger's method. The results indicated that torrefied LL pellets have sufficiently high-energy yield and density, with consistent torrefaction energy index values particularly for torrefaction temperature above 250°C. Although hardness of torrefied LL pellets was found to have decreased over increasing torrefaction temperature, it is suggested to compensate this problem with reduction in holding time. Kinetic analysis during thermal decomposition showed highest activation energy when LL samples were torrefied at maximum temperature of 300°C, which subsequently suggest better thermal stability and regarded as an advantage during storage and handling. A further study in decomposition kinetics using isoconversional/model-free methods and model fitting methods is needed to relate reaction conversion with torrefaction temperature and holding time effects, as well as for the determination of reaction mechanism. In summary, temperature has more significant effect than holding time during torrefaction in enhancing energy properties of LL pellets and may be further validated via torrefaction parameter optimization.

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