Comparative Study of the Synergistic Effects of Blending Raw/ Torrefied Biomass and Vietnamese Anthracite Using Co-pyrolysis

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Cite This: ACS Omega 2021, 6, 29171−29183

ABSTRACT: Biomass can be upgraded via torrefaction, and torrefied kenaf (TK) is a fuel that allows blending with coal at high ratios. In the present study, raw kenaf (Hibiscus cannabinus L.) (RK) was torrefied at 523 K for 30 min and then mixed with Vietnamese anthracite (NinhBinh, NB) before co-pyrolysis. Thermogravimetric (TG) analysis was used to evaluate the behavior of RK, TK, and blended RK/TK during co-pyrolysis at biomass blending ratios (BBRs) of 0, 25, 50, 75, and 100 wt %. The TG and derivative thermogravimetry curves of a mixture of NB and RK (NBRK) were similar to those of RK. The decomposition curves of a mixture of NB and TK (NBTK) depended on the mass fraction of TK. Based on weight loss differences between the experimental and calculated data for the fuel blends, no interaction between the RK and anthracite was observed for all BBRs, whereas anthracite involving 50 and 75% TK exhibited synergistic effects. The temperature range for synergy and degree of synergy for NB and TK depended on the heating rate and mass ratio of TK. Kinetic parameters were calculated using the Friedman−non-isothermal free kinetic method at heating rates of 10, 20, and 40 K/min. The results showed that the activation energy ($E$) values of the NBRK at conversion ratios of 0.2−0.5 were equal to those of the RK, whereas they were superior at NB decomposition ratios of 0.6−0.8. NBTK1-1 (BBR of 50%) showed $E$ values higher than those of NB at some conversion ratios, thus demonstrating a negative impact of blending. Further, NBTK1-3 (BBR of 75%) and NBTK3-1 (BBR of 25%) exhibited $E$ values between those of NB and TK. The present study suggests that a high TK mass fraction (75%) in the blend for co-pyrolysis is optimal for the activation energy and volatile matter yield.

1. INTRODUCTION

Coal remains a significant contributor to energy systems around the world, accounting for 38% of global electricity generation. According to a review on world energy, coal, oil, and gas accounted for approximately 84% of primary energy in 2019, and the associated CO$_2$ emissions attained a historic high of 33.1 Gt.\textsuperscript{1} To meet the requirements of electricity production, Vietnam will need to import approximately 50, 80, and 88 million tons of coal by 2025, 2030, and 2035, respectively.\textsuperscript{2} Therefore, to meet fuel demand, improving the fuel supply autonomy and minimizing the supply disruption risk are vital.\textsuperscript{3} Owing to the thriving agriculture in Vietnam, biomass energy can be produced from other sources, such as bagasse, wood chips, rice husks, and rice straw. Exploiting this massive biomass energy potential will minimize dependence on traditional energy sources, such as coal and oil, and reduce environmental pollution through low carbon emissions.\textsuperscript{4,5}

Despite the benefits of biomass utilization, their high oxygen contents can destabilize products characterized by low calorific values, which create corrosion problems.\textsuperscript{4,7,8} The torrefied biomass overcomes the shortcomings of raw biomass, such as high moisture content, low energy density, and low calorific value.\textsuperscript{4} In this process, biomass is heated at 473−573 K to eliminate moisture, decompose hemicellulose (HE), and partially decompose cellulose (CE) and lignin (LG). Synergistic effects can be exploited for higher pyrolysis yields by utilizing a mixture of materials. Concerning co-pyrolysis, Wu et al.\textsuperscript{9} reported that blends of low-rank coal and microalgae biomass produced higher volatile matter compared to samples of each component, while Moghtaderi\textsuperscript{10} reported that the temperature for evolution of volatile matter from such a blend was lower than that for coal. Thus, co-pyrolysis of coal and biomass/torre$fi$ed biomass can improve the commercial competitiveness of the associated fuels.

During pyrolysis, the complex structure of the carbonaceous feedstock comprising aromatic, aliphatic, and polar compo-
Table 1. Chemical Analysis Data for the NB, TK, and RK

| fuels   | proximate analysis (wt %, AR) | ultimate analysis (wt %, DAF) | FR (FC/VM) | H/C | O/C | HHV (AR) [kJ/kg] |
|---------|------------------------------|-------------------------------|------------|-----|-----|-----------------|
| NB      | 2.31                         | 12.97                         | 60.42      | 24.30 | 90.57 | 3.06 | 4.15 | 1.37 | 0.85 | 4.66 | 0.40 | 0.03 | 22,740 |
| RK      | 8.73                         | 73.64                         | 14.15      | 3.48 | 46.71 | 6.71 | 45.32 | 1.21 | 0.05 | 0.19 | 1.71 | 0.73 | 17,405 |
| TK      | 2.96                         | 49.04                         | 42.57      | 5.43 | 52.27 | 5.27 | 41.49 | 0.87 | 0.11 | 0.85 | 1.21 | 0.60 | 20,836 |

*M, moisture; VM, volatile matter; FC, fixed carbon; DAF, dry ash-free; C, carbon; H, hydrogen; O, oxygen; N, nitrogen; S, sulfur; FR, fuel ratio; HHV, higher heating value; AR, air received. NB: NinhBinh; RK: raw kenaf; and TK: torrefied kenaf.

The pyrolysis of solid feedstocks can be simulated using complex multistep reactions. Thermogravimetric analysis (TGA) is suitable for modeling this thermal decomposition behavior of the feedstock by measuring the rate of weight loss as a function of temperature and time. The thermal behavior and product evolution during co-pyrolysis of coal and raw/torre biomass have been investigated in numerous studies to assess possible synergistic effects. According to some studies, no interaction or synergy is discernible in the mass loss patterns linked to co-pyrolysis, whereas some studies indicate otherwise. For example, Lu et al. indicated that the characteristics of pyrolyzed mixtures of raw/torre wood and coal can be predicted through the weight loss of the individual materials. Alam et al. indicated that the decomposition of the torrefied bamboo sawdust was inhibited by the addition of the linear low-density polyethylene. Conversely, Wu et al. reported that the effects of HE and LG on char yields depend on the mixing ratio and temperature range. In addition, Mallick et al. indicated that minerals in the ash of biomass enhance the reaction kinetics during co-pyrolysis by increasing the decomposition intensity and reducing the activation energy, and Zhang et al. showed that during co-pyrolysis of cattle manure and textile dyeing, sludge enhanced the volatile yield from the early devolatilization stage but had a negative interaction effect in the second pyrolysis stage. Song et al. pointed out the main interaction up to 673 K and the greatest effect on the HE and CE decomposition of Pteris vittata (biomass) during co-pyrolysis.

In Vietnam, anthracite coal is the main fuel for the energy industry, supplying 18 power plants with only coal and 12 power plants with mixed anthracite. The characteristics of anthracite include low volatile content and difficulty in ignition and exhaustion. Raw kenaf (RK) is a herbaceous biomass co-fired with coal in Korean power plants and has a relatively lower production cost than other biomass types. Furthermore, the effects of torrefaction of Kenaf on thermal behavior under N2 and CO2 atmospheres were compared, and the characteristics of kenaf and torrefied kenaf under pyrolysis conditions using three methods (FWO, KAS, and DAEM) were investigated. Studies on the effects of RK or TK on the blend with coal, which are critical considerations for industry energy, are lacking. However, despite numerous studies on single and blended coal pyrolysis kinetics, kinetic studies using Vietnam anthracite as a raw material have not yet been reported. Accordingly, in the present study, synergistic effects on the yields of volatiles and the activation energy were investigated using blends of raw biomass (kenaf)/torrefied kenaf and Vietnamese anthracite. The thermal behavior of the feedstock during co-pyrolysis was evaluated at biomass blending ratios (BBRs) of 0, 25, 50, 75, and 100 wt % using a thermogravimetric analyzer. Kinetic parameters were calculated using the Friedman–non-isothermal free kinetic method at ramp rates of 10, 20, and 40 K min⁻¹. Our results provide insight into the interaction between Vietnamese anthracite and RK/TK during co-pyrolysis.

2. RESULTS AND DISCUSSION

2.1. Role of Torrefaction. Data from proximate and ultimate analyses of the NinhBinh (NB), RK, and TK samples are presented in Table 1. The torrefaction process significantly impacted the proportions of fixed carbon and volatile matter in the products, and the properties of TK changed based on the carbon content. In RK, the oxygen content is beneficial for combustion, although its calorific value is low due to the high oxygen content. Therefore, torrefaction is utilized to reduce undesired constituents, such as hydrogen and oxygen, thereby imparting the TK with chemical properties comparable to those of coal. Fuel properties of the NB, RK, TK, and three other types of coals were compared using a van Krevelen diagram (Figure 1).

Figure 1. The van Krevelen diagram showing H/C and O/C ratios for raw biomass, torrefied biomass, and three types of coals. NB coal: Vietnamese coal, NCA coal, Adaro coal, RK: raw kenaf, and TK: torrefied kenaf.

The NCA coal (bituminous coal) and Adaro coal (sub-bituminous coal) in Figure 1 are imported coals used in power plants in South Korea. The RK is characterized by high H/C and O/C ratios, while the coals (Adaro, NCA, and NB) show lower ratios to the left of RK. The TK highlights the transformation of the properties of RK to those of coal.

2.2. Chemical and Structural Properties of Raw and Torrefied Biomass. The three main components of the RK and TK, including CE (700–1500 cm⁻¹), HE (1600–2000 cm⁻¹), and LG (1200–1700 cm⁻¹), are highlighted in Figure 2. Bands at approximately 3300–3600 cm⁻¹ are attributed to O–H stretching vibrations of hydroxyl and carboxyl groups.
The lower peak of the O–H group in the TK compared to that in the RK is caused by its hydrophobicity. Peaks between 1700 and 1620 cm⁻¹ are assigned to stretching vibrations of C=O groups of HE in RK, which are absent in the TK. This indicates that decarboxylation and acetylation reactions occur during the torrefaction. C=O–C vibrations of CE between the 1170 and 1150 cm⁻¹ region are lower for the TK, and this suggests that CE partially decomposes during torrefaction. The major peak at 1045 cm⁻¹ corresponds to the C–O–H stretching of primary and secondary alcohols, while the absorption peak at 1085 cm⁻¹ is assigned to the C–O–C glycosidic bond stretching, and those between 1450 and 1600 cm⁻¹ are characteristic of LG. In addition, the higher peak at 2970 cm⁻¹ for the RK compared to the TK is likely because of C–H deformation within methoxyl groups of LG.

2.3. Thermal Degradation of Individual Feedstock.
Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for the NB, RK, and TK samples obtained under an N₂ atmosphere at heating rates of 10, 20, and 40 K min⁻¹ are shown in Figure 3. The decomposition curves of all samples exhibit three stages and two prominent DTG peaks. The first stage mainly involves the evaporation of moisture, which is characterized by a peak before 373 K (100 °C). The second stage represents the principal phase of the pyrolysis process. In general, the main DTG peak of the RK corresponds to CE degradation, while the slopes represent partial HE and LG decomposition. Owing to the torrefaction, the DTG peak to CE degradation, while the slopes represent partial HE and the second stage represents the principal phase of the pyrolysis (7.81 to 30.35% min⁻¹, respectively).

Regarding RK and TK, decomposition mainly occurred between 523 and 693 K, and this is likely because of the degradation of HE, CE, and LG. In the DTG curves, RK shows peaks at 596.5, 609.5, and 622.5 K, while TK displays peaks at 602.4, 610.7, and 627.7 K, for heating rates of 10, 20, and 40 K min⁻¹, respectively. The third stage involves LG decomposition and biochar or coal char formation, with no distinct peak for all samples. This stage is associated with temperatures ranging between 500 and 1000 K. At a heating rate of 20 K min⁻¹ up to 1173 K, samples for RK, TK, and NB produced 19.12, 45.82, and 86.20 wt % of residues, respectively.

As shown in Figure 3, as the ramp rate increased, the DTG peak shifted toward higher temperatures. The temperature at the maximum decomposition rate for NB was higher than that for RK and TK, suggesting a higher temperature gradient in NB. This can be explained by examining the total surface area of the sample during the heating. Brunauer–Emmett–Teller (BET) analysis data for biomass and single char heated at 1173 K are presented in Table 3.

The BET surface area of RK/TK has been presented in our previous study. According to the data in Table 3, torrefaction failed to improve the surface area of TK (0.568 m² g⁻¹) compared with RK (0.528 m² g⁻¹). The high surface area of the biochar (420.3142 m² g⁻¹) indicates that devolatilization created micropores. This difference is attributed to the decomposition of LG, which involves the rapid release of H₂ and CH₄, followed by the condensation of aromatics as the temperature increases. The biochar from the RK and TK was characterized by a higher specific surface area compared with char (coal char) from NB (56.0257 m² g⁻¹). This implied that internal temperature gradients were significantly lower for the RK/TK compared with those of NB. The lower surface area of the coal char is probably because the inorganic material partially fills or blocks its micropores. The volatile–volatile and volatile–char interactions during co-pyrolysis at high temperatures also impact meso- and macroporosity. Plausibly, volatiles produced by RK and TK can condense on the coal char surface as carbonaceous deposits.

The devolatilization index (D_i) reflects the rate of release of volatiles during pyrolysis, which is calculated using eq 10. As displayed in Figure 4, the D_i increased as the heating rate increased; moreover, the higher the D_i is, the easier is the release of gases. At a heating rate of 20 K min⁻¹, the D_i values for RK, TK, and NB were 76.5, 4.51, and 1.56, respectively, and these demonstrate that HE significantly influences the production of volatiles.

2.4. Pyrolysis Characteristics of Mixed Feedstock at Different Heating Rates. 2.4.1. Pyrolysis Characteristics. Pyrolysis characteristics of NB mixed with RK and TK at three heating rates (10, 20, and 40 K min⁻¹) are shown in Figure 5, while data for parameters associated with the blends are presented in Table 4. TG and DTG curves for three ratios of NB and RK, including NBRK1-3 (75% RK), NBRK1-1 (50% RK), and NBRK3-1 (25% RK), were similar to those of the original RK. During pyrolysis, the initial low devolatilization temperature (T_m) indicates better activities for the blends. According to the data in Table 4, T_m values of mixtures of RK and NB were slightly higher than those of RK at all heating rates but lower than those of NB. The decomposition curves of
the NBRK samples also exhibited three stages characterized by different DTG peak temperatures. The peak temperature for the evolution of water in the first stage for the single feedstock showed no major difference relative to that for the blends. In the second stage, the peak for NBRK1-1 and NBRK1-3 were 2 and 3 times higher than those of NBRK3-1 because of the increasing proportion of RK in the blends. In the third stage, the decomposition increased slightly between 700−800 and 900−1000 K, as both the mass fraction of NB and the heating

![Figure 3. TG (weight loss) and DTG (derivative thermogravimetry) curves at different heating rates for (a) NB, (b) RK, and (c) TK samples as well as (d) at 20 K min−1 for all samples.](image)

| Table 2. Data for Pyrolysis Parameters of the NB, RK, and TK at Different Heating Ratesa |
|---------------------------------|----------------------------------|------------------|
| heating rate | T_in (K) | T_peak (K) | R_max % min−1 |
| 10 K/min | 587 | 744.5 | 0.39 |
| 20 K/min | 592 | 749.1 | 0.77 |
| 40 K/min | 593 | 763.9 | 1.53 |

| RK |
|------------------|
| T_in (K) | T_peak (K) | R_max % min−1 |
| 517 | 596.5 | 7.81 |
| 525 | 609.5 | 15.24 |
| 536 | 622.5 | 30.35 |

| TK |
|------------------|
| T_in (K) | T_peak (K) | R_max % min−1 |
| 564 | 602.4 | 2.07 |
| 569 | 610.7 | 3.26 |
| 588 | 627.7 | 6.29 |

aT_in, initial devolatilization temperature; T_peak, temperature at the maximum decomposition rate; and R_max, maximum decomposition rate.

| Table 3. Surface Area Analysis Data for RK, TK, Biochar, and NB Char |
|-----------------|------------------------------|
| samples | BET surface area, m² g⁻¹ |
| RK | 0.528 |
| TK | 0.568 |
| biochar | 420.3142 |
| NB char | 56.0257 |

the evolution of water in the first stage for the single feedstock showed no major difference relative to that for the blends. In the second stage, the peak for NBRK lies between the peaks of RK and NB. During this stage, R_max values of 2.14, 4.25, and 8.82 min⁻¹ appeared at 599, 612, and 627 K at heating rates of 10, 20, and 40 K min⁻¹, respectively, for NBRK3-1. Observably, R_max values of NBRK1-1 and NBRK1-3 were 2 and 3 times higher than those of NBRK3-1 because of the increasing proportion of RK in the blends. In the third stage, the decomposition increased slightly between 700−800 and 900−1000 K, as both the mass fraction of NB and the heating
rate increased. This is because the macromolecular structure of RK, which contains abundant volatile components, is decomposed at lower temperatures. The \( D_i \) of the NBRK increased gradually as the RK proportion increased from 30.6 to 100% at 20 K min\(^{-1}\), indicating that the release of volatiles from the mixture is significantly influenced by the RK proportion.

In contrast to the NBRK, decomposition curves for three mixes of NB and TK (i.e., NBTK), including NBTK1-3 (75% TK), NBTK1-1 (50% TK), and NBTK3-1 (25% TK), depended on the TK mass ratio. The NBTK blends’ decomposition also showed three main stages involving different peak temperatures. TK addition to NB increased the peak intensity in the second stage from 0.76% min\(^{-1}\) (NBTK3-1) to 2.33% min\(^{-1}\) (NBTK3-1) at 20 K min\(^{-1}\). TG and DTG curves for NBTK1-1 and NBTK1-3 exhibited trends similar to those of the TK, while NBTK3-1 showed similarity with the NB. Pyrolysis peaks associated with LG in the TK and NB were observed between 700 and 800 K because the decomposition of NB and LG overlapped. At TK proportions of 50 and 75%, the decomposition mainly occurred between 600 and 700 K, which was similar to that for the unblended TK. However, at a TK proportion of 25%, decomposition was principally between 700 and 800 K, which is within the zone for NB. At TK proportions of 50 and 75%, the \( T_a \) values of NBTK1-1 and NBTK1-3 were lower than those of TK and NB. For example, at a heating rate of 20 K min\(^{-1}\), the \( T_a \) values of NBTK1-1 and NBTK1-3 were 568 and 566 K, respectively, and 569 and 592 for TK and NB. These results suggest that these differences are linked to the interactions between the NB and TK.

2.4.2. Raw/Torrefied Kenaf and Anthracite Interactions.

To highlight synergistic effects, the \( W_{\text{exp}} \) and \( W_{\text{cal}} \) versus the RK/TK mass ratios at a heating rate of 20 K min\(^{-1}\) are displayed in Figure 6a. The maximum relative errors between the experimental and calculated weight loss values for various blends are presented in Table S. Figure 6a reveals that the experimental values were higher than the calculated values, whereas at other heating rates, the data are almost identical. Therefore, interactions between RK and NB appear to be limited. The presence of alkali and alkaline (AAEMS) earth metal in RK on pyrolysis could affect the cracking of volatiles. The inhibition of the RK mixture in co-pyrolysis by NB may be attributed to the activation of AAEMS in RK with aluminosilicate minerals in NB coal to produce the stable inert crystals. Also, the melting and fusing of LG may block the pore of NB coal and the gap between NB and LG. Thus, the releasing of volatile may be hampered, i.e., negative synergistic effect (SE).18,34

Figure 6b shows that curves for samples with 25 and 50% TK at 20 K min\(^{-1}\) are similar to those for NBRK. This implies that at TK proportions of 2% and 50% for a heating rate of 20 K min\(^{-1}\), interactions with NB are restricted. However, at a TK proportion of 75%, the \( W_{\text{exp}} \) was lower than \( W_{\text{cal}} \) or the volatiles produced were higher than the calculated values until the temperature reached 759 K, thus highlighting an SE. The weight loss difference (\( \Delta W \)) reached a maximum of 2.99% at 529 K when the proportion of TK was 75%. These results reveal that the SE of the NBTK is associated with a high proportion of TK (75%) in the mixture.

2.4.3. Effect of Heating Rates on Torrefied Kenaf and Anthracite Blend Synergy.

To demonstrate the SE associated with the co-pyrolysis of TK and NB mixtures at different heating rates (10, 20, and 40 K min\(^{-1}\)), the measured and calculated volatile matter generated based on the weighted average and weight loss difference is exhibited in Figure 7. As the heating rate increased, an increase in the proportion of TK elevated the synergy temperature (\( T_{\text{se}} \)) and the weight loss difference (\( \Delta W \)). Therefore, the SE for a TK proportion of 75 wt % was higher compared with that for 25 and 50 wt %.

Regarding sample NBTK1-3, the calculated weight loss values were higher than the measured values until the temperatures reached 692 and 759 K at heating rates of 10 and 20 K min\(^{-1}\), respectively, and for all temperatures at a heating rate of 40 K min\(^{-1}\). The maximum \( \Delta W \) increased from 2.42% at 536 K at a heating rate of 10 K/min to 3.54% at 574 K at a heating rate of 40 K min\(^{-1}\) for a TK proportion of 75%. These results suggest that the interaction between TK and NB likely involves the swelling of TK, which then expands the microchannels between TK and NB during TK decomposition. Sample NBTK1-1 showed \( T_{\text{se}} \) values of 582 and 630 K for heating rates of 20 and 40 K min\(^{-1}\), respectively, whereas no SE was associated with a heating rate of 10 K min\(^{-1}\). However, a TK proportion of 25% negatively affected the decomposition in sample NBTK3-1, except between 961 and 1173 K at a heating rate of 40 K min\(^{-1}\), which was probably caused by LG devolatilization. Overall, these results indicate that the extent of synergy for NB and TK blends depends on the proportion of TK and the heating rate.

The SE of NBTK may be due to the catalytic effect of Fe(III) in TK for active interaction with NB coal and the deceleration of the cross-linking reaction and repolymerization by hydrogen radicals via inorganic matter in TK.18,33 Those radicals promoted the formation of volatiles. During the co-pyrolysis, the competition of positive of the three main compounds (CE, HE, and LG) of TK may compete against each other on the char generation for SE. The co-pyrolysis destroyed the weaker chemical bonds and accelerated the thermal degradation.34,35

2.5. Kinetic Parameter Analysis.

To gain insights into the kinetic parameters of the pyrolysis of the samples, Friedman method was used to determine the apparent activation energy (\( E \)) and pre-exponential factor (\( A \)) values of the single and mixed feedstocks at heating rates of 10, 20, and 40 K min\(^{-1}\). \( E \) was calculated from the slope of the ln(\( \alpha \)) versus the 1/RT plot (based on eq 8) and conversion degree (\( \alpha \)) values between 0.2 and 0.8 since the correlation
coefficients were less than 0.9 at $\alpha$ values $>0.8$. Kinetic parameters like activation energy and pre-exponential factor are the important indicators in the efficient design of thermochemical processes. Activation energy is the minimum
amount of energy required to start a reaction. Activation energy is also used to know the reactivity of a fuel. \(^\text{18,19}\)

E values of the coal were higher than those of RK and TK under all conversions (Figure 8) since, similar to anthracite, NB contains low volatiles and its reactivity is low. \(^\text{37}\) The E values gradually increased in all regions (0.2−0.8). The RK sample exhibited two regions, with E values of 0.3−0.6 in the first region followed by a slight increase. TK values slightly increased at α ranging from 0.2 to 0.5, whereas these significantly increased during the last stage of the reaction because of LG decomposition. Based on the Friedman method, E values for NB varied between 211.81 and 971.69 kJ mol\(^{-1}\), while those for RK and TK ranged between 159.85 and 225.1 kJ mol\(^{-1}\) and 120.8 and 479.73 kJ mol\(^{-1}\), respectively. These values were consistent with those reported in previous studies. \(^\text{14,38}\)

An evaluation of the synergy in co-pyrolysis in relation to E is displayed in Figure 9. Overall, E values of all samples increased as the conversion degree increased. Interactions of mixtures in the pyrolysis were estimated based on changes in the E values after blending. A comparison of the E values for the NBRK, NBTK, NB, RK, and TK is presented in Table 6.

Table 4. Pyrolysis Parameter Data for NB with RK and TK at Different Heating Rates and Blend Ratios\(^a\)

| Heating Rate | \(T_{\text{in}}\) (K) | \(T_p\) (K) | \(R_{\text{max}}\) (\%/min) | \(\Delta T_{1/2}\) (K) | \(D_1\) (\(^{\circ}\)) | \(T_{\text{in}}\) (K) | \(T_p\) (K) | \(R_{\text{max}}\) (\%/min) | \(\Delta T_{1/2}\) (K) | \(D_1\) (\(^{\circ}\)) | \(T_{\text{in}}\) (K) | \(T_p\) (K) | \(R_{\text{max}}\) (\%/min) | \(\Delta T_{1/2}\) (K) | \(D_1\) (\(^{\circ}\)) |
|--------------|----------------|------------|-----------------|----------------|----------------|----------------|------------|-----------------|----------------|----------------|----------------|------------|-----------------|----------------|----------------|----------------|----------------|
| NBRK1-3      | 10 K/min       | 520        | 601             | 6.19           | 30.6           | 522           | 600         | 4.22            | 21.1           | 525           | 599           | 2.14        | 63              | 10.8          |                |
|              | 20 K/min       | 529        | 613             | 12.14          | 68             | 530           | 613         | 8.11            | 37.2           | 533           | 612           | 4.25        | 65              | 20.0          |                |
|              | 40 K/min       | 539        | 627             | 23.97          | 70             | 540           | 627         | 16.5            | 68.8           | 543           | 627           | 8.82        | 69              | 37.6          |                |
| NBRK1-1      |                |            |                 |                |                | NBRK3-1       |            |                 |                |                |                |            |                 |                |                |
|              | 10 K/min       | 558        | 603             | 1.18           | 200            | 559           | 603         | 0.65            | 268            | 0.72          | 573           | 745          | 0.42         | 373            | 0.26          |                |
|              | 20 K/min       | 566        | 615             | 2.33           | 200            | 568           | 616         | 1.35            | 257            | 1.50          | 580           | 748          | 0.76         | 495            | 0.36          |                |
|              | 40 K/min       | 574        | 628             | 4.21           | 213            | 576           | 629         | 2.79            | 247            | 3.11          | 600           | 762          | 1.91         | 501            | 0.83          |                |

\(^{a}\)\(T_{\text{in}}\): initial devolatilization temperature; \(T_p\): temperature at the maximum decomposition rate; and \(R_{\text{max}}\): maximum decomposition rate. (\(\ast\)): (10\(^{-8}\)/min K).

Table 5. Experimental and Calculated Weight Loss Data for Different Feedstock Blends Based on a Heating Rate of 20 K/min\(^{-1}\)

| BBR \(^b\) | \(W_{\text{raw}}\) \(^a\) | \(\Delta W\) | \(W_{\text{Torrefied}}\) \(^a\) | \(\Delta W\) |
|------------|----------------|------------|----------------------------|------------|
| 75         | 50             | 25         |                            |            |
| \(W_{\text{raw}}\) \(^a\) | 571 | 604 | 1073 |                |
| experiment | 83.16 | 79.01 | 74.85 |                |
| calculation | 78.85 | 75.30 | 71.78 |                |
| \(\Delta W\) | +4.31 | +3.69 | +3.07 |                |
| \(W_{\text{Torrefied}}\) \(^a\) | 529/1073 | 529/1073 | 857 |                |
| experiment | 92.09/64.75 | 95.29/75.02 | 88.80 |                |
| calculation | 95.10/64.20 | 95.82/70.81 | 84.32 |                |
| \(\Delta W\) | −2.99/−2.55 | −0.47/+4.21 | +4.48 |                |

\(^{a}\) BBR: biomass blending ratio. \(^{b}\) Temperature at the maximum weight loss difference.
RK, indicating that RK is the only component of the mixture that was pyrolyzed. This was also the region in which HE and CE were removed from the RK. In the region with $\alpha$ values between 0.6 and 0.8, $E$ values significantly increased, and this corresponded to the temperature range for the generation of volatile matter in NB and biomass LG decomposition. Therefore, a nonsynergistic behavior existed between the RK and NB.

The trend, however, differed significantly when anthracite was blended with TK (NBTK). As shown in Figure 9, $E$ values associated with a 50% TK proportion (NBTK1-1) were higher than those for 25% TK (NBTK3-1). $E$ values for NBTK1-1 increased from 299.96 to 601.74 kJ mol$^{-1}$, while those for NBTK3-1 slightly varied between 209 and 362.73 kJ mol$^{-1}$. The $E$ values of NBTK1-1 were higher than those of NB in the 0.2–0.4 and 0.7 regions, with a negative impact in the 0.2–0.4 region and synergy at 0.5, 0.6, and 0.8. Variations in $E$ values

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**Figure 7.** Experimental and calculated weight loss (TG) and weight loss difference ($\Delta W$) plots of NBTK showing the (a) TG curve for NBTK1-3, (b) $\Delta W$ for NB blended with TK in NBTK1-3, (c) TG curve for NBTK1-1, (d) $\Delta W$ for NB blended with TK in NBTK1-1, (e) TG curve for NBTK3-1, and (f) $\Delta W$ for NB blended with TK in NBTK3-1.
probably indicate changes in the solid structure, such as melting and softening of the carbonaceous structure.\textsuperscript{9,12} Regarding NBTK1-3 (75% TK), the $E$ values were lower than those of NB but higher than those of TK at all conversions, indicating that 75% TK is favorable for the pyrolysis process. These values increased slightly from 172 to 261 and then 522 kJ mol$^{-1}$ for $\alpha$ values of 0.2, 0.6, and 0.8, respectively. The change in $E$ values indicated the varying reaction mechanisms and chemical structures of NBTK, possibly caused by catalytic effects of Fe(III) in TK or the competition of positive of the three main compounds (CE, HE, and LG) of TK during decomposition. Therefore, the TK proportion significantly affected the $E$ values of blended samples. At a proportion of 75% TK, these effects are likely linked to the changing NB structure, such as bond dissociation and polymerization.

Values of the frequency factor ($A$) obtained from eq 9 at a heating rate of 20 K min$^{-1}$ are presented in Table 7, and trends at other heating rates are similar and within the same range. The frequency factor is used to describe the frequency of molecular collisions with the proper orientation to cause reactions between particles at an appropriate temperature. Frequency factor values increased with increasing conversion for all samples, and this indicated that the collision intensities of molecules were high at elevated temperatures. According to the data in Table 7, frequency factor values can be divided into three groups. Group 1 included the NBTK1-3 sample, with values $<10^{16}$ s$^{-1}$, while Group 2 included the NB, RK, TK, and NBTK3-1 samples, with values of approximately $10^{20}$ s$^{-1}$. Group 3, which comprised the NBRK3-1, NBRK1-1, NBRK1-3, and NBTK1-1 samples, is characterized by high frequency factor values.

3. CONCLUSIONS

The addition of raw kenaf/torrefied kenaf showed different trends for both mass loss and activation energy curves of mixtures with anthracite coal (NB coal) in co-pyrolysis treatments. Based on the weight loss difference between the experimental and calculated data of fuels from the blends, no interaction could have possibly occurred between RK and NB at all BBRs. The results showed that the activation $E$ values of NBRK were equal to those of RK at conversion ratios of 0.2–0.5, suggesting that RK is the only mixture component with pyrolyzed values. At conversion ratios of 0.6–0.8, $E$ values significantly increased, which corresponded to the temperature range for the generation of volatile matter in NB and biomass LG decomposition, whereas the addition of TK exhibited a higher synergy by increasing the volatile matter release of mixtures. The temperature range and degree of synergy for the NB and TK blends depended on the heating rate and TK proportion. The results suggest that the blending of TK and NB has synergistic effects at TK proportions of 50 and 75%. Particularly, a high TK mass fraction (75%) in the blend for co-pyrolysis is optimal for the activation energy and volatile matter yield. The results of the present study highlight the utility of biomass/torrefied biomass as a resource for the energy industry in Vietnam.

**Figure 8.** Plot of activation energy versus conversion degree for single feedstock samples.

**Figure 9.** Plots showing variations in activation energies of mixed samples with progressive conversion for (a) NBRK and (b) NBTK.
4. MATERIALS AND METHODS

4.1. Sample Preparation. In the present study, NB, RK, and TK samples were utilized for thermal conversion experiments. NB is an anthracite used as a fuel in power plants in North Vietnam, while RK is a type of jute fiber common in South Asia. TK was obtained from torrefaction of RK in a thermogravimetric analyzer under N$_2$ at 523 K for 30 min. This mild temperature was selected because the associated energy density exceeds that of other torrefaction temperatures.\textsuperscript{15} The blending of RK/TK and NB included ratios of 0, 25, 50, 75, and 100% (wt %, dry basis).

4.2. Thermodynamic Analysis. Samples were ground and sieved to obtain average particle sizes of 75 and <100 $\mu$m for the coal and biomass, respectively. Approximately 15 mg of samples was placed in alumina crucibles of the TGA (SDT Q600, TA Instruments Co.) and heated from room temperature to 1173 K using heating rates of 10, 20, and 40 K min$^{-1}$ under N$_2$ flowing at 100 mL min$^{-1}$. TG and derivative thermogravimetry (DTG) data were acquired using the TA universal analysis software.

4.3. Fourier Transform Infrared Spectroscopy and Surface Area Analysis. Fourier transform infrared (FT-IR) spectroscopy (IRAffinity-1, Shimadzu, Japan) was conducted to determine functional groups in the RK and TK. The samples were analyzed after mixing with KBr and compressed to form pellets at ambient temperature, and the scanning range varied between 450 and 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.\textsuperscript{16} The surface areas of the RK, TK, biochar of the kenaf, and NB char were determined using N$_2$ sorption measurements. Analyses were performed using a Micromeritics ASAP 2020 physisorption analyzer, which was degassed at 373 K for 7 h to nondestructively measure the BET pore volumes of samples.\textsuperscript{40}

4.4. Kinetic Parameter Determination. The devolatilization of solid feedstock is primarily represented by the conversion rate to volatile products.\textsuperscript{17,27,28,43} The devolatilization rate ($da/dt$) is a function of a temperature-dependent reaction rate, expressed as follows:

$$\frac{da}{dt} = f(T)f(\alpha) \tag{1}$$

where $f(\alpha)$ is the degradation mechanism reaction model and rate constant.

The conversion ($\alpha$) versus time is expressed as follows:

$$\alpha = \frac{m_b - m_i}{m_b - m_f} \tag{2}$$

where $m_b$ and $m_i$ are masses of a sample at the beginning and end of the reaction, respectively; $m_i$ is the sample mass at reaction time $t_i$; and $k(T)$ is the rate constant of devolatilization at temperature $T$. $k(T)$ can be expressed as follows:\textsuperscript{46}

$$k(T) = A \exp \left(\frac{-E}{RT}\right) \tag{3}$$

where $A$, $E$, and $R$ represent the pre-exponential factor (s$^{-1}$), activation energy (J mol$^{-1}$), and universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$).
K$^{-1}$ mol$^{-1}$), respectively. By combining eqs 1 and 3, the devolatilization rate can be rewritten as follows:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)$$  \hspace{1cm} (4)

Under non-isothermal conditions involving a fixed heating rate, $\beta = dT/dt$ (K s$^{-1}$), and eq 1 can be expressed as:

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha)$$  \hspace{1cm} (5)

Equation 5 can be rearranged into eq 6.

$$\frac{dx}{f(\alpha)} = \frac{A}{\beta} \frac{dT}{RT}$$  \hspace{1cm} (6)

Integration of eq 6 produces the following:

$$g(\alpha) = \int_{0}^{\alpha} \frac{dx}{f(\alpha)} = A \int_{T_a}^{T} \exp\left(-\frac{E}{RT}\right) dT$$  \hspace{1cm} (7)

where $g(\alpha)$ is the integrated form of the conversion-dependent function $f(\alpha)$ and $T_a$ denotes the initial temperature of the experiment.

By applying natural log on both sides of eq 4, the following expression is generated:

$$\ln\left(\frac{dx}{dt}\right) = -\frac{E}{RT} + \ln(Af(\alpha))$$  \hspace{1cm} (8)

The activation energy, $E$, can then be obtained by plotting $\ln(dx/dt)$ versus $1/RT$ at a given $\alpha$. TG experiments were conducted at ramp rates ($\beta$) of 10, 20, and 40 K min$^{-1}$. The Friedman method was employed to estimate kinetic parameters without including the details of the reaction mechanism.

The pre-exponential factor can be calculated as follows:

$$A = \frac{\beta E \exp(E/RT_{\text{peak}})}{RT_{\text{peak}}^2}$$  \hspace{1cm} (9)

where $T_{\text{peak}}$ is the temperature corresponding to the highest peak on the DTG curve.

To quantify the pyrolysis yields of volatile products at various heating rates utilized, a devolatilization index was defined as follows:

$$D_1 = \frac{R_{\text{max}}}{T_{\text{in}} T_{\text{p}} \Delta T_{1/2}}$$  \hspace{1cm} (10)

where $R_{\text{max}}$ is the maximum decomposition rate, $T_{\text{in}}$ is the initial devolatilization temperature, $T_{\text{p}}$ is the maximum mass loss temperature, $\Delta T_{1/2}$ is the temperature at which $R/R_{\text{max}}$ is $1/2$, and $R$ is the decomposition rate. $T_{\text{in}}$ and $T_{\text{p}}$ assist in describing the kinetic evolution of several products during pyrolysis.

The synergistic effects or interactions during the co-pyrolysis of NB and RK/TK can be estimated using the weight loss difference ($\Delta W$), where $\Delta W = W_{\text{exp}} - W_{\text{cal}}$ and $W_{\text{cal}} = x_1 W_{1c} + x_2 W_{2c}$ biomass where $W_{\text{exp}}$, $W_{\text{cal}}$, $W_{1c}$, and $W_{2c}$ biomass correspond to the experimental, calculated, coal, and biomass weight losses (%). The parameters $x_1$ and $x_2$ represent the mass fractions of the coal and the biomass in the blend, respectively, while the degree of synergy is evaluated using $\Delta W$. A positive $\Delta W$ implies that blending caused no interaction or inhibited interaction. Conversely, a negative $\Delta W$ indicates that volatiles increased after blending compared with the individual solid components, and thus, synergy was achieved.

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### Author Contributions

The manuscript was written through contributions of all authors. V.T.T., B.-H.L., and C.-H.J. conceived and planned the research. T.V.T. carried out experiments for this research. T.V.T., B.-H.L., and T.-Y J. contributed to the analysis of the results. T.V.T., T.-Y J., B.-H.L., and C.H.J. contributed to the review of original and revised paper. V.T.T. wrote the manuscript. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was conducted under the framework of the Research and Development Program of the Korea Institute of Energy Research (C1-2428-01).

### REFERENCES

1. International Energy Agency Global Energy Review 2020; OECD Publishing 2020, DOI: 10.1787/a60abbf2-en.

2. Vietnam Electricity (EVN) Annual Report; Vietnam Electricity 2018.

3. Merdun, H.; Laouge, Z. B. Kinetic and Thermodynamic Analyses during Co-Pyrolysis of Greenhouse Wastes and Coal by TGA. Renewable Energy 2021, 163, 453–464.

4. Gouws, S. M.; Carrier, M.; Bunt, J. R.; Neomagus, H. W. J. P. Co-Pyrolysis of Coal and Raw/Torrefied Biomass: A Review on Chemistry, Kinetics and Implementation. Renew. Sustain. Energy Rev. 2021, 135, 110189.

5. GmbH, D. G. für I. Z. (GIZ) Sub-Sector Analysis Study of Sugar and Timber Industry in Vietnam; Deutsche Gesellschaft für Internationale Zusammenarbeit 2017.

6. The World Bank Final Report on Biomass Atlas for Vietnam; The World Bank 2020.

7. Kim, G. M.; Jeong, J. W.; Jeong, J. S.; Kim, D. Y.; Kim, S. M.; Jeon, C. H. Empirical Formula to Predict the NOx Emissions from Coal Power Plant Using Lab-Scale and Real-Scale Operating Data. Appl. Sci. 2019, 9, 2914.
Biomass Model Components Blend with Bituminous Coal. *Bioresour. Technol.* 2014, *169*, 220–228.