Effect of Torrefaction on Thermal and Kinetic Behavior of Kenaf during Its Pyrolysis and CO2 Gasification

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ABSTRACT: Torrefaction is an appealing pretreatment method for improving the fuel properties of kenaf biomass before its utilization in thermochemical processes. This study evaluated and compared the impact of torrefaction on thermal behavior and kinetics during pyrolysis and gasification. Thermogravimetric analysis experiments were conducted at temperatures of 300–1173 K at several heating rates under N2 and CO2 atmospheres. The raw and torrefied kenaf (RK and TK) during CO2 gasification in the low-temperature region (<900 K) was found to exhibit a tendency that was similar to that of N2. However, TK during CO2 gasification resulted in a lower maximum mass loss rate, delayed initiating temperature, and lower devolatilization index due to lower reactivity. In addition, the gasification reaction of CO2 and char was observed to occur in the high-temperature region (> 900 K), thus improving conversion efficiencies. The activation energy for TK in a CO2 atmosphere depending on the conversion was calculated using the distributed activation energy method. The activation of RK during CO2 gasification was higher than that of N2. However, TK during CO2 gasification exhibited a lower activation energy compared to that of N2, indicating its potential as a better feedstock during the CO2 gasification process and the ability to save energy.

1. INTRODUCTION

Gasification aims to produce biomass as a gas, which is converted to syngas for liquid biofuel production.1 The produced gas may also be used directly to generate heat and power through combustion.2 Integrated gasification combined cycle systems have higher thermal efficiency compared to direct combustion of biomass. Currently, most gasification plants use coal as a resource, and replacing coal with biomass would be beneficial as biomass is converted into value-added products. However, the direct utilization of biomass as a gasification feedstock is limited by its high moisture content, low grindability, low energy content, and low bulk density.3 Therefore, biomass gasification has been investigated extensively to date, and increasing gasification efficiency through feedstock upgrade using pretreatment methods such as torrefaction is an important research topic.

Torrefaction is also known as mild pyrolysis and in recent years has been preferred for the improvement of the characteristics of biomass as fuel before thermochemical processes. Biomass is heated at 473–573 K in inert gas to produce high-quality solid fuel.1,5 After drying during the torrefaction process, hemicellulose and some cellulose in biomass are thermally decomposed and biochar is produced.6,7 This biochar has a higher calorific value and improved grindability compared to raw biomass and is more effective for application in advanced gasification and combustion technologies.8 Owing to the aforementioned advantages, many studies have focused on evaluating the fuel properties of torrefied biomass, and research is gradually expanding in terms of the gasification kinetics of torrefied biomass.9,10 Gasification kinetics are crucial and have an essential impact on the design, process control, and efficiency of gasification.11 The design and optimization of gasifiers for industrial-scale applications require in-depth understanding of reliable kinetic data and characteristics during gasification.12,13 Although several researchers have studied the effect of torrefied fuel on gasification kinetics and thermal behavior, this subject has not been systematically investigated. Tran et al.5 reported that temperatures of torrefaction had a significant effect on the CO2 gasification of forest residues, and the gasification activation energy of the three samples varied from 260 to 290 kJ/mol. Chew et al.10 evaluated the impact of torrefaction on the gasification behavior and kinetics of three oil palm biomasses: empty fruit bunch, methyl-furans, and palm kernel shells. They

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reported that torrefied oil palm biomass showed reduced gasification reactivity relative to the nontorrefied analogues due to the removal of volatile matter from biomass after torrefaction. In addition, biomass reactivity during CO₂ gasification was affected by the gasification temperature, biomass type, and pretreatment method. Zhang et al. investigated the distribution of solid products and the effects of torrefaction conditions on char gasification reactivity, as well as cogasification with coal and torrefied solids. They noted that char produced by torrefied biomass showed faster conversion compared to char produced by raw biomass during CO₂ gasification.

Kenaf, which grows in Korea, is an important source of herbaceous biomass. The life cycle of kenaf among herbaceous biomass is relatively short and production costs are relatively low. Owing to the price competitiveness, kenaf is expected to replace woody biomass. Therefore, we investigated the characteristics of kenaf in terms of various aspects, such as the effect of torrefaction and how kenaf compares with woody biomass. Furthermore, we investigated the torrefaction-improved features such as grindability, hydrophobicity, and carbonization. However, to date, studies on the gasification kinetics of torrefied kenaf (TK) biomass, which are essential for large-scale application development, are lacking. In addition, the applicability of N₂ and CO₂ atmospheres for TK has not been studied and compared comprehensively. Therefore, this study aims to examine the effect of torrefaction on the CO₂ gasification behavior and kinetics of kenaf compared to N₂ pyrolysis. In addition, we evaluated and compared the CO₂ gasification kinetics of raw kenaf (RK) and TK biomass using the distributed activation energy method (DAEM). This study elucidates the kinetics and thermal behavior of the gasification process for TK.

2. RESULTS AND DISCUSSION

2.1. Thermal Analysis. Figures 1 and 2 show the mass loss (TG, thermogravimetry) and mass loss rate (DTG) curves for RK and TK under pyrolysis (N₂) and gasification (CO₂) at a heating rate of 10 K/min. The effects of ambient gas on thermal decomposition of RK and TK were investigated by comparing and evaluating the TG and DTG results in N₂ and CO₂ atmospheres. Water evaporation, devolatilization, and char reaction are evident in Figure 1. The 300–400 K region was associated with surface moisture and adsorbent water in the sample. In the N₂ atmosphere, the devolatilization of RK started at approximately 450 K and reached the maximum mass loss rate at 586 K. The mass loss rate decreased, and
there was no change in mass when the temperature was over 900 K, indicating that the thermal decomposition was complete. The decomposition of hemicellulose and cellulose occurred mainly during the initial region of the thermal decomposition, and that of lignin occurred in the latter region. This is similar to previous results showing that there are two thermal decomposition regions for lignocellulose biomass.\(^\text{18}\) In the CO\(_2\) gasification experiments shown in Figure 1, the mass loss tendency of RK and TK in the CO\(_2\) atmosphere was similar to that of N\(_2\) when the temperature was less than 900 K. However, the maximum mass loss rate of CO\(_2\) was less than that of N\(_2\) because of the greater heat capacity and lower reactivity of CO\(_2\). Nevertheless, an additional mass loss was clearly observed at temperatures exceeding 900 K in the CO\(_2\) atmosphere, indicating that the CO\(_2\) gasification reaction occurred in the remaining char. These results are consistent with the findings of previous studies.\(^\text{9,10}\)

Char produced by thermal decomposition still contains a large amount of carbon, and incomplete carbonation during the process of thermal decomposition in conjunction with CO\(_2\) facilitates the gasification reaction of the remaining char.\(^\text{20,21}\) Hydrogen and oxygen-related compounds are gradually compressed in the char matrix with increasing temperature, and the fixed carbon content of the remaining char increases, resulting in an inevitable gasification reaction between CO\(_2\) and fixed carbon.

Figure 2 shows the thermal decomposition behavior of TK in both N\(_2\) and CO\(_2\) atmospheres. Evidently, the first strong shoulder on the first half of the devolatilization peak found in RK is not observed for TK, indicating a significant reduction of hemicellulose content.\(^\text{23}\) In addition, most of the weight loss occurred from 500 to 700 K with the maximum rate and temperature of mass loss at 8.3 mg/min and 599.8 K in N\(_2\) and 6.44 mg/min and 599.4 K in CO\(_2\), respectively, which was almost identical to the behavior of the cellulose region.\(^\text{24}\) Furthermore, the maximum mass loss rate of TK was significantly more pronounced than that of RK, and the second shoulder was generally associated with the thermal decomposition of lignin; hence, this observation shows that lignin content increases after the torrefaction process. Yan et al. also reported that the lignin fraction of lignocellulosic biomass was significantly increased as a result of torrefaction.\(^\text{25}\) Figures 1 and 2 show that the maximum mass loss rate and temperature of the DTG peaks in the CO\(_2\) gasification region for RK and TK occurred at 3.72 mg/min and 1086.8 K and 2.58 mg/min and 1117.9 K, respectively, indicating that the increased lignin content in char resulted in a greater reaction with CO\(_2\).

There are no significant changes in reaction time and thermal progression delay of the sample was observed with respect to heat transfer, indicating that the peak moved into the high-temperature region.\(^\text{26}\) In addition, the

### Table 1. Effect of Heating Rates on Key Thermal Parameters for RK (a) and TK (b) under Pyrolysis (N\(_2\)) and Gasification (CO\(_2\))\(^\text{24}\)

| heating rate (K/min) | \(T_{\text{ini}}\) (K) | \(T_{\text{peak}}\) (K) | \(R_{\text{max}}\) (mg/min) | \(\Delta T_{1/2}\) (K) | \(D_i\) (10\(^{-5}\) K/\(\Delta T_{1/2}\)) |
|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| (a) RK              |                 |                 |                 |                 |                 |
| N\(_2\) (pyrolysis) |                 |                 |                 |                 |                 |
| 5                   | 537.01          | 589.23          | 3.79            | 22.63           | 52.19           |
| 10                  | 546.10          | 599.85          | 8.30            | 26.87           | 94.28           |
| 20                  | 555.70          | 612.23          | 16.37           | 28.27           | 170.23          |
| CO\(_2\) (gasification) |                 |                 |                 |                 |                 |
| 5                   | 543.96          | 589.23          | 3.79            | 22.63           | 52.19           |
| 10                  | 547.91          | 599.46          | 7.32            | 25.78           | 76.03           |
| 20                  | 560.26          | 609.20          | 12.73           | 24.47           | 152.43          |
| (b) TK              |                 |                 |                 |                 |                 |
| N\(_2\) (pyrolysis) |                 |                 |                 |                 |                 |
| 5                   | 346.86          | 585.60          | 4.08            | 119.60          | 16.77           |
| 10                  | 368.83          | 596.66          | 7.81            | 113.92          | 31.17           |
| 20                  | 377.98          | 609.63          | 15.24           | 115.82          | 57.08           |
| CO\(_2\) (gasification) |                 |                 |                 |                 |                 |
| 5                   | 378.13          | 587.74          | 4.06            | 104.31          | 17.49           |
| 10                  | 394.89          | 596.19          | 7.32            | 100.65          | 30.90           |
| 20                  | 403.75          | 605.90          | 13.57           | 101.08          | 54.88           |

\(^{\text{a}}\) \(T_{\text{ini}}\). Initial devolatilization temperature at a conversion of 10%; \(T_{\text{peak}}\). Maximum peak temperature; \(R_{\text{max}}\). Maximum mass loss rate; \(\Delta T_{1/2}\). Temperature interval when \(R/R_{\text{max}}\) is 1/2; \(D_i\). Devolatilization index.
maximum mass loss rate during the thermal decomposition increased, and the conversion rate decreased on increasing the heating rate at the same temperature owing to the thermal hysteresis phenomenon caused by heat resistance. This is attributable to the delay in the heat transferred to the internal bulk sample, resulting in the central temperature of the particle being lower than the surface temperature. The increased heating rate increased this temperature difference; furthermore, the sample interior was not supplied with sufficient energy to decompose on time. The higher CO$_2$ gasification reaction of carbon was also observed to occur more significantly at temperatures exceeding 900 K and at a higher heating rate, as mentioned in section 2.1.

To compare and evaluate processes quantitatively, the key thermal parameters of pyrolysis (N$_2$) and gasification (CO$_2$) heated at several heating rates are described, which include the initiating temperature ($T_{in}$), peak temperature ($T_{peak}$), maximum mass loss rate ($R_{max}$), and devolatilization index ($D_i$), as summarized in Table 1 and Figure 5. In this study, the $D_i$ was used to investigate the release behavior of the volatile materials, as shown by He et al.$^{27}$ and in eq 1 below:

\begin{align*}
D_i &= \frac{\text{Mass loss at temperature } T}{\text{Initial mass}}
\end{align*}

Figure 5. Effect of heating rates on (a) $R_{max}$ and (b) $D_i$ for raw and torrefied kenaf.

Figure 6. Conversion ratio versus temperature for the pyrolysis and gasification at different heating rates in the reaction during stage I (a, b) and II (c).
higher than that of N₂, but the $k_\text{min}$ was 5% less than that of the N₂ atmosphere, implying $R_K$ under N₂, indicating that gasification as a function of temperature for reaction stages I was higher than that of $R_K$.

In addition, the residuals for CO$_2$ decreased by approximately 74% for RK and 84% for TK because the gasification reaction of the remaining char with CO$_2$ and the reduction ratio for TK was higher than that of RK.

### Table 2. Activation Energy, Pre-Exponential Factor, and Correlation Coefficient According to the Conversion Ratio in the Reaction during Stage I (a, b) and II (c)

| Conversion Ratio | Activation Energy (kJ/mol) | Pre-Exponential Factor (1/s) | $R^2$ |
|------------------|-----------------------------|-----------------------------|--------|
| **(a) RK (stage I)** |                            |                             |        |
| N₂ (pyrolysis)   |                             |                             |        |
| 0.1              | 180.73                      | 9.54E+14                    | 0.9971 |
| 0.2              | 182.06                      | 6.44E+15                    | 0.9987 |
| 0.3              | 186.63                      | 1.25E+15                    | 0.9965 |
| 0.4              | 188.11                      | 7.09E+14                    | 0.9981 |
| 0.5              | 183.71                      | 1.35E+14                    | 0.9990 |
| 0.6              | 180.20                      | 3.59E+13                    | 0.9996 |
| 0.7              | 181.59                      | 2.76E+13                    | 1.0000 |
| 0.8              |                             |                             |        |
| 0.9              |                             |                             |        |
| Average          | 183.29                      | 1.36E+15                    | 0.9984 |
| CO₂ (gasification) |                             |                             |        |
| 0.1              | 206.72                      | 2.038E+18                   | 0.9891 |
| 0.2              | 215.26                      | 2.332E+18                   | 0.9903 |
| 0.3              | 232.05                      | 2.827E+19                   | 0.9900 |
| 0.4              | 243.50                      | 1.124E+20                   | 0.9915 |
| 0.5              | 235.08                      | 7.365E+18                   | 0.9940 |
| 0.6              | 218.63                      | 1.122E+17                   | 0.9953 |
| 0.7              | 205.72                      | 4.064E+15                   | 0.9961 |
| 0.8              | 192.57                      | 1.123E+14                   | 0.9827 |
| 0.9              | 122.65                      | 6.40E+06                    | 0.9412 |
| Average          | 222.42                      | 2.18E+19                    | 0.9923 |
| **(b) TK (stage I)** |                             |                             |        |
| N₂ (pyrolysis)   |                             |                             |        |
| 0.1              | 175.49                      | 3.14E+13                    | 1.0000 |
| 0.2              | 172.59                      | 5.26E+13                    | 1.0000 |
| 0.3              | 176.67                      | 2.17E+13                    | 1.0000 |
| 0.4              | 178.12                      | 1.85E+13                    | 0.9999 |
| 0.5              | 184.13                      | 4.09E+13                    | 0.9998 |
| 0.6              | 216.38                      | 1.37E+16                    | 0.9981 |
| 0.7              | 320.37                      | 1.04E+24                    | 0.9976 |
| 0.8              | 385.15                      | 2.24E+27                    | 0.9985 |
| 0.9              | 457.93                      | 1.19E+30                    | 0.9948 |
| Average          | 251.87                      | 1.32E+29                    | 0.9987 |

\[ D_i = \frac{R_{\text{max}}}{T_i T_i^2 \Delta T_{i/2}} \]  

\[ (1) \]

Owing to the thermal hysteresis, the $T_{\text{peak}}$, $R_{\text{max}}$, and $D_i$ increased as the heating rate increased, as observed in both atmospheres, and the $D_i$ value for TK was higher than that of RK at all heating rates. For comparison between N₂ and CO₂ atmospheres, the $D_i$ value for CO₂ at 5 K/min was slightly higher than that of N₂, but the $D_i$ value for CO₂ at 10 and 20 K/min was 5% less than that of the N₂ atmosphere, implying that the CO₂ devolatilization performance dropped below that of N₂ as the heating rate increased. In addition, $D_i$ and $R_{\text{max}}$ values for TK under CO₂ were significantly lower than those of RK under N₂, indicating that gasification results in less reactivity with lignin-like compounds produced by torrefaction, which is consistent with the results obtained by other studies.28 In addition, the residuals for CO₂ decreased by approximately 74% for RK and 84% for TK because the gasification reaction of the remaining char with CO₂ and the reduction ratio for TK was higher than that of RK.

#### 2.3. Kinetic Parameter Analysis

Figure 6 shows conversion as a function of temperature for reaction stages I and II in the N₂ and CO₂ atmospheres for RK and TK. The model-free activation energy was analyzed using the DAEM. Stages I and II indicate the low-temperature (< 900 K) and high-temperature regions (> 900 K), respectively. In addition, the reaction during stage II only represented CO₂ because there was no reaction during stage II for N₂. Thus, the kinetic analysis for stage II was only carried out in the high-temperature regions (> 900 K), respectively. In addition, the reaction during stage II only represented CO₂ because there was no reaction during stage II for N₂. Thus, the kinetic analysis for stage II was only carried out in the high-temperature region, as shown in Table 2. The model-free activation energy using the DAEM at each conversion was obtained from the slope of the linear regression method. The activation energy changed as the reaction progressed during pyrolysis and gasification. This phenomenon occurred because the material was not a pure compound but a mixture of other elements with complex chemical bond structures. Figure 7 shows the variation of activation energies according to conversion for RK and TK under pyrolysis (N₂) and
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cation (CO₂) in stage I. The conversion graph in the reaction during stage I for N₂ and CO₂ appears similar for both RK and TK. The activation energy according to conversion for RK was higher in the case of CO₂ compared to that of N₂, yielding average values of 222.42 and 183.29 kJ/mol, respectively. This indicates that the reactivity of CO₂ is lower than that of N₂. In the case of TK, the activation energies for CO₂ were higher as the conversion ratio increased to 0.6, and activation energies for N₂ increased significantly when the conversion ratio exceeded 0.6. This shows a higher activation energy of lignin derived from hemicellulose and cellulose by torrefaction during the final stage of the reaction, a tendency that was also observed in a previous study.27 However, the activation energies for CO₂ did not change significantly even after the conversion ratio exceeded 0.6, indicating varying patterns in the CO₂ atmosphere. Thus, with respect to TK, the average activation energy for CO₂ is lower than that of N₂.

Figure 7. Variation of activation energies according to conversion for raw (a) and torrefied kenaf (b) under pyrolysis (N₂) and gasification (CO₂) during stage I.

Figure 8. Variation of activation energies according to conversion for raw and torrefied kenaf under gasification (CO₂) during stage II.

whose average values are 218.29 and 251.87 kJ/mol, respectively. These results show that the energy needed for gasification in the case of TK is lower than that needed for pyrolysis. Figure 8 shows the variation of activation energies according to conversion ratio for RK and TK under a CO₂ environment during stage II. The activation energies for stage II (197.94 and 197.62 kJ/mol for RK and TK, respectively) under a CO₂ atmosphere were similar for both the samples. The activation energy gradually decreased as the conversion ratio increased. Furthermore, all samples showed kinetic compensation effects with simultaneous increase or decrease in activation energy and pre-exponential factors for N₂ and CO₂, as shown in Table 2. This behavior was consistent with the findings of previous studies.30,31 These results suggest that the energy required in the gasification system using TK as feedstock is less than that of RK, which implies that energy can be saved in the system.

3. CONCLUSIONS

The effect of torrefaction on kenaf under N₂ and CO₂ atmospheres was examined using thermogravimetric analysis (TGA) data at different heating rates. In the low-temperature region (<900 K), the thermal effect on gasification for TK was similar to that of pyrolysis. However, from the analysis of essential thermal parameters, TK under CO₂ gasification resulted in a lower maximum mass loss rate, delayed initiating temperature, and lower Dₙ at the different heating rates, indicating that CO₂ gasification has a lower reactivity. However, in the high-temperature region (> 900 K), the gasification reaction of CO₂ and char occurred, resulting in high conversion efficiencies in the CO₂ atmosphere. In addition, torrefaction led to a larger reaction of CO₂ gasification with increased char, which was confirmed by the residual char. The activation energies were analyzed using the DAEM with distinctive stages I and II. TK under a CO₂ atmosphere in the entire region remarkably exhibited a lower average activation energy compared to RK, which opposes the tendency observed in the results of RK. The activation energies for the CO₂ reaction with char at high temperatures had similar values for both samples. These results suggest that the energy needed for TK under gasification is less than that
needed for RK and could thus contribute to saving energy in the system.

4. MATERIALS AND METHODS

4.1. Materials. Kenaf was used as fuel (Hibiscus cannabinus L.), a sample of which was pretreated by torrefaction. Then, 5 g of RK was added to a sample crucible and N₂ was passed through a tube at 1.5 cm³/min to form an inert atmosphere. TK was produced in a fixed-bed furnace under inert N₂ gas conditions at 523 K for a residence time of 30 min. The RK and TK samples were prepared at a particle size of < 100 μm using a grinder, and the properties of each sample are listed in Table 3.

Table 3. Fuel Properties of RK and TK

| sample            | RK    | TK    |
|-------------------|-------|-------|
| proximate analysis (wt %, as-received) |       |       |
| moi.              | 9.18  | 1.96  |
| VM                | 69.42 | 62.12 |
| FC                | 17.91 | 30.48 |
| ash               | 3.48  | 5.43  |
| FR                | 0.26  | 0.49  |
| ultimate analysis (wt %, dry basis) |       |       |
| C                 | 43.36 | 52.27 |
| H                 | 5.69  | 5.27  |
| N                 | 0.66  | 0.87  |
| O                 | 50.21 | 41.49 |
| S                 | 0.08  | 0.11  |
| O/C               | 1.158 | 0.794 |
| H/C               | 0.131 | 0.101 |
| HHV (MJ/kg, AR)   | 17.4  | 20.8  |

*Calculated by difference.

4.2. Experimental Procedures. The experiments of RK and TK during pyrolysis and gasification were conducted using a thermogravimetric analyzer (SDT Q600, TA Instruments Co.) at three heating rates (5, 10, and 20 K/min). The heating rate was selected as a TGA experiment in which kinetic analysis can be performed using the DAEM. In a ceramic crucible, the samples were distributed evenly in a thin layer (17 mg ± 2 mg), and the mass and temperature of the samples were continuously recorded on increasing the temperature at a set heating rate until the final temperature of 1173 K. In the pyrolysis experiments, ultrapure N₂ was injected into the thermogravimetric analyzer at a constant flow rate of 100 mL/min, creating an inert gas environment; in the case of gasification experiments, a constant flow rate of ultrapure CO₂ was continuously supplied.

4.3. Distributed Activation Energy Model. In this study, kinetic analysis was conducted using the DAEM and a single-step reaction model based on the TGA data on the pyrolysis and gasification of RK and TK to compare and evaluate the characteristics of samples during thermal degradation.35,34 Thus, converting raw materials into products is assumed to be a single-step process.34 The rate constant of the reaction (k) according to the Arrhenius method is expressed as follows:

\[
    k = A e^{-E/RT}
\]

where \( k \) is the reaction rate constant, \( A \) is the pre-exponential factor (1/s), \( E \) is the activation energy (kJ/mol), \( R \) is the gas constant (8.314 J/mol-K), and \( T \) is the absolute temperature (K). For biomass conversion from solid to volatile states, the rate equation is expressed as follows:

\[
    \frac{d\alpha}{dt} = k(\alpha)
\]

The conversion ratio (\( \alpha \)) is calculated using eq 4

\[
    \alpha = \frac{m_i - m_f}{m_i - m}\n\]

where \( m_i \) is the initial mass, \( m_f \) is the mass at time \( t \), and \( m \) is the final mass.

By combining eqs 2 and 3, we get

\[
    \frac{d\alpha}{dt} = A e^{-E/RT}(\alpha)
\]

Rearranging eq 5 into a logarithmic form using the simplified DAEM for the Arrhenius equation yields the following:

\[
    \ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E} \right) + 0.6075 - \frac{E}{RT}
\]

From eq 6, the plot of \( \ln \left( \frac{\beta}{T^2} \right) \) versus \( 1/T \) yields a straight-line equation. \( \frac{AR}{E} \) provides the slope of the equation and \( \ln \left( \frac{AR}{E} \right) \) provides the intercept value, while the value 0.6075 is kept constant for simplicity.

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B.-H.L., T.V.T., and C.-H.J. conceived and planned the study. T.V.T. conducted the experiments for this research. B.-H.L. and C.-H.J. contributed to the analysis of the results. All authors helped shape the research, discussed the results, and contributed to the final manuscript.

Notes

The authors declare no competing financial interest.

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