The effect of torrefaction on the thermo-kinetics of thermally processed black pine

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Abstract
This paper investigates the kinetic behaviour of thermal decomposition of pre-treated pine needles. The model-free methods of Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Kissinger, are used to determine the kinetic parameters of the processed pine needles. For a comparative analysis, the kinetic characteristic of the pre-treated pine needles is equated to the thermal decomposition of the raw pine needles. For torrefaction of the raw substrate, some changes related to the design have been made to the furnace. The raw material has been thermally pre-treated at a temperature of 523 K for 5 minutes. The volumetric rate of nitrogen during the torrefaction process is 42 L·min⁻¹, while the purge flow rate of nitrogen gas is 0.2 L·min⁻¹ for the thermogravimetric analysis. The temperature range for the thermal degradation of the torrefied pine needles is 308 K-873 K. The activation energies determined by the FWO and the KAS methods are 157.08 kJ·mol⁻¹ and 160.54 kJ·mol⁻¹, respectively, whereas it is 137 kJ·mol⁻¹ by the Kissinger method. The activation energy computed by the FWO and the KAS schemes for the raw material is found to be 1.3% less than that of the processed pine needles. The aromaticity of the thermally processed pine needles is increased by 13.61%. Thermal immunity or stability due to the increasing fraction of lignin causes the activation energy and frequency factor of the pre-treated pine needles to slightly elevate. The redistribution of the pyrolysis stages has been observed for the torrefied pine needle sample, the temperature scale at a constant heating rate increases slightly by 0.34% during the char formation.

KEYWORDS
biomass, kinetics, model-free methods, pre-treatment, thermal decomposition

INTRODUCTION
The rate by which chemical transformations take place in a physical structure during a process is defined by chemical kinetics. It can either be governed by the probabilistic models such as quantum mechanics, statistical mechanics, or the semi-empirical rate laws deduced from the physical models. The phenomenological models or semi-empirical rate laws are also referred to as engineering kinetics or global kinetics because they serve the...
application purpose rather than developing a framework for the chemical problem. These models mainly focus on the lumped chemical mechanism that denotes the cumulative progress of a set of related reactions. These set of reactions are represented by a differential equation that expresses the formation and decomposition of products and reactants in terms of conversion ($\alpha$), respectively. The corollary of the lumped chemical mechanism further classifies the kinetic analysis under two main headings: model-free analysis and model-fitting methods.

These methods are used to derive a kinetic expression for the condensed phase reactions, but both depend on some assumptions. The model-free analysis is further classified based on its computational procedure. Isoconversional methods support the model-free kinetics but are not assumption-free. The basic principle of the methods states that the same reactions occur in the same ratio and would be independent of temperature at a particular extent of reaction. However, it is not a hard-and-fast rule that the reactions must follow the course line of isoconversional methods; for example, the independent parallel reactions, which differ in their relative reactivity, are the function of temperature since they have different activation energies.\(^1\)

Another example of disagreement is with a set of the competitive reactions having different activation energies, which cause the overall reaction pathway to be changed at different temperatures.\(^2\) Some isoconversional methods have good computational accuracy, and they would help to construct a robust kinetic model.\(^3\) Some of the isoconversional methods which are often used for computational purpose are the differential method developed by Friedman,\(^4\) the integral method coined by Flynn-Wall-Ozawa (FWO),\(^5-8\) and the modified version of FWO given by Kissinger-Akhira-Sunose (KAS).\(^9\) Within the same group, the Kissinger model is the simplest kinetic model,\(^10\) which is not an isoconversional method, but in some cases, has proximity with its group members. It uses the maximum reaction rate to determine the kinetic parameters (activation energy and frequency factor). It is highly precise and isoconversional for first-order reactions.\(^11\) It provides an accurate approximation for the following reaction regimes: $n^{th}$ order reactions,\(^12\) nucleation-growth,\(^13\) and distributed reactivity reactions.\(^14\) As mentioned, there are some set of reactions which do not comply with the assumptions of isoconversional methods, but in some cases, it explains the reaction mechanism effectively.\(^15\)

Some kinetic studies based on the isoconversional methods are conducted on invasive species.\(^16-18\) Alves et al examined aquatic macrophytes and reported that water hyacinth and yellow velvetleaf are relatively good for thermal application as compared to other biomasses. This is due to the high content of volatiles, carbon, hydrogen, and oxygen.\(^16\) The activation energies for water hyacinth and yellow velvetleaf are found to vary from 105 kJ ÷ mol$^{-1}$ to 219.49 kJ ÷ mol$^{-1}$.\(^16\) Similarly, Dhaundiyal et al studied the effect of carrot grass on the highlands of the Greater Himalaya and Karakoram ranges.\(^17\) The estimated value of activation energy from the isoconversional methods has been found to vary from 145.44 kJ ÷ mol$^{-1}$ to 145.81 kJ ÷ mol$^{-1}$, whereas it is 148 kJ ÷ mol$^{-1}$ for the Kissinger method. As a low bulk density fuel, the released energy per unit mass for the carrot grass is found to more than other feedstocks have at the same temperature.\(^17\) Havilah et al have conducted the experiments on the perennial shrub and lantana camera, for energy generation. In their kinetic analysis, they estimated that the activation energy derived from the isoconversional methods is in the range of 184 kJ ÷ mol$^{-1}$-197.8 kJ ÷ mol$^{-1}$, whereas the determined value from the Kissinger method is found to be relatively low (105.83 kJ ÷ mol$^{-1}$). They used oxidising atmosphere and reported that the TG curves deviates with the increasing heating rate. They observed that the activation energy increases until a 60% conversion of the substrate is achieved. They have concluded that the bond energies vary with temperature, which eventually leads to fluctuation in the activation energy with the conversion.\(^18\)

It has been found that isoconversional methods are much more promising than the model-fitting approach to determine kinetic parameters; however, the diffusion models provide the goodness-of-fit (GOF) with the thermogravimetric data.\(^17\) In another experimental study, the apparent activation energy for the pyrolysis of wheat straw was found to be 130 kJ ÷ mol$^{-1}$-175 kJ ÷ mol$^{-1}$. A marginal deviation in the activation energy is seen while computing its values from the isoconversional methods. The activation energy during thermal decomposition is highly influenced by the conversion of wheat straws with respect to time. It has been established that during the pyrolysis process, the iterative integral method could also be grouped among the other isoconversional methods.\(^19\) During decomposition of nitroimidazoles, it has been seen that the Friedmann method provides higher values of activation energy than the FWO.\(^20\) The kinetics analysis of thermal decomposition of wood chips has also been performed by the isoconversional methods, and it has been concluded that the composition and concentration of the main components determines the reaction pathway in wood chips.\(^21\) The kinetic study based on pyrolysis of rice straw concludes that the KAS and FWO are the most efficient compared with other isoconversional methods to delineate the thermal degradation mechanism of rice straw.\(^22\) A similar observation has been made with melon seed when its kinetic
behaviour was examined by the isoconversional methods. It has been concluded that the KAS and the FWO are much more promising than the other methodologies.[23] Seeing their computational performances as a benchmark for the kinetic analysis, they have been adopted to examine the kinetics of pyrolysis of the torrefied pine needles.

This paper discusses the kinetic behaviour of the thermal decomposition of processed pine needles with respect to the raw pine needles. The kinetic parameters for thermal decomposition of both materials are obtained from the model-free methods. Based on the derived solution for both cases (thermally pre-treated and the raw material), a qualitative assessment of kinetic activities is performed. The chemical characteristic of the torrefied pine needles and the variation in its constituents have been investigated. By the thermo-kinetic analysis of the torrefied pine needles, the yield of the various products formed during pyrolysis can be comparatively examined for both materials. The procedure and novelty of the work involves the use of an improvised muffle furnace rather than microwave heating for the torrefaction process. The torrefaction has been carried out without a non-linear ramping temperature profile. It was also ensured that the mass loss during conversion would be minimal. Thermodynamically, the quasi-static approach has been taken to carry out thermal decomposition of the substrate.

2 MATERIALS AND METHODS

2.1 Experimental installation

The raw material (pine needles) for the torrefaction purpose was collected from the Pest county in Central Hungary. A mass of 4 kg of the raw material was mechanically processed by the milling machine. To pre-treat the raw material at the given temperature, the digitally programmed furnace (Nabertherm GmbH, Lilienthal, Germany) was slightly modified to make a pilot-scale torrefaction unit. The hinged gate of the furnace was replaced with a clamped gate. The modified gate has two ducts for inert gas, a plunger, a cooling fan, and a hollow cylinder. The milled pine needles were injected into the main unit from a protruded hollow cylinder, which was welded with the gate, when the furnace reached a chosen torrefaction temperature. A steel vessel was connected to the weighing unit through a mechanical link. After torrefaction of the raw pine needles, the calorific value and the elemental composition of the sample were calculated. A nitrogen cylinder having a maximum pressure of 50 bar was reduced to 1.5 bar by the regulating valve. The purge rate of nitrogen for the furnace was set at 42 L · min⁻¹. The milled pine needles were torrefied at a temperature of 523 K for the duration of 5 minutes.

The chemical analysis of the pine needles/torrefied pine needles were performed with the help of the CHNS analyzer (Vario MACRO cube, Langenselbold, Germany), whereas the percentage composition of oxygen was determined by the difference method.[24] Tableting the pre-treated samples with tungsten (VI) oxide (WO₃) was performed using a tin foil. Tungsten oxide was used as a reagent to facilitate the oxidation of the sample. Before using the CHN analyzer, it was calibrated with the birch leaf, so that it could ensure that the analyzer was functioning properly. Initially, the analyzer was heated to 1473 K for 30 minutes. Upon reaching the pre-combustion temperature, the encapsulated samples were fed into the chamber by the rotating disc. Helium gas, a carrier gas, was used to carry away the products of combustion to different reduction columns, where the elements of gas were separated by using a trap or purge chromatography. Each element was detected by a thermal conductivity detector (TCD). The function of a TCD is to generate an electric pulse that is proportional to the concentration of the elementary components of a material. The heating value of the torrefied sample was calculated by oxygen bomb calorimeter (IKA-WERKE, Staufen, Germany). For the calibration of the calorimeter, a benzoic tablet was used. Once it was calibrated, the samples were then kept inside a stainless-steel vessel. The maximum operating pressure of the calorimeter was fixed to 23 MPa. The temperature of the water measured by the temperature sensor was 298 K. The energy provided to initiate the process was less than 40 kJ. The IKA WERKE C2000 interface software was used to compute the heating value of the pre-treated samples.

Thermogravimetric analysis (Seiko Instruments Inc, Chiba, Japan) was performed at the Indian Instrumentation Centre, the Indian Institute of Technology, Roorkee, UK, India. The thermobalance used for testing purpose was a horizontal differential type. The derivative thermogravimetric (DTG) measurement range for the instrument was 0.5 mg · min⁻¹-1000 mg · min⁻¹. The samples underwent thermal decomposition at the heating rates of 5°C · min⁻¹, 10°C · min⁻¹, and 15°C · min⁻¹. The temperature of heating the chamber varied from 308 K to 873 K. The duration of the thermal decomposition of the processed and raw material was 60 minutes. The mass of the sample used for the analysis purpose was 10 mg. A Type R thermocouple (Platinum/ Rhodium- 13%/ Platinum) was used to measure the temperature of the chamber. The volumetric flow rate of nitrogen selected for the pyrolysis process was 0.2 L · min⁻¹. The physical configuration of the balance beam was horizontal so that the
buoyance effect might influence the thermogravimetric analysis. The reference material used for the thermogravimetric analysis was alumina powder.

The change in constituent composition (cellulose, hemicellulose, and lignin) of the thermally pre-treated pine needles samples was also examined. The standard protocol followed to measure the significant constituents of biomass is the NREL method. Before measuring the constituents of the biomass, the dry matter was calculated. The samples of 0.5 g of torrefied/ raw pine needles were chemically treated with 2.5 mL of H₂SO₄ (72% concentrated). The samples of 0.5 g of torrefied/ raw pine needles were loaded in an autosampler, and later injected into the mobile solvent (the HPLC grade water) was filtered by a 0.2 μm membrane filter so that the impurities in the mobile solvent was detected by a detector diode through the flow cell. The generated UV spectrum was collimated by a deuterium lamp was used as a UV light source. The generated UV spectrum was collimated by a slit and allowed to diffract from the mobile phase and get absorbed by the analytes. A deuterium lamp was used as a UV light source. The generated UV spectrum was collimated by a deuterium lamp was used as a UV light source.

After completion of the process, the same sample was diluted with 75 mL of distilled water. Thereafter, it was autoclaved for one more hour. A sintered filter was used to carry out the filtration process of the autoclaved solution in a vacuum flask with its side-arm attached to an aspirator. The filtered solution was sent to an autosampler, and later injected into the mobile solvent by a hypodermic syringe. A UV-VIS detector was used to identify and detect the relative fractions of xylose, glucose, and arabinose with the help of light absorption and the impurities of the binary solution and also prevent the C18 column (Nucleosil, USA) from getting damaged.

Perform liquid chromatography, the samples were loaded in an autosampler, and later injected into the mobile solvent by a hypodermic syringe. A UV-VIS detector was used to identify and detect the relative fractions of xylose, glucose, and arabinose with the help of light absorption and the impurities of the binary solution and also prevent the C18 column (Nucleosil, USA) from getting damaged.

Table 1 shows the chemical characteristics of the pine needles and the torrefied pine needles (dry basis). The energy consumption of the furnace as well as the milling machine was calculated by the energy logger (Volcraft, Hirschau, Germany). The physical parameters related to the raw and processed pine needles are shown in Table 2. Figure 1 illustrates the equipment used for processing the raw material. Table 3 provides information about the fraction of cellulose, hemicellulose, and lignin present in the raw and processed pine needles.

### 2.2 Kinetic theory

It is often assumed that for a non-ideal situation, the dependence of the conversion on the intensive properties of a system (P and T) can be written down in a single differential equation. The set of chemical reactions can be denoted by the rate law, which includes the rate of disappearance of reactants or the rate of appearance of products. The first-order differential equation in terms of the appearance of the products (α) is used throughout in this study:

\[
\frac{d\alpha}{dt} = f(\alpha)g(P)k(T)
\]

where \(\alpha = \frac{m_0 - m_t}{m_0 - m_r}\) and \(m_0\), \(m_t\), and \(m_r\) represent the initial mass, instantaneous mass, and the residual mass of the sample, respectively.

Therefore, the differential equations for the above reaction can be written as follows:

\[
\frac{d\alpha}{dt} = f(\alpha)g(P)k(T)
\]

or

\[
-\frac{d(1-\alpha)}{dt} = f(\alpha)g(P)k(T)
\]

Here, \(P\) and \(T\) denote the pressure and temperature of the system, respectively, and the differential form of the conversion function \(f(\alpha)\) is determined by selecting the solid-state reaction regimes. The \(k(T)\) and \(g(P)\) represent the rate constant and the pressure function, respectively. The weightage of the pressure dependence is

### Table 1

| Material     | C%   | H%   | N%   | O%   | S%   | Ash%  | *F.C% | *V.M% |
|--------------|------|------|------|------|------|-------|-------|-------|
| Raw          | 49.68| 5.98 | 0.52 | 40.80| 0.10 | 2.92  | 1.11  | 89.92 |
| Processed    | 53.40| 6.54 | 0.68 | 39.13| 0.09 | 0.16  | 93.44 | 3.210 |

Note: *F.C, Fixed carbon; *V.M, Volatile matter.
TABLE 2  The physical parameters related to the raw and processed pine needles

| Material   | Heating Value (MJ·kg⁻¹) | Energy density (GJ·m⁻³) | Mass loss (%) | Energy gain (%) | Electricity consumption (kW·h) |
|------------|--------------------------|--------------------------|---------------|-----------------|-------------------------------|
| Raw        | 19.054                   | 3.680                    | 0             | 0               | 0                             |
| Processed  | 23.446                   | 4.201                    | 7.5           | 10              | 0.076                         |

FIGURE 1  Equipment used for torrefaction and milling purpose: A, furnace; B, milling machine; and C, schematic diagram.
mainly for the gas-solid reactions, where the partial pressure of gaseous products \( (P) \) and the equilibrium vapour pressure \( (P_{eq}) \) are taken into consideration

\[
P(P) = 1 - \frac{P}{P_{eq}}.
\]

For example: (a) reduction of calcium carbonate into calcium oxide and carbon dioxide, (b) hydrogen cracking, where the relative change in the pressure causes deviation in initiation, propagation, and termination of reactions, which eventually causes the variation in the overall activation energy of the reactions,[27] and (c) the reaction rate of volatile gases with the unpyrolysed material (autocatalytic reactions) is accelerated by the moderate increase in the pressure.[28] On the other hand, drastic change in pressure also causes the reduction in the reaction rate of the autocatalytic reactions by increasing the diffusion resistance.[29] Another important aspect of Equations (2) and (3) is that the materials subjected to decomposition are homogenous in nature. On the contrary, the thermally processed biomass and the raw biomass have moieties which might show different reactivity, therefore carrying on the kinetic analysis by bifurcating reactions into the set of parallel reactions can be simplified if the pressure dependence is assumed to be absent. The progress of these parallel reactions can also be grouped into three classes: (a) acceleratory, (b) deceleratory, and (c) sigmoidal. Here, the sigmoidal reactions are formed by grouping the acceleratory and declaratory phases, which are connected by an inflexion point where the deviation of the mass fraction with respect to time and temperature is constant. A solid-state reaction that propagates from the core of a sphere, and a chain reaction having a branching fraction greater than 1 are some of the examples of acceleratory reactions. In contrast, the decomposition of biomass, which is initially accelerated by the secondary pyrolysis reactions and accompanies the dissipation of released heat and pressure, would lead to the sigmoidal phase.[30]

2.2.1 | Methods of kinetic analysis

The isoconvensional methods begin with the assumption in Equation (2) or Equation (3) that the function \( g(P) \) is supposed to be one. Friedman has envisioned the differential method by assuming no pressure dependence, and the value of \( f(\alpha) \) must be constant at a particular extent of \( 1-\alpha \) if the chemical pathway is independent of the temperature.[4] The interpretation of the isoconvensional analysis is illustrated in Figure 2:

\[
\ln\left(-\frac{d(1-\alpha)}{dt}\right) = \ln(A) + \ln(f(\alpha)) - \frac{E}{RT}.
\]

Plotting natural logarithm of the reaction rate against the \((1/T)\), Equation (4) provides the slope \( E/R \) and an intercept of \( \ln(A, f(\alpha)) \). It has been reported that the plot of \( \ln(A, f(\alpha)) \) versus \( \ln(1-\alpha) \) would be linear, and the slope of the line would be \( n \) for the \( n^{th} \)-order reaction. But in actual practise, the \( E/R \) is not usually constant with the unreacted mass \( (1-\alpha) \) and the plot is hardly able to determine the reaction order linear. Friedman originally gave this method in the context of the unreacted mass. Apart from the

### Table 3

| Material | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|----------|---------------|-------------------|------------|
| Raw      | 29.144        | 19.937            | 33.905     |
| Processed| 25.774        | 14.080            | 38.521     |
The differential method of Friedman, the integral approach gained more popularity due to its relatively high accuracy in determining activation energies.[31] The dependency of the rate constant on the thermodynamic temperature, \( T \), can be expressed by the Arrhenius equation:

\[
k(T) = Ae^{-\frac{E_a}{RT}}
\]

Without assuming pressure dependence, substitute \( k(T) \) in Equation (2) and we get Equation (6):

\[
\frac{d\alpha}{dt} = f(\alpha).Ae^{-\frac{E_a}{RT}}
\]

The right-hand side of Equation (6) is also called the kinetic triplet. For non-isothermal thermal history, the time dependence of conversion (\( \alpha \)) can be written down in terms of temperature, \( T \), by replacing it with the heating rate, \( \beta \):

\[
\frac{d\alpha}{dt} = f(\alpha).\frac{A}{\beta}e^{-\frac{E_a}{RT}}
\]

Here, \( \beta \) is the rate of change of temperature with time:

\[
\beta = \frac{dT}{dt}
\]

After the rearrangement of Equation (7), we have the following:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int \left( \frac{E_a}{RT} \right)
\]

The temperature integral \( \int \left( \frac{E_a}{RT} \right) \) has no exact solution and it can be approximated by various proposed numerical or asymptotic methods,[32-39] but the most commonly used method for isoconversional models has been proposed by Doyle.[40]

The solution of Equation (9) using Doyle’s approximation (Equation (10))[40] provides the FWO method,[5,6] which can be written as Equation (11):

\[
I \left( \frac{E_a}{RT} \right) \approx -5.331 - \frac{1.052E_a}{RT\alpha}
\]

\[
\ln(\beta_i) = \ln \left( \frac{AR}{g(\alpha)E_a} \right) - 5.331 - \frac{1.052E_a}{RT\alpha}
\]

Here the subscript \( \alpha_i \) represents a fixed conversion at different heating rates (\( \beta_i \)). The plot of Equation (11) provides a straight line having a slope \(-\frac{1.052E_a}{RT}\).

Furthermore, the more accurate version of temperature integral leads to the KAS method,[9] which is also recommended by the ICTAC reports for kinetic analysis.[3] However, it is useful to use both integral and differential methods since each method has some demerit, and it might show anomalies at different conditions.

The temperature integral approximation for Kissinger-Akahira-Sunose (KAS) is given by Equation (12), where \( I \left( \frac{E_a}{RT} \right) \) is replaced by the approximated term \( I \left( \frac{E_a}{RT} \right) \approx e^{-\frac{E_a}{RT\alpha}} \). This approximation is valid for the range of \( 20 \leq \frac{E_a}{RT\alpha} \leq 50 \).[41]

Therefore, Equation (9) can also be rewritten as follows:

\[
\ln \left( \frac{\beta_m}{\alpha} \right) = \ln \left( \frac{AR}{g(\alpha)E_a} \right) - \frac{E_a}{RT\alpha}
\]

The apparent activation energy can thus be computed by plotting \( \ln \left( \frac{\beta_m}{\alpha} \right) \) against \( \frac{1000}{T_m} \).

The ASTM E698 method presents a different interpretation which dwells between model-based methods and model-free analysis.[42] Unlike isoconversional method, the activation energy is not estimated at each conversion for the Kissinger method. It considers the model-free approach to determine the activation energy. At the peak reaction rate, the derivative of the reaction rate is zero. Differentiate Equation (3) by putting the value of \( g(P) = 1 \) and \( k(T) = Ae^{-\frac{E_a}{RT}} \), we obtain:

\[
\beta E_a \frac{R}{T_m^2} + Ae^{-\frac{E_a}{RT_m}} \left( \frac{df(\alpha)}{d(1-\alpha)} \right) = 0
\]

For first order reaction, \( \frac{df(\alpha)}{d(1-\alpha)} = -1 \).

Taking the natural logarithm of Equation (13), we get Equation (14), which is the required expression for model-free method:

\[
\ln \left( \frac{\beta}{R.T_m^2} \right) = \ln \left( \frac{AR}{E_a} \right) - \frac{E_a}{RT_m}
\]
method is more reliable than the model-fitting methods for estimating the global conversion of a starting material. Furthermore, the dependence of the activation energy $E$ and the frequency factor $\Lambda$ on the conversion can be more easily incorporated in the model-free method than the model-fitting methods.

3 | RESULTS AND DISCUSSION

The samples of the raw pine needles were thermally pre-treated in an improvised torrefaction unit. The change in the elemental composition (Table 1) and the physical parameters of the processed pine needles clearly show that the relative fraction of carbon as compared to the oxygen and hydrogen was increased, which also indicates the influence of thermal maturity on the application of the forest waste in a co-fired power plant. The torrefaction was conducted at 523 K for a duration of only 5 minutes. The breakage of the inter- and the intramolecular bonds and the emission of hydrophilic extractives led to the decrease in the fractions of hydrogen and oxygen of the biomass. However, there was a mass loss of 7.5% that took place during the thermal pre-treatment process, but in contrast to the mass loss, energy gain fraction increased by 10%. The energy density that directly influences the transportation cost of biomass also shot up to 4.201 GJ m$^{-3}$. The calorific value was also increased by 23.04% during the torrefaction process. Besides the chemical characteristics and the combustion-related parameters, structural transformation also occurred, which was experimentally determined by the HPLC method (Table 3). The cellulose and hemicellulose fractions of the pine needles were decreased by 11.56% and 29.37%, respectively. On the other hand, acid-insoluble lignin (AIL) in the thermally processed material was 13.61% higher than the parent material. An increasing fraction of lignin indicates that the aromaticity of the thermally processed pine needles was enhanced due to the thermal treatment. This occurred due to cleavage of lignin ether bonds ($\beta$-O-4 linkage decomposes at 518 K) and decomposition of carbohydrates which could re-condense to form 15 aromatic C-C and C-H bonds.$^{[43-45]}$

The effect of torrefaction on the lignin fraction altered the reaction pathway of different polymers, and consequently, the yield of the end products was affected.

It should be noted that the percentage fractions of the volatile matter and fixed carbon (Table 1) were also impacted during the thermal pre-treatment. As a matter of fact, the hemicellulose fraction of biomass is crucial in determining the yield of volatile gas rather than the yield of tar and char, whereas cellulose compared to hemicellulose provides more tar and char, and less gaseous products. The reason why the hemicellulose fraction is severely affected during torrefaction can be understood by this fact that the thermal immunity of hemicellulose is strongly related to its amorphous structure (strained structure) and lower molecular mass. Soltes and Elder$^{[46]}$ have reported that hemicellulose is thermally very sensitive, and it decomposes in the temperature range of 473 K-533 K; whereas lignin decomposes when the biomass is heated in the temperature range of 553 K-773 K.$^{[46]}$ The decomposition of hemicellulose takes place in two steps: (a) decomposition of polymer into solubler fragment or converts into monomers (b) transformation of monomer into light volatile products. In the case of cellulose, the dominant process is the reduction in the degree of polymerisation at a temperature of less than 573 K.$^{[47]}$ The yield of char is predominately determined by the fractions of lignin and cellulose in the biomass. In addition to the volatile content and fixed carbon, the ash content of the pine needles decreases by a margin of 94.52%. This reduction influences fouling of the surface of a pyrolysis reactor and the ancillary components of a biomass plant.

Apart from the physical and chemical changes, the influence of torrefaction on the conversion of biomass encouraged thermo-kinetic analysis to be performed, which was also compared with the kinetic behaviour of the unprocessed pine needles sample. Therefore, the overall assessment of the processed pine needles bifurcates the analysis process under the subsequent headings.

3.1 | Thermogravimetric analysis

The mass loss curves (TG) for the thermal decomposition of the torrefied and raw pine needles are plotted at three different heating rates (5°C min$^{-1}$, 10°C min$^{-1}$, and 15°C min$^{-1}$) (Figures 3 and 4). The boundaries of the degraded mass for both cases are demarcated by three different zones: dehydration, devolatilization, and the char formation. It is quite clear from the comparative perspective that the redistribution of the boundaries has taken place due to the thermal pre-treatment of the pine needles. The dehydration process of the pre-treated pine needles varies from 321.9 K-367.2 K, whereas the thermal range required for the raw pine needles to expel moisture lies in the domain of 321.5 K-381.9 K, which shows a 3.8% decrease in the upper thermal bound of the dehydration phase. The significance of the moisture reduction can be known from the fact that the local condensation of volatile in the cracks influence the overall tar yield and thus influence the local surface temperature due to endothermic evaporation.$^{[48]}$

Similarly, the devolatilization stage is in the range of 461.4 K-630.7 K for the raw pine needles. On the other
hand, the temperature scale for the same devolatilization phase gets shifted by 1.79%-1.99% from the lower bound scale of the raw pine needles for the torrefied pine needles. The devolatilization of torrefied pine needles is in a temperature range of 469.7 K-631.6 K, which is subject to vary with the heating rates. It can be inferred that the active pyrolysis of the torrefied pine needles is delayed, or the thermal immunity of the processed sample is relatively high as compared to the thermal sensitivity of the raw material at a constant heating rate. Apart from the devolatilization phase, the charring of processed pine needles is also get influenced by thermal pre-treatment. The range of temperature for the char formation varies from 636.5 K-830.6 K, whereas the range of temperature is 619 K-829 K for the raw material. A shift in the temperature scale of the torrefied pine needles sample has been seen at the onset of the char formation phase. Unlike the thermal decomposition of the raw pine needles, the expansion of the char formation has been seen with an increasing heating rate for the torrefied pine samples. On the contrary, the char formation phase gets shifted to a higher temperature domain for the raw material. The reason behind the rearrangement of the thermochemical phases is the structural change in the raw material due to the thermal treatment. The raw material which has undergone thermal treatment is mechanically and thermally immune due to carbonization and the cross-linking reaction. [48,49]

Even though the mass yield obtained at higher torrefaction temperatures is low, it improves the density of the biomass. With the change in the density of loose biomass, the kinetics of thermal decomposition of pre-treatment is also affected. Increasing density increases the residence time of the volatile gases inside the solid matrix, which in turn promotes the secondary pyrolysis (autocatalytic reactions) and the char formation. The density also influences the heat and mass-transfer properties of a biomass material. The manner in which a sample is heated in a reactor also leads to the rearrangement of the phases. Roberts[49] and Matsumoto et al.[50] concluded in their heat transfer modelling that the dependency of the thermal conductivity on the density cannot

**FIGURE 3** Thermogravimetric (TG) curves of the torrefied pine needles at different heating rates

**FIGURE 4** Thermogravimetric (TG) curves of the raw pine needles at different heating rates
be ignored; however, the direct proportionality between them has been refuted while comparing the experimental data with the predicted model.\textsuperscript{[49]} Even the porosity and anisotropy get affected during the thermal treatment, which eventually influences the permeability of the pyrolysis gases across a biomass material.\textsuperscript{[51]} The residual fraction after pyrolysis of the pre-treated sample varies from 2.2%-3.2%, whereas, at the same heating rate, the fraction of the residue obtained from the raw pine needles is in the range of 3.4%-3.96%, which is 21.7%-55.8% higher than that of the torrefied pine needles. With the increasing heating rate, the residual mass also increases by 15.4%-47.9%, whereas the relative change in the residual mass (mostly char) of the pre-treated pine needles with the heating rate is 17.8%-35.8% lower than its raw form.

The DTG curves of the thermally pre-treated and the raw pine needles are shown in Figures 5 and 6. The active and passive pyrolysis stages of the torrefied and raw pine needles can be distinguished by the global and local minima (maximum decomposition rate of cellulose) on the DTG curves obtained at the different heating rates. The rate of mass loss during the dehydration $\frac{dm}{dt}$, varies from 327.3 K-346.9 K, whereas the decomposition of cellulose $\frac{dm}{dt}$ is found to take place in the temperature range of 596.4 K-616.2 K. The decomposition of lignin occurs during the active as well as passive pyrolysis, however, the local minima $\frac{dm}{dt}$, (decomposition of lignin) is more perceivable in the temperature range of 725.6 K-743.6 K for the torrefied pine needles. It has been noticed that the temperature range for lignin is relatively wide as compared to cellulose and hemicellulose, but the rate of mass loss is far more uniform and slower than mass loss during the decomposition of cellulose and dehydration. It is worth mentioning that the peaks of the hemicellulose decomposition overlap with the cellulose peaks for both materials (thermally processed and the raw pine needles). Unlike in the decomposition of wood, lignin plays a pivotal role in the decomposition of the coniferous species (eg, pine needles and Cedrus deodara leaves). However, the overlapping of hemicellulose and cellulose peaks has also been observed during decomposition of wood,\textsuperscript{[52]} but in the case of the thermally processed pine needles as well as the raw pine needles, hemicellulose decomposition takes place alongside the cellulose, which in turn contributes to the mass loss during the cellulose decomposition. Similarly, for the raw pine needles, any significant shift in the temperature range as well as magnitude of rate of decomposition have not observed in the characteristic of DTG curves.

The range of temperature required for mass loss during the dehydration process varies from 328.9 K-346.9 K, which is negligibly higher than that of the range of temperature corresponding to the dehydration in the torrefied pine needles. On the other hand, the mass loss during the dehydration process is 4.45%-5.70% higher than the corresponding mass loss that occurs in a thermally pre-treated sample of pine needles. The decomposition of cellulose for the raw pine needles occurs in the temperature range of 591.8 K to 613.9 K, which is relatively narrow in comparison with that of the thermally pre-treated pine needles. Furthermore, the rate of mass loss during the cellulose decomposition (the raw pine needles) is 6.5%-8.8% lower than the rate at which cellulose decomposes in the torrefied pine needles. The lignin decomposition, in the case of the raw pine needles, takes place in the temperature range of 725.8 K-750.5 K. The temperature scale gets shifted to the right during the thermal degradation of lignin. The rate at which lignin decomposes in the raw pine needles is relatively low (7.58%-11.76%) compared to the rate of decomposition of lignin in the torrefied pine needles. However, the relative margin gets lowered with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Derivative thermogravimetric (DTG) plot of the torrefied pine needles at different ramp rates.}
\end{figure}
increasing heating rate. It can be concluded from the DTG analysis that the cellulose and lignin decomposition lead to increases in the overall char formation, in the case of the torrefied pine needles, whereas the rate of conversion is relatively slow in the raw pine needles, which causes expansion of the temperature range for the decomposition of a similar constituent of material. It implies that cross-linking, repolymerization, and cracking of cellulose are promoted during the thermal decomposition of the thermally pre-treated sample. Though there would be some mass transfer, it is relatively low for the raw pine needles. Moreover, it implies that the residence time of the volatile is slightly higher, and its pressure-driven flow inside the specimen is reduced.

To comprehend the mass transfer at high temperatures, information about the grain orientation, particle size, and internal structure must be known. Moreover, the propagation of thermal energy through the char layer is carried out by conduction, and the energy that flows through the non-pyrolysed solid also depends upon the temperature gradient and its physical dimensions.[53]

### 3.2 Investigation of the kinetic behaviour

The kinetic analysis of the torrefied pine needles is examined by the model-free methods (Kissinger, FWO, and

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**TABLE 4** Kinetic parameters of thermal decomposition of the torrefied pine needles

| Conversion (α) | FWO          | KAS          |
|---------------|--------------|--------------|
|               | E_a (kJ · mol⁻¹) | A (min⁻¹) | R² | E_a (kJ · mol⁻¹) | A (min⁻¹) | R² |
| 0.05          | 69.07        | 4.17 × 10¹¹ | 0.99 | 69.68        | 1.43 × 10⁸ | 0.99 |
| 0.10          | 144.83       | 1.01 × 10¹⁷ | 0.99 | 148.23       | 1.10 × 10¹⁴ | 0.99 |
| 0.15          | 161.92       | 1.17 × 10¹⁸ | 0.99 | 165.96       | 1.53 × 10¹⁵ | 0.99 |
| 0.20          | 175.14       | 1.07 × 10¹⁹ | 0.99 | 179.71       | 1.27 × 10¹⁶ | 0.99 |
| 0.25          | 179.64       | 1.03 × 10¹⁹ | 0.99 | 183.33       | 1.56 × 10¹⁶ | 0.99 |
| 0.30          | 180.17       | 5.99 × 10¹⁸ | 0.99 | 184.79       | 8.98 × 10¹⁵ | 0.99 |
| 0.35          | 178.22       | 2.30 × 10¹⁸ | 0.99 | 182.65       | 3.31 × 10¹⁵ | 0.99 |
| 0.40          | 175.24       | 7.75 × 10¹⁷ | 0.99 | 179.43       | 1.05 × 10¹⁵ | 0.99 |
| 0.45          | 172.20       | 2.77 × 10¹⁷ | 0.99 | 176.31       | 3.78 × 10¹⁴ | 0.99 |
| 0.50          | 171.56       | 1.70 × 10¹⁷ | 0.99 | 176.15       | 4.18 × 10¹⁴ | 0.99 |
| 0.55          | 167.78       | 5.53 × 10¹⁶ | 0.99 | 171.37       | 6.62 × 10¹³ | 0.99 |
| 0.60          | 153.65       | 1.87 × 10¹⁵ | 0.99 | 156.37       | 1.83 × 10¹² | 0.99 |
| 0.65          | 139.32       | 4.92 × 10¹⁴ | 0.99 | 141.11       | 3.79 × 10¹⁰ | 0.99 |
| 0.70          | 130.47       | 4.29 × 10¹² | 1   | 131.58       | 2.78 × 10⁹  | 1   |
| Average       | 157.08       | 2.95 × 10¹⁹ | 1   | 160.54       | 4.41 × 10¹⁶ | 1   |
| Kissinger     | 137          | 2.46 × 10⁸  | 0.97 |
TABLE 5  Kinetic parameters of thermal decomposition of the raw pine needles

| Conversion (α) | FWO          | KAS          |
|----------------|--------------|--------------|
|                | Eₐ (kJ · mol⁻¹) | A (min⁻¹) | R² | Eₐ (kJ · mol⁻¹) | A (min⁻¹) | R² |
| 0.05           | 74           | 2.92 × 10⁻¹² | 1.00 | 74.98         | 1.18 × 10⁰  | 1.00 |
| 0.10           | 149.67       | 1.53 × 10⁻¹⁴ | 0.98 | 153.48        | 1.90 × 10⁰⁵ | 0.98 |
| 0.15           | 152.58       | 3.44 × 10⁻¹⁷ | 0.99 | 156.26        | 4.13 × 10⁰⁴ | 0.99 |
| 0.20           | 162.58       | 1.05 × 10⁻¹⁴ | 0.99 | 166.59        | 1.37 × 10⁰⁵ | 0.99 |
| 0.25           | 173.72       | 5.27 × 10⁻¹⁸ | 0.99 | 178.18        | 7.64 × 10⁰⁵ | 0.99 |
| 0.30           | 176.07       | 4.15 × 10⁻¹⁸ | 0.99 | 180.05        | 6.01 × 10⁰⁵ | 0.99 |
| 0.35           | 174.13       | 1.47 × 10⁻¹⁸ | 0.99 | 178.40        | 2.05 × 10⁰⁵ | 0.99 |
| 0.40           | 172.50       | 6.33 × 10⁻¹⁷ | 0.99 | 176.60        | 8.49 × 10⁰⁴ | 0.99 |
| 0.45           | 170.36       | 2.60 × 10⁻¹⁷ | 0.99 | 174.26        | 3.34 × 10⁰⁴ | 0.99 |
| 0.50           | 170.00       | 1.59 × 10⁻¹⁷ | 0.99 | 173.72        | 2.01 × 10⁰⁴ | 0.99 |
| 0.55           | 170.20       | 9.79 × 10⁻¹⁶ | 0.99 | 174.94        | 1.40 × 10⁰⁴ | 0.99 |
| 0.60           | 161.03       | 1.02 × 10⁻¹⁶ | 1.00 | 164.19        | 1.11 × 10⁰³ | 1.00 |
| 0.65           | 138.89       | 5.86 × 10⁻¹⁵ | 1.00 | 140.70        | 4.52 × 10⁰⁰ | 1.00 |
| 0.70           | 124.16       | 1.72 × 10⁻¹² | 1.00 | 125.78        | 1.23 × 10⁰⁹ | 1.00 |
| Average        | 155          | 1.49 × 10⁻⁸   | 1.00 | 158.43        | 2.09 × 10⁰⁶ | 1.00 |
| Kissinger      | 127.66       | 4.21 × 10⁻⁷   | 1.00 |
activation energies and ratios of the rate of reactions of both material will be affected by the relative thermal deviation between the pre-treated biomass and its parent form if the frequency factors are assumed to be constant. In other words, the ratio is independent of activation energy of the reactions. It could be concluded that the response of thermally pre-treated biomass at given range of temperature affects the rate of reaction of thermal decomposition of the pre-treated biomass at inflexion points in the TG curves or at the vicinity of these points. A similar trend of deviation in the activation energies has been observed for both the FWO and KAS methods, however, the relative magnitude differs (Figure 7). The variation in the activation energy with respect to the extent of conversion ($\alpha$) is illustrated in Figure 8. It is clear from the plot that the variation of the activation energy is higher in the raw material than thermally processed pine needles. On the other hand, a uniform rise in the activation energy of the pre-treated pine needles samples has been observed. The reason for the shift in the characteristic peaks in DTG plot is the variation in physical and thermal properties of the material, which also leads to the abrupt change in the chemical kinetics of the material. The variation in the bulk density due to the thermal degradation leads to the sudden change in the apparent activation energies and the heat of reaction.

In an experiment on a wood dowel, the activation energy of the wood increases by 21.6% due to structural breakdown,\(^{54}\) which is quite reasonable assertion of increasing activation energy of the torrefied pine needles during pyrolysis. Another study claims that the overall kinetics of pyrolysis is determined by the reactivity of cellulose where it is necessary to include the influence of autocatalytic reactions on the kinetic parameters at lower temperature range, however, the secondary reactions (autocatalytic) have no crucial role in the kinetics analysis at higher temperature regime. During the thermal decomposition of the pure form of cellulose and lignin, it has been found that the autocatalysis of the secondary pyrolysis by the products of the primary stages might cause the frequency factor $A$ to be increased up to 12 times. It has been assumed that the autocatalytic reactions have a negligible influence on $E$.\(^{49}\) The residence
time of volatile in the solid matrix decreases with the increase in the temperature and thus, the reaction rate increases less rapidly as it does in the presence of these reactions. Due to the thermal immunity, the light volatile products (CO, CO₂, fixed gases, ester, ketones, organic acids, aldehydes, and free radicals) are unable to inhibit cross-linking and repolymerization reactions in a cellulose matrix, which eventually, increases the char formation.

The shifting of the curves towards higher temperature regimes in the TG and DTG curves with the increasing heating rate is due to the drawback of heat transfer from the furnace to the sample. A longer time is needed to allow the inert gas to meet a steady state with the temperature of the furnace of the sample, which is not efficiently performed owing to a shorter reaction time at higher thermal history and hence the high temperature required to obtain the same mass conversion.

4 | CONCLUSIONS

From the preliminary physical and chemical analysis, it has been found that a mass loss of 7.5% occurs during the torrefaction, whereas energy gain in terms of calorific value is 10%. The energy density of torrefied pine needles is also increased to 4.210 GJ·m⁻³. During the torrefaction of pine needles, the cellulose and hemicellulose fractions are reduced by 11.56% and 29.37% respectively, whereas the AIL is increased by 13.61%. Thermal immunity and increasing lignin caused the overall apparent activation energy of torrefied pine needles to be raised by a margin of 1.34%. The structural breakdown during the pre-treatment process can also influence the kinetics of thermal decomposition of torrefied pine needles. The temperature range during the dehydration process varies from 321.9 K-367.2 K for the pre-treated pine needles, whereas for the raw pine needles it is 321.5 K-381.9 K. The temperature scale during the devolatilization is increased by 1.79%-1.99%. A marginal dilation in the temperature range of the thermally processed pine needles was seen during the char formation. The rearrangement of the pyrolysis phases is caused by the structural change in the raw pine needles during the thermal pre-treatment process. Thermal immunity and mechanical transformation in the torrefied pine needles are the attributes of promotion of carbonization and cross-linking during the torrefaction process.

The rate of decomposition in the raw pine needles was found to be 7.58%-11.76% lower than that of the torrefied pine needles. From the DTG analysis, the rate of mass loss during dehydration phase was observed at 327.3-346.9 K, whereas the decomposition of cellulose was found to occur in the temperature range of 596.4-616.2 K. The activation energy obtained from the FWO and KAS methods for the torrefied pine needles was 157.08 and 160.54 kJ·mol⁻¹, respectively, whereas the value of activation energy estimated from FWO and KAS for the raw pine needles was 155 and 158.43 kJ·mol⁻¹, respectively. Alternatively, the value of the activation energy computed from the Kissinger method for the torrefied pine needles was 137 kJ·mol⁻¹; whereas it was 127.6 kJ·mol⁻¹ for the raw pine needles.

The relative variation of the activation energy of the torrefied pine needles from the activation energy of the raw pine needles is in range of −0.066 to 0.0773 kJ·mol⁻¹ for the FWO method. In a similar manner, the relative deviation of the activation energy varies from −0.0707 to 0.0788 kJ·mol⁻¹ for the KAS scheme. It has been found through this comparative analysis of pine needles and their processed form that the char production in a pyrolysis reactor can be enhanced without much disturbing the reactivities of major constituents of pine needles. The rate of devolatilization is affected by the primary char formation during thermal decomposition of processed biomass (Figures 5 and 6). As the moisture content is almost absent in the processed pine needles, the condensation of volatile at the cracking would be relatively low, and thus it could reduce the overall tar production. As the moisture content influences the solid-temperature history due to endothermic evaporation and affects the intraparticle energy balance, therefore thermogravimetric behaviour of processed pine needles has been examined to determine the drift in the reaction pathway.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

Alok Dhaundiyal: Conceptualization, analysis, writing, validation, supervision, data collection, reviewing, and editing. Gabor Bercesi: Electrical assistance. Istvan Bacskai: Lab assistance.

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[51] E. J. Kansa, H. E. Perlee, H. E, R. F. Chaiken, *Combust. Flame* 1977, 29(C), 311. https://doi.org/10.1016/0010-2180(77)90121-3.

[52] L. Gašparovič, J. Labovský, J. Markoš, L. Jelemenský, *Chem. Biochem. Eng. Q.* 2012, 26(1), 45.

[53] C. Di Blasi, *Fuel* 1997, 76(10), 957. https://doi.org/10.1016/S0016-2361(97)00096-3.

[54] E. R. Tinney, *Symp. (Int.) Combust.* 1965, 10(1), 925. https://doi.org/10.1016/S0082-0784(65)80235-1.

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