



Article

Assessment of Co-Pyrolysis of a Cyanobacterium and Waste Textile Polymer: Investigating Kinetics, Thermodynamics, Reaction Mechanism and Synergism

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Abstract

Algal cultivation has attracted significant attention due to CO₂ biocapture and potential for biofuel generation. Enormous generation of waste polymer often poses an environmental problem due to non-biodegradability. This study comprehensively analyses the thermal degradation characteristics of blue-green alga, *Leptolyngbya subtilis* JUCHE1 (LS) and waste textile polyester (WTP) and their mixtures (LS1P3 (1:3); LS1P1 (1:1); LS3P1 (3:1)) during co-pyrolysis. The interaction between LS and WTP during co-pyrolysis has been assessed through the verification of synergism using different blending ratio and through the comparison of the corresponding values of the Comprehensive Pyrolysis Index (CPI). The composite, LS1P3, exhibited the highest synergism and the maximum value of CPI. Isoconversional models (FWO, Starink, Bosewell and Tang) have been used to predict the activation energies (E_a). Thermodynamic parameters, namely, heat of reaction (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS), have also been determined for all. The average value of E_a for LS1P3 is also the lowest (96.015 kJ/mol) among all composites. The Master plot method identifies that there is a shift of reaction mechanism from phase boundary type (R2 and R3) for LS and WTP to a P2-type acceleratory reaction rate mechanism for LS1P3. The lowest average value of ΔH and the highest values of ΔG and ΔS for LS1P3 co-pyrolysis also support the least consumption of energy and the highest favorability under present conditions. The product yield distribution of co-pyrolysis in the isothermally operated conditions (450 °C) also establishes the superiority of LS1P3. Yields of pyro-oil and pyro-gas are the highest among all composites. The study ensures the future application prospects of co-pyrolysis of LS and WTP as a means for generation of energy resources (pyro-oil and pyro-gas) and chemicals (pyro-char).

Keywords: algae; textile waste; thermogravimetric analysis; co-pyrolysis; kinetic analysis; thermodynamics; reaction mechanism; product yields of co-pyrolysis

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1. Introduction

Valorization can be described as the process for maintaining or enhancing the value of a resource. The rapid advancement of industrialization and globalization has led to unprecedented economic growth and technological progress during the 19th and 20th

century. It has also significantly burdened the environment and strained the available resources, resulting in the advent of valorization of carbonaceous materials, generated as wastes or byproducts of anthropological activities, as a strategy for aligning with the United Nation's Sustainable Development Goals (UN-SDGs). Primary environmental concerns include climate change, energy scarcity, resource depletion, pollution due to increasing population and associated waste generation [1,2]. The increasing demands for affordable clothing for the growing population has resulted in textile industries adapting polyester-based fabrics. Though such materials make clothing affordable, it should be kept in mind that such materials exhibit poor recyclability [3–5]. While the advent of polyester-based textile has made fashion and clothing affordable, it has also brought into focus the issue of the disposal of such textile materials after use [6]. Due to poor recyclability, these materials end up filling landfills that raise some serious issues in the context of waste management. Polyester-based textiles are synthetic fibers derived from petroleum [7]. They resist natural decomposition and complete breakdown takes over centuries in landfills. Furthermore, commercial garments have polyester blended with other fibers that makes textile-to-textile recycling economically unfeasible. Therefore, in landfills, these fibers become a major source of microplastic pollution contaminating ground and water due to leaching [8].

On the other hand, in many countries, coal-based thermal power plants are indispensable to meet the energy demand [9–11]. Thermal plant waste (like coal ash) and nuclear power plants create favorable habitats for cyanobacteria and algae. The growth of these organisms poses a critical challenge, particularly by fouling the heat transfer surface in cooling systems of power plants [12–14]. Interestingly, algae were recognized as third-generation feedstock for biofuel generation which can accelerate the energy transition [15–17]. They are also sources of a variety of important secondary metabolites. In the present scenario, the power plant algae are merely considered as waste without any valorization. In recent times, a few pioneering research studies have been reported on co-pyrolysis of algae with polymeric wastes [18,19]. There is evidence of beneficial interaction between these feedstocks during co-pyrolysis [20]. In-depth kinetic and thermodynamic analyses, essential for the scale-up of such co-pyrolytic units, have also been reported for a few combinations of algal strains and polymer wastes. Although a few reports are available on co-pyrolysis of different polymeric wastes and algae, there is dearth of information on the co-pyrolysis using polymeric textile wastes and algae [20–22].

The present study focuses on the co-pyrolysis of a cyanobacterium isolated from thermal power plant cooling towers and polyester waste from the textile industry. In this context, thermal decomposition characteristics of individual materials as well as their composites are assessed using thermogravimetric analysis (TGA). Based on thermal decomposition data, model-free kinetics and thermodynamic parameters were determined. The synergistic correlation between the cyanobacterial biomass and waste textile polymer during the co-pyrolysis of their mixtures is assessed. The underlying reaction mechanisms of pyrolysis of LS and WTP and co-pyrolysis of LS-WTP mixtures are determined. The effect of the mixing ratio of cyanobacterial biomass and waste textile polyester (WTP) on the product array is determined by conducting lab-scale pyrolysis and co-pyrolysis studies in a semi-batch reactor. This study is a novel undertaking as limited literature exists on co-pyrolysis of algal biomass and textile wastes, even less for algae and polyester-based textile waste. The findings presented in this paper will provide insights into the co-pyrolysis of a mixture of a blue-green algae and waste textile polymer. The kinetic and thermodynamic data, supported by the assessment of synergism and a reaction mechanism, will facilitate a large-scale reactor design and the selection of the proper blending ratio of algal biomass and textile wastes.

2. Materials and Methods

2.1. Algal Strain and Textile Waste

The algal strain, *Leptolyngbya subtilis* JUCHE1 (LS), was previously isolated from Sagardighi (India) thermal power plant cooling towers and maintained in M18 medium [23]. For the experiment, the strain was cultured in M18 medium for 21 days at 37 °C. Light requirements were met by providing continuous illumination maintained at 2.5 kLux. At the end of the run, the biomass was harvested, washed and dried overnight at 60 °C. The dried LS biomass was ground into fine powder-like consistency for the upcoming experiments. Simultaneously, waste textile polyester was sourced from a local tailoring shop at Jadavpur, Kolkata, India. It was used without any pretreatment apart from shredding into bits of 2 mm × 5 mm size followed by drying in an oven set at 60 °C for an overnight time period.

2.2. Sample Characterization

Elemental analysis of the individual components was carried out using CHNS analyzer (Elementar, Langenselbold, Germany) and the results are provided in Table 1. Oxygen content of the samples was calculated by difference.

Table 1. CHNS analysis of LS and WTP.

	LS	WTP
C	57.74	64.57
H	14.06	4.6
N	12.37	1.54
S	0.937	0.85
O	14.893	28.44

2.3. Thermogravimetric Experiments

For the thermogravimetric (TG) experiments, feed samples were prepared with the following weight compositions and codes: 100% LS (LS), 100% WTP (WTP), 25% LS + 75% WTP (LS1P3), 75% LS + 25% WTP (LS3P1) and 50% LS + 50% WTP (LS1P1). Thermogravimetric analysis was conducted using the Simultaneous Thermal Analyzer STA 6000 (Perkin Elmer, Waltham, MA, USA). Approximately 4 ± 0.2 mg of dried biomass was placed in a ceramic crucible and subjected to a heating program from 35 °C to 850 °C at linear heating rates (β) of 20, 30, 40 and 50 °C/min under a continuous nitrogen flow of 2 mL/min to maintain inert conditions. The TGA experiments were conducted in triplicate. The statistical analysis of the TG (m% versus temperature) and DTG (time derivative of m% versus temperature) data was carried out. TG and DTG plots have been generated after assessment of the reliability of the data using Origin Pro (2024).

2.4. Experiments in Pyrolyser

The experimental runs were conducted in a vertical quartz tube pyrolyser, as described in a previous article [24]. The individual feedstocks, i.e., LS and WTP along with the different composites (LS1P1, LS1P3 and LS3P1), 2 g each, were pyrolysed for 45 min under isothermal conditions at 450 °C. The operating temperature was selected on the basis of introspection of the decomposition behavior of LS and WTP during thermogravimetric analysis, as detailed in Section 3.1. An inert atmosphere was created by the flowing nitrogen gas. The volatile products, generated during pyrolysis, were passed through a separation train and the condensed volatiles, i.e., the pyro-oil was collected. The weight of pyro-gas and pyro-char were determined using the standard protocol, explained in

previous publications [25]. The pyrolysis experiments were conducted in triplicate. The mean and standard deviations were calculated.

The yield, $Y_{k,j}$, of any product, k , from any material j has been calculated as follows:

$$Y_{k,j}(\%) = \frac{\text{Mass of any product, } k \text{ from any feed material, } j}{\text{Mass of any feed material, } j (= \text{LS or WTP or LS - WTP composites})} \times 100 \quad (1)$$

where k = gas, oil or char and j = LS or WTP for pyrolysis and LS-WTP composites for co pyrolysis.

2.5. Comprehensive Pyrolysis Index

The Comprehensive Pyrolysis Index (CPI) reflects the intensity of pyrolysis for any material based on the TG and DTG data. The CPI can be defined as follows [26]:

$$CPI_j = \frac{\left(\frac{dm\%}{dt}\right)_{in,j} \left(\frac{dm\%}{dt}\right)_{mean,j} (1 - (f)_{t \rightarrow \infty,j})}{T_{in,j} T_{m,j} (\Delta T)_{1/2,j}} \quad (2)$$

where

$\left(\frac{dm\%}{dt}\right)_{in,j}$ = Initial decomposition rate (%/min) for any material, j

$\left(\frac{dm\%}{dt}\right)_{mean,j}$ = Mean decomposition rate (%/min) for any material, j

$(f)_{t \rightarrow \infty,j}$ = Dimensionless fractional residue remaining after the TGA experiment = $(m\%)(t \rightarrow \infty)/100$ for any material, j

$T_{in,j}$ = Initial pyrolysis temperature for any material, j (°C)

$T_{m,j}$ = Temperature corresponding to the highest peak (°C) for any material, j

$(\Delta T)_{1/2,j}$ = The temperature ranges corresponding to half the maximum decomposition rate (°C) for any material, j

j = LS or WTP for pyrolysis and LS – WTP composites for co – pyrolysis

The unit of CPI is $(\%m)^2/\text{min}^2 \text{ } ^\circ\text{C}^3$.

2.6. Synergism

Based on the analysis of TGA and DTG plots, the interactive correlation of feedstocks can be adjudged. One way of carrying this out is by the comparison of the TGA mass loss data of mixtures with the value predicted by the linear model. Following the linear model, i.e., non-interacting behavior of pyrolysis, the residual mass ($m\%$) and decomposition rate, $\frac{dm\%}{dt}$ of a mixture, i.e., $(TG)_{\text{mixModel}}$ and $(DTG)_{\text{mixModel}}$ at any temperature, T , during TGA can be determined by the weighted average. For any mixture, j , the equation is as follows [27]:

$$(TG(T))_{\text{mixModel},j} = \sum_i w_{i,j} \times (m\%(T))_{i,j} \quad (3)$$

$$(DTG(T))_{\text{mixModel},j} = \sum_i w_{i,j} \times \left(\frac{dm\%}{dt}(T)\right)_{i,j} \quad (4)$$

where $w_{i,j}$ = weight fraction of i th pyrolysing material (LS or WTP) in the mixture, j
 $(m\%(T))_{i,j}$ = $m\%$ data of i th pyrolysing material in the mixture, j at any temperature, T
 $\left(\frac{dm\%}{dt}(T)\right)_{i,j}$ = $\frac{dm\%}{dt}$ of i th pyrolysing material in the mixture, j at any temperature, T .

$\Delta TG(T)_j$ i.e., the difference of experimental $((m\%_{\text{mix}}(T))_{\text{mixExp},j})$ and model-predicted $((m\%_{\text{mix}}(T))_{\text{mixModel},j})$ values of mass (%) for mixture, j at any temperature, T during co-pyrolysis is calculated as follows:

$$\Delta TG(T)_j = (m\%_{\text{mix}}(T))_{\text{mixExp},j} - (m\%_{\text{mix}}(T))_{\text{mixModel},j} \quad (5)$$

For the overall assessment of synergism in case of any LS-WTP composite, j , values of $\Delta TG(T)_j$ have been plotted against the entire range of pyrolysis temperature for LS-WTP composites in figures discussed in Section 3.

According to the linear model, DTG for any mixture, j can be calculated at any temperature (T) as follows:

$$\left(\frac{dm\%}{dt}(T)\right)_{\text{mix}_{\text{Model}}} = \sum_i w_{i,j} \left(\frac{dm\%}{dt}(T)\right)_{i,j} \quad (6)$$

Similar to $\Delta TG(T)_j$, the values of $\Delta DTG(T)_j$ for any mixture, j can be calculated at any temperature (T) as follows:

$$\Delta DTG(T)_j = \left(\frac{dm\%}{dt}(T)\right)_{\text{mix}_{\text{Exp},j}} - \left(\frac{dm\%}{dt}(T)\right)_{\text{mix}_{\text{Model},j}} \quad (7)$$

As values of $\frac{dm\%}{dt}$ are inherently negative, for DTG plots, $-\frac{dm\%}{dt}$ have been plotted against temperature. The synergistic and antagonistic interactions for any mixture, j can be established by the negativity and positivity of $\Delta TG(T)_j$ respectively. Similarly, the negativity and positivity of $\Delta DTG(T)_j$ respectively, represent synergism and antagonism in any mixture, j . The units of ΔTG and ΔDTG are $m\%$ and $m\%/min$.

2.7. Model-Free Kinetic Analysis

LS and WTP and their mixtures are complex feedstocks. These are constituted of different components like carbohydrates, lipids and proteins due to the presence of the biomass and monomers from the textile polymer. The thermal decomposition involves a network of reactions instead of a single reaction. Therefore, single-step order-based models, assuming a constant mechanism throughout pyrolysis cannot represent the process properly. According to the literature review, model-free isoconversional distributed activation energy models (DAEM), considering activation energy (E_a) as a function of the degree of conversion (α), are more appropriate [28]. Accordingly, the following equations (Equations (8) and (9)) are applicable for pyrolysis and co-pyrolysis of any material, j , i.e., for LS or WP and for LS-WP mixtures, respectively. However, in these equations, the suffix, j , as used in Equations (1)–(7), is dropped to avoid unnecessary complications.

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = k(T)f(\alpha) = Ae^{\left(\frac{-E_a}{RT}\right)}f(\alpha) \quad (8)$$

where $\alpha = \frac{m_0 - m(t)}{m_0 - m_f}$ considering m_0 , m_f and $m(t)$ to be the mass of sample at start, end and at any time (t) during the TG experiment, respectively. If $\beta = \frac{dT}{dt}$, Equation (8) can be written as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)}f(\alpha) \quad (9)$$

$$\int_0^1 \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\left(\frac{-E_a}{RT}\right)}dT = g(\alpha) \quad (10)$$

$$\text{If } e^{\left(\frac{-E_a}{RT}\right)} = x,$$

$$g(\alpha) = \frac{AE_a}{R\beta} \int_0^\infty x^{-2} e^{-x} dx = \left(\frac{AE_a}{\beta R}\right)p(x) \quad (11)$$

Since the exact analytical solution to determine $p(x)$ is almost impossible, different mathematical approximations are used [29]. Some integral methods, namely the Flynn–Wall–Ozawa (FWO) Method, Tang Method, Boswell Method and Starink Method, as represented in Table 2, have been attempted under the present study. As represented in Table 2, appropriate ordinates have been plotted against $\frac{1}{T}$ at a constant value of α for different methods using TGA data. The values of activation energy, E_a , have been estimated from the slope of each plot generated using all models in the range of α varying from 0.1 to 1.0.

The plot using the FWO model is presented in Section 3. The similar plots for other isoconversational models are provided in the Supplementary Material (Figure S6). For each method, the average E_a has been calculated by taking the average of all values over the entire range of α , as presented in Section 3 and Table S8.

Table 2. Model-free isoconversational methods.

Method	Temperature Integral Function	Plot	References
FWO	$\ln(\beta) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{RT}$	$\ln(\beta)$ against $\frac{1}{T}$	[29]
Tang	$\ln\left(\frac{\beta}{T^{1.894661}}\right) = -1.052 \frac{E_a}{RT} + \ln\left(\frac{AR}{E_a g(\alpha)}\right)$	$\ln\left(\frac{\beta}{T^{1.894661}}\right)$ against $\frac{1}{T}$	[28]
Boswell	$\ln\left(\frac{\beta}{T}\right) = C - \frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T}\right)$ against $\frac{1}{T}$	[30]
Starink	$\ln\left(\frac{\beta}{T^{1.92}}\right) = C - 1.0008 \frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T^{1.92}}\right)$ against $\frac{1}{T}$	[31]

2.8. Master Plot Method

There are multiple approaches to the Master plot method, based on different forms of kinetic equations like differential ($f(\alpha)$ method), integral ($g(\alpha)$ method) or a combination of two forms ($z(\alpha)$ method) [32,33]. Under this study, isoconversational integral methods, described in Section 2.7, were used to determine E_a as a function of conversion. For the Master plot method, the normalized values of $g(\alpha)$, defined in Equation (11), have been calculated for standard kinetic mechanisms by taking the ratio of $g(\alpha)$ to $g(\alpha = 0.5)$. The normalization has been carried out with respect to the value of $g(\alpha)$ at $\alpha = 0.5$ because $g(\alpha = 0.5)$ is constant for any particular kinetic mechanism. Applying Equation (11), the normalization can be carried out as follows:

$$\frac{g(\alpha)}{g(0.5)} = \frac{\int_{T_0}^T e^{\left(\frac{-E_a}{RT}\right)} dT}{\int_{T_0}^{T_{0.5}} e^{\left(\frac{-E_a}{RT}\right)} dT} \quad (12)$$

It is obvious that Equation (12) is applicable for the pyrolysis and co-pyrolysis of any material, j , i.e., for LS or WP and for LS–WP mixtures, respectively. Unlike in Equations (1)–(7), the suffix, j , is dropped to avoid unnecessary complications.

The reaction mechanism has been searched by using fifteen standard forms, three under power law model (P2, P3, P4); three under the chemical reaction model (F1, F2, F3); four under the diffusion-controlled model (D1, D2, D3, D4), two under the phase boundary model (R2, R3) and three under the Avrami–Erofeev-type nucleation and growth model (A2, A3, A4). From the standard correlations of $g(\alpha)$ with α for each reaction mechanism, as represented in Table S1, the values of LHS of Equation (12) have been determined at different conversions (α) for each kinetic mechanism, attempted under the present study [34–38]. The evaluation of RHS is carried out through numerical integration using the values of activation energy obtained through different isoconversion models (FWO, Tang, Boswell, Starink) at each conversion. On the RHS, the upper limit, T , of integration in the numerator, signifies the temperature at any value of α . The upper limit, $T_{0.5}$, of integration in the denominator signifies the temperature corresponding to $\alpha = 0.5$. Both the numerator and the denominator have been evaluated through numerical integration using the Trapezoidal rule with the aid of function `trapz` in MATLAB R2025a. The evaluation of statistical deviations has been carried out using the MATLAB R2025a program for Root Mean Square Error (RMSE), defined as follows:

$$RMSE = \sqrt{\frac{1}{M} \sum_{i=1}^M (\hat{y}_i - y_{exp,i})^2} \quad (13)$$

where M is the total number of data, $y_{\text{exp},i}$ is any experimental value or the value, calculated based on experimental data; $\hat{y}_i$ is the corresponding model-predicted value.

2.9. Statistical Analysis of Data

The reliability of experimental data is measured by the spread of replicate observations and the uncertainty in mean values of replicate observations. The standard deviation of replicate observations and the standard error in their mean values have been determined for this purpose [39]. The lower the values of SD and SEM, the more reliable the data are.

2.9.1. Standard Deviation

$$\text{Standard Deviation (SD)} = \sqrt{\frac{\sum_{i=1}^{i=N} (y_i - \bar{y})^2}{(N - 1)}} \quad (14)$$

where $\bar{y}$ is the mean of any number of observations, y_i , and can be calculated as follows:

$$\bar{y} = \frac{\sum_{i=1}^{i=N} y_i}{N} \quad (15)$$

N is the total number of observations.

2.9.2. Standard Error of Mean

$$\text{Standard Error of Mean (SEM)} = \frac{\text{SD}}{\sqrt{N}} \quad (16)$$

For the TGA data, the maximum, minimum and median of the values of SDs and SEMs over the entire TGA temperature range (35 °C to 850 °C) for LS, WTP and their composites have been calculated at each heating rate. The built-in functions of Origin Pro have been used for the calculations of statistical parameters.

2.10. Determination of Thermodynamic Parameters

The thermodynamic parameters, namely, enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) have been evaluated using the values of activation energies, E_a , determined at different fractional conversion, α for different heating rates (20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min) applying all isoconversional models. The following equations have been used for the determination of ΔH , ΔG and ΔS for pyrolysis and co-pyrolysis of any material, j , i.e., for LS or WTP and for LS–WTP mixtures, respectively [40]:

$$\Delta H_j = E_{a,j} - RT_{\alpha,j} \quad (17)$$

$$\Delta G_j = E_{a,j} + RT_m \ln \left(\frac{k_B T_m}{hA} \right) \quad (18)$$

$$\Delta S_j = \frac{\Delta H_j - \Delta G_j}{T_m} \quad (19)$$

Where, T_m is the maximum degradation temperature in K, h is Planck's constant and k_B is Boltzmann's constant and j denotes LS or WTP and LS–WTP mixtures.

3. Result and Discussion

3.1. TGA and DTG Patterns

3.1.1. Statistics of TGA Data

Tables S2 and S3 provide the maximum, minimum and median of the values of SDs and SEMs of TG and DTG data from the triplicate observations of TGA over the entire temperature range (35 °C to 850 °C) for LS, WTP, LS1P1, LS1P3 and LS3P1 at each heating rate, β . The tables also include the number of data points, situated at an interval of 0.002 min, for the TGA runs at all heating rates. From the analysis of the tables, it is evident that the values of both SD and SEM of TG and DTG data are very low. The very low values of SD and SEM prove the reliability of measurement. Hence, the triplicate observations at each point are very close to each other over the entire range of TGA experiment at all heating rates. Hence, the mean values of triplicate observations reliably represent the thermal characteristics of each sample. Similar to a reported analysis of TGA data of the textile component, Figure 1 shows TG and DTG plots of all samples at the $\beta = 40$ °C/min with SD. Since the number of data points are very large, ranging from 19,560 to 7824 with the variation of β from 20 °C/min to 50 °C/min, the mean can reliably represent the thermal behavior of each sample. Hence, mean values have been used to generate the TG and DTG plots for all feed samples, namely, LS, WTP, LS1P1, LS1P3 and LS3P1 in Figures 2–4. In all further analysis and calculations using TG and DTG data, these TG and DTG plots have been used.

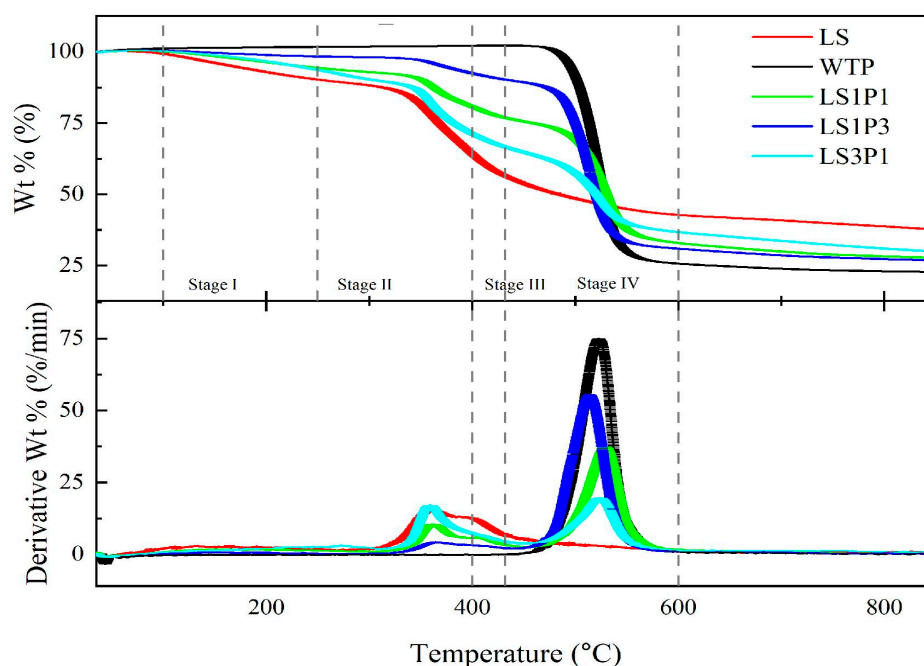


Figure 1. TG and DTG plots of LS, WTP, LS1P1, LS1P3 and LS3P1 at heating rates, $\beta = 40$ °C/min with standard deviation included.

3.1.2. Individual Feedstocks

The TG and DTG profile of LS in Figure 2 reveals that the biomass follows a four-stage mass loss pathway. Irrespective of heating rates, TG as well as DTG patterns of LS maintain similar characteristics. The initial phase occurs in the temperature range from 100 to ~250 °C. This signifies the initial loss of bound and unbound moisture in the sample [41]. The TG profile also indicates that this amounts to about ~12% mass loss in the sample due to moisture loss. In the second (250–400 °C) and third (400–470 °C) stages, the organic constituents like carbohydrates, lipids and proteins undergo thermal degradation and

produce volatiles. The combined second and third stages cumulatively result in ~50% of mass loss as seen in the figure. Lastly, the carbonization of biomass occurs beyond 470 °C. According to the reported literature, the thermal decomposition of all carbohydrates occurs in the second phase. The complex proteins and lipids are decomposed in the later phases [42,43]. Similarly, the literature review also sheds light on the carbonization of residual mass in the last stages of the reaction [44,45]. The protein disintegrates quicker under thermal stress in comparison to the lipids that are more complex and require higher temperatures to undergo degradation.

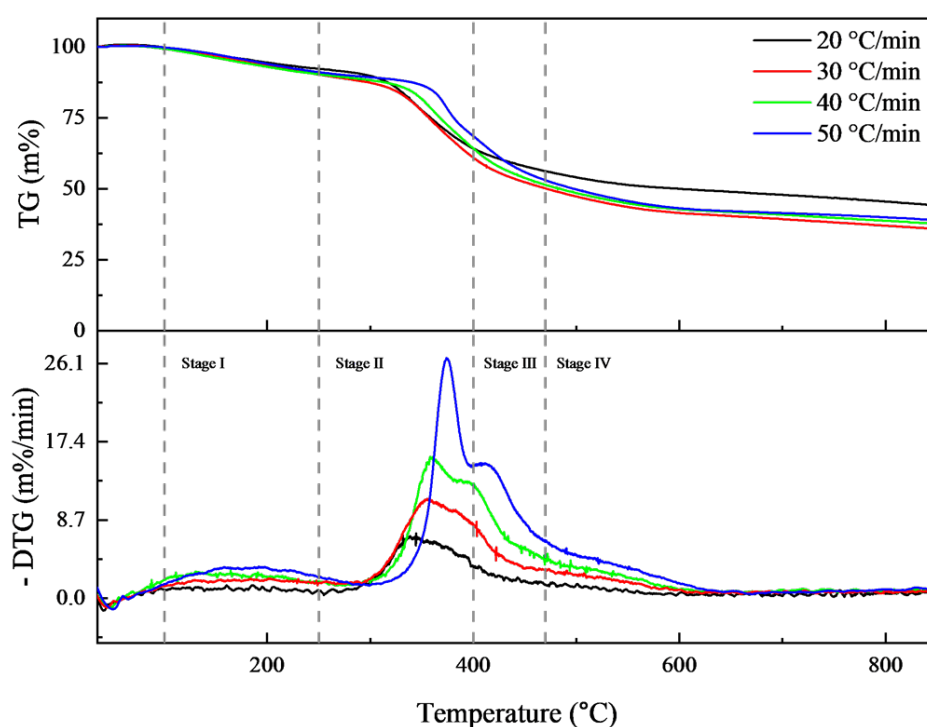


Figure 2. TGA-DTG profiles of LS at different heating rates, $\beta = 20$ °C/min to 50 °C/min.

Interestingly, as the heating rate increases, the degradation peaks become distinguishable and peak shoulders become observable. This signifies a thermal lag in decomposition with the enhancement of β . The lowering of residence time for devolatilization at each temperature might result in the thermal lag causing unequal heat transmission or low thermal conductivity within the sample. This also leads to a large temperature gradient across the reactor. This may result in a slower diffusion rate of volatiles delaying the decomposition of pyrolysing material [46,47]. With an increase in heating rate, the maximum degradation temperature (T_{max}) shifts from 338 °C at $\beta = 20$ °C/min to 375 °C at $\beta = 50$ °C/min. The overall shift towards higher temperatures at higher heating rates can be associated with thermal hysteresis. Very similar thermal behavior of different algal species has been observed by other researchers [48–53]. At the heating rate, $\beta = 20$ °C/min, the presence of higher residual mass after stage-II up to 850 °C has been observed. This can be due to the increase in residence time for the carbonization reaction of volatile products [45].

The TG and DTG profile of WTP in Figure 3 reveals that the material demonstrates a single-step sharp decomposition zone occurring in the temperature range of 450 to 545 °C. This can be justified by the uniformity of composition of polymer compounds, unlike algal biomass. In this step, the polymer chain scission occurs, which leads to the generation of volatiles and a mass loss of approximately 75%. The DTG plot also reveals that with the increase in β values, the maximum decomposition rate also increases. The increase in the

peak temperature from 504 °C to 544 °C, corresponding to the maximum decomposition rate with the increase in the value of β from 20 °C/min to 50 °C/min, is also observable, similar to that in the case of LS. A similar mass loss pattern for active pyrolysis of other polymeric and textile wastes has also been reported in the literature [54–56]. To demonstrate the similarity of the thermal behavior of LS and WTP with the literature data, the Supplementary Material provides two supportive tables (Tables S4 and S5).

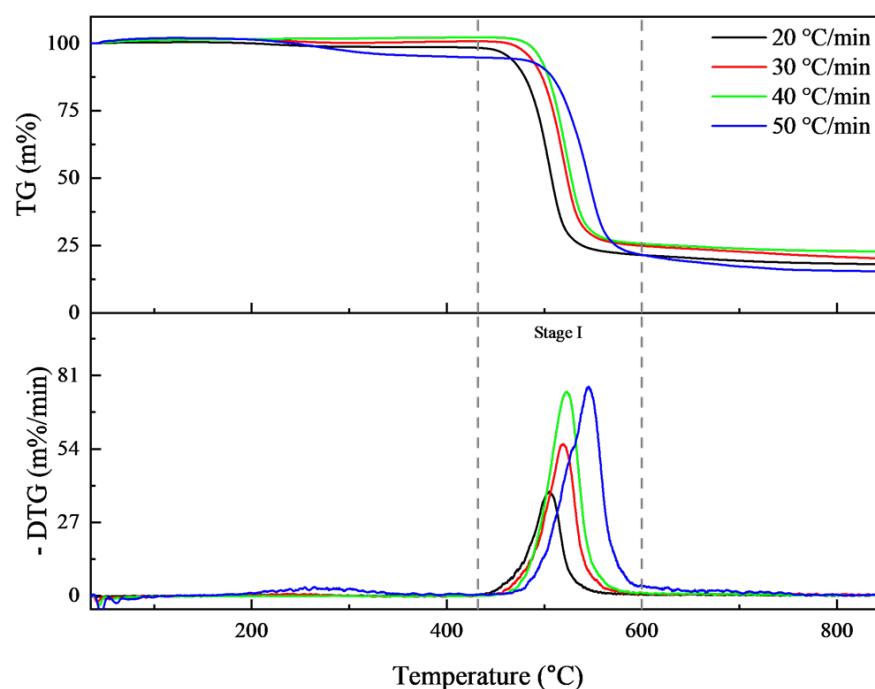


Figure 3. TGA-DTG profile of WTP at different heating rates, β = 20 °C/min to 50 °C/min.

3.1.3. Mixed Feedstock

Figure 4A–C represents the TGA and DTG plots for all the LS-WTP mixtures for samples labelled LS1P1, LS1P3 and LS3P1 at different heating rates. From the introspection of the figures, it is clear that at each value of β , the thermal decomposition profiles of the LS-WTP mixtures are very distinct compared to those of either LS or WTP. There exists a strong influence on thermal behavior of the composites based on the ratio between of their constituents (LS and WTP) in them. All the LS-WTP blends exhibit a four-stage mass loss. It is evident from the plots that LS corresponds to the first three major mass loss zones (100–470 °C), i.e., moisture loss and degradation of biomolecules. The DTG plot shows that the fourth zone (450–545 °C) comprises of a single-step decomposition that is similar to the pyrolysis characteristics of WTP. The last stage of LS degradation, i.e., residual carbonization, actually overlaps with the initiation of WTP decomposition, which may suggest an inhibitory phase where LS char covers the WTP surface causing uneven heat distribution and encapsulation leading to volatile release blockage, as evident from the SEM image of char samples of composites shown in Section 3.5. The effect of heating rate (β) on T_{max} and overall shifting of the reaction towards higher temperatures is similar to that in the case of individual feeds. The thermal fingerprints are distinct for each mixture. In the case of balanced (LS1P1) and high-polymer mixtures (LS1P3), the presence of polymer dominates the thermal behavior exhibited by the blends and thus, overshadow the four stages of algal decomposition. Meanwhile, the high algae composite (LS3P1) exhibits an evenly distributed thermal signature establishing the dominance of the LS behavior.

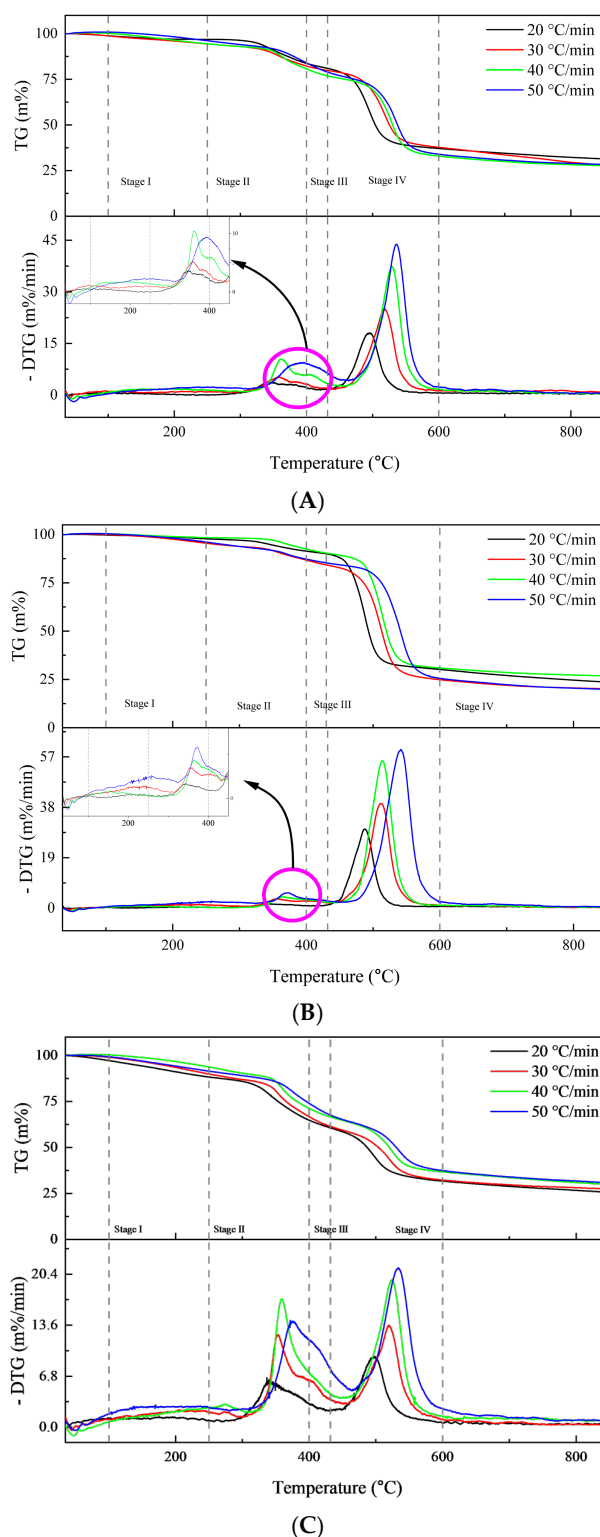


Figure 4. TGA-DTG profile of (A) LS1P1; (B) LS1P3 and (C) LS3P1 at different heating rates, $\beta = 20$ °C/min to 50 °C/min.

An interesting observation when comparing the TG and DTG profiles of the individual feedstocks and the blended mixtures at a fixed heating rate is that the overall thermal fingerprints of the blended mixtures exhibit decomposition peaks at the same temperature ranges as the individual components. While the blends did not have any significant temperature shift during the degradation of the LS component, LS1P3 showed a shift to lower temperature in comparison to LS1P1 and LS3P1. Simultaneously, increasing the ratio of

WTP added with LS led to a lower residual mass in comparison to only the LS sample but remained more than that obtained during thermal degradation of only the WTP sample. A comparative table between this study and other similar works is provided in the Supplementary Material (Table S6)

3.2. Patterns of Comprehensive Pyrolysis Index

The Comprehensive Pyrolysis Index (CPI) acts as a direct metric for feedstock quality, where a higher value indicates superior reactivity and ease of conversion. The pyrolysis parameters required for the calculation of CPI are derived from the DTG plots. To evaluate the synergism, the relevant parameters were obtained from the DTG diagram generated by plotting the simulated values of $\left(\frac{dm\%}{dt}(t)\right)_{mix}$ against pyrolysis temperature. The characteristic parameters, $\left(\frac{dm\%}{dt}\right)_i$, $\left(\frac{dm\%}{dt}\right)_{mean}$, $(f)_{t \rightarrow \infty}$, T_i , T_{max} , $\Delta T_{1/2}$, are represented (Table S7) in the Supplementary Material for all composites at all values of β . CPI has been evaluated for each sample using the triplicate TGA experimental data at each heating rate (20–50 °C/min). The mean values of CPI against heating rate are represented in a bar-plot in Figure 5.

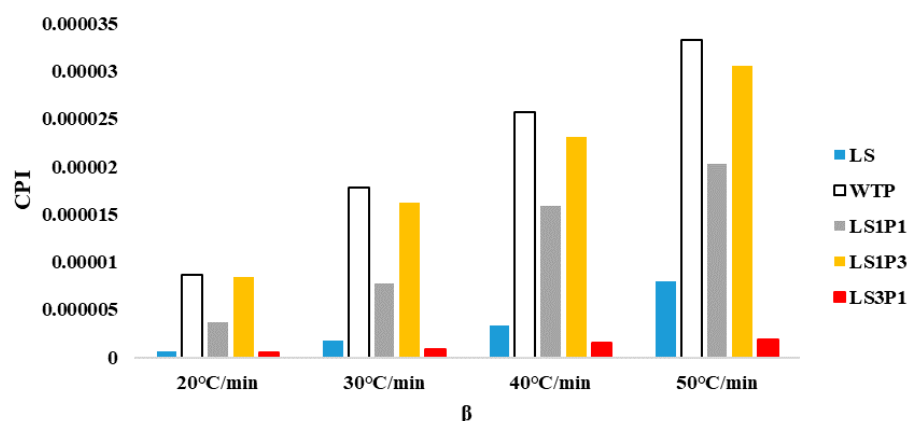


Figure 5. CPI values for LS, WTP, LS1P3, LS1P1 and LS3P1 at different heating rate, $\beta = 20$ °C/min to 50 °C/min.

From Figure 5, the CPI values are in the sequence $WTP > LS1P3 > LS1P1 > LS > LS3P1$ over the entire range of β . The highest value for the CPI index of WTP reflects a mechanism dominated by rapid radical chain scission, allowing for unhindered devolatilization essential for efficient bio-oil production [57]. Among the composites, LS1P3 has the highest values of CPI at all heating rates. Conversely, LS3P1 represents the poorest feedstock option. Its exceptionally low CPI signals a refractory material where the biomass component promotes excessive char formation rather than useful generation of gas through pyrolysis. The CPI values of LS1P1 are in between those of LS3P1 and LS1P3.

3.3. Assessment of Synergism

The inspection of the nature of $m\%_{mix}$ or ΔT_{Gmix} and $\Delta\left(\frac{dm\%}{dt}(t)\right)_{mix}$ or ΔDTG_{mix} clearly reveals the type of interaction between the LS and WTP in each mixture during their co-pyrolysis. The predictions of the additive model correspond to a non-interacting situation where the other influences neither the pyrolysis of LS nor that of WTP. The synergistic and antagonistic interactions can be established by the negativity and positivity of values of $\Delta m\%_{mix}$ and $\Delta\left(\frac{dm\%}{dt}\right)_{mix}$ with respect to the values of $m\%_{mix}$ and $\left(\frac{dm\%}{dt}\right)_{mix}$, predicted by the additive model.

In Figure 6A–D, the values of ΔTG_{mix} , as calculated according to Section 2.6, have been plotted against the temperature for all LS-WTP mixtures using $\beta = 20, 30, 40$ and $50\text{ }^{\circ}\text{C}/\text{min}$. The LS1P1 composite shows different interactive effects at different temperature zones. The pattern of interaction also varies with the value of β . At $\beta = 20\text{ }^{\circ}\text{C}/\text{min}$, an antagonistic effect, characterized by positive deviations, is observed in the temperature range $210\text{--}476\text{ }^{\circ}\text{C}$, i.e., almost entire pyrolysis zone of algal biomass and initial part of WTP degradation. At $\beta = 30\text{ }^{\circ}\text{C}/\text{min}$, the synergism, indicated by the negative deviations, has been observed only up $345\text{ }^{\circ}\text{C}$, beyond which antagonism is observed. For $\beta = 20\text{ }^{\circ}\text{C}/\text{min}$ and $50\text{ }^{\circ}\text{C}/\text{min}$, synergism is observed at $498\text{ }^{\circ}\text{C}$ and $543\text{ }^{\circ}\text{C}$, showing a positive effect of the pyrolysis product of algal mass on WTP degradation. At $\beta = 40\text{ }^{\circ}\text{C}/\text{min}$, an antagonistic effect is observed at $527\text{ }^{\circ}\text{C}$, which corresponds to the degradation peak of WTP. In the combined carbonization zone of algal mass and WTP, observed beyond the WTP degradation zone, antagonism has been indicated at all values of β except $40\text{ }^{\circ}\text{C}/\text{min}$. The presence of thermal antagonism can be a sign of thermal retardation due to char formation, radical scavenging interactions, chemical cross-linking reactions, limited mass and heat transfer [58–61]. The antagonism effectively begins with initiation biomass degradation at $300\text{ }^{\circ}\text{C}$, but under higher heating rates, this antagonism is suppressed which may be due to lesser residence time leading to lesser char formation. The LS3P1 composite moderately demonstrates a consistent, synergistic effect throughout the temperature range, as evident from a continuous negative deviation. The extent of synergism, however, decreases with the increase in heating rate, β . In contrast, the LS1P3 composite displays strong synergism, specifically, in the region of thermal degradation of WTP. Across all the heating rates, a sharp, deep negative peak between $500\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$ is observed. The values of ΔTG , i.e., those of $-15\text{ m\%}$ at $500\text{ }^{\circ}\text{C}$; $-12\text{ m\%}$; $-10\text{ m\%}$ and $-5\text{ m\%}$ at $550\text{ }^{\circ}\text{C}$, are observed for heating rates of $\beta = 20\text{ }^{\circ}\text{C}/\text{min}$, $\beta = 30\text{ }^{\circ}\text{C}/\text{min}$, $\beta = 40\text{ }^{\circ}\text{C}/\text{min}$ and $\beta = 50\text{ }^{\circ}\text{C}/\text{min}$, respectively. This indicates a rapid destabilization of WTP due to the presence of LS pyrolysis products that is much beyond the prediction of summative model prediction. The increase in the extent of synergism with the decrease in heating rate is due to the increase in residence time of decomposition.

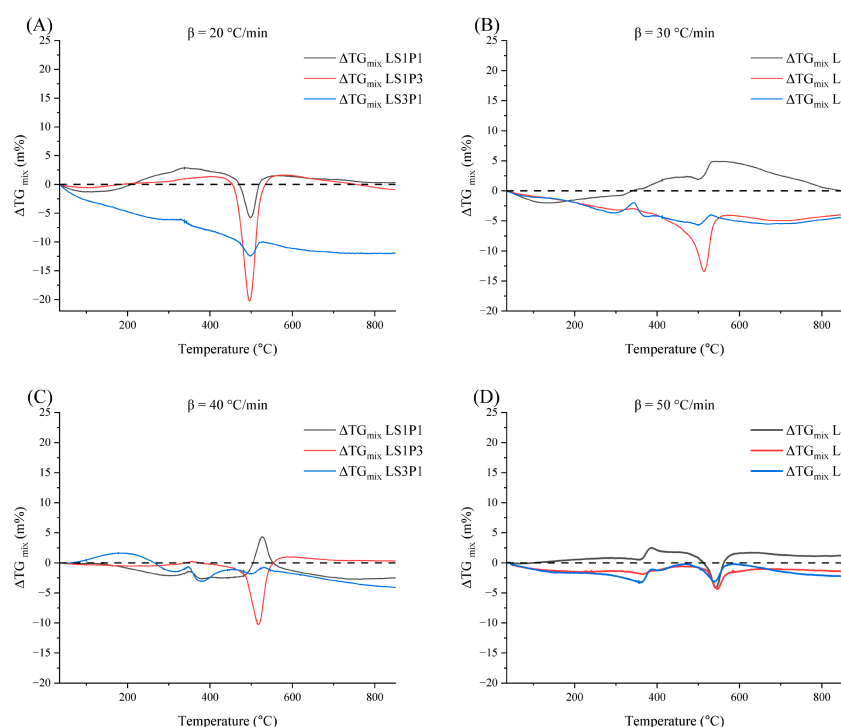


Figure 6. Analysis of the difference in thermogravimetric values of experimental data and predictions of the summative model for different composites at (A) $\beta = 20^\circ\text{C}/\text{min}$ (B) $\beta = 30^\circ\text{C}/\text{min}$ (C) $\beta = 30^\circ\text{C}/\text{min}$ (D) $\beta = 20^\circ\text{C}/\text{min}$.

The temperature trajectories ΔDTG , as plotted in Figure 7A–D for different composites corresponding to $\beta = 20^\circ\text{C}/\text{min}$, $30^\circ\text{C}/\text{min}$, $40^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$, respectively, reveal the pattern of interaction between the components and their products during the co-pyrolysis. The LS1P1 composite displays high sensitivity of the interaction pattern of LS and WTP towards the heating rate; while it shows synergism in WTP degradation at $\beta = 20^\circ\text{C}/\text{min}$, $30^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$, the pattern is the reverse for $\beta = 40^\circ\text{C}/\text{min}$. In all cases, the effect of interaction is, however, very low. Meanwhile, the LS3P1 composite shows minimal deviation in the main decomposition region compared to the others, with its interactions primarily confined to minor fluctuations in the lower temperature range ($300\text{--}400^\circ\text{C}$), indicating it does not significantly alter the thermal stability of the main polymer matrix. As LS3P1 is dominated by LS, which has the main pyrolysis region ahead of WTP, the effect of the presence of the latter does not affect that of the former. The TG and DTG patterns of LS3P1, as shown in the figures, are predominantly governed by LS degradation. The LS1P3 composite consistently demonstrates the most significant synergistic effect across all heating rates; its curves exhibit a prominent “negative-followed-by-positive” wave pattern in the $450\text{--}550^\circ\text{C}$ range with the negative peak at 485°C , 506°C , 506°C and 536°C for $\beta = 20^\circ\text{C}/\text{min}$, $30^\circ\text{C}/\text{min}$, $40^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$. The values of negative peak temperature closely correspond to the degradation peaks of WTP (504°C , 518°C , 522°C and 544°C) at those heating rates. This signifies that the presence of LS pyrolysis products simultaneously lowers the degradation temperature of WTP in the composite along with acceleration of rate. The trends also establish antagonism in the carbonization zone similar to the findings of ΔTG trends. In general, synergism has increased with the increase in WTP fraction in the composite and similar observations have been reported in some research studies on algae–polymer co-pyrolysis. In co-pyrolysis studies by Weng et al. (2025) on algal biomass and waste polymer pairs, synergism was observed wherein co-pyrolysis significantly reduces activation energy [20]. An antagonistic relationship has also been reported in cases of some algae–polymer pairs like between *Chlorella vulgaris* and poly vinyl chloride where the occurrence of stage-specific synergism was observed, and while promotion was observed in early stages, inhibition occurred at later stages due to char formation [18]. Xu et al. (2024) characterized synergism as a combination of promoting and inhibitory effects during the co-pyrolysis of Spirulina and waste tires [22]. The enhancement of the pyrolysis rate of algal biomass in the presence of waste polymer widens the scope of bioenergy generation using the biorefinery concept.

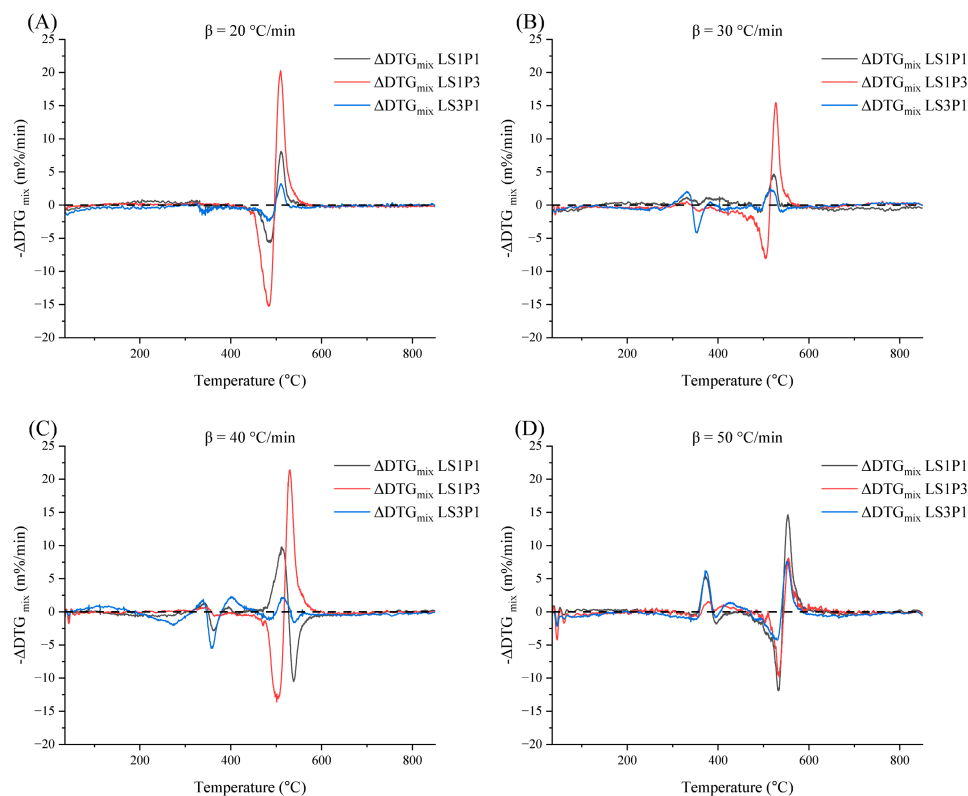


Figure 7. Analysis of the difference in derivative thermogravimetric values of experimental data and additive data at different β values for different composites at (A) $\beta = 20^\circ\text{C}/\text{min}$ (B) $\beta = 30^\circ\text{C}/\text{min}$ (C) $\beta = 30^\circ\text{C}/\text{min}$ (D) $\beta = 20^\circ\text{C}/\text{min}$.

3.4. Kinetic Analysis

Based on the isoconversional plots in Figure 8, it can be seen that in the case of only the polyester sample, the lines were linear and nearly parallel throughout all the conversion values, which indicates a single-step reaction wherein the reaction rate is likely to be constant throughout the degradation process. However, in the case of only the LS sample, the lines were also found to be linear but displayed variation in slope with increasing conversion (α). This represents an overlapping multi-component degradation wherein different biomolecules require slightly different activation energies.

In the case of balanced composite (LS1P1), the lines are parallel with a bend at low temperatures. The occurrence of the bend represents a transition zone wherein early degradation of biomass (LS) is followed by later decomposition of polyester. Meanwhile, high-polymer composite (LS1P3) is tightly grouped, parallel and steep, which closely resembles LS1P1. It can be inferred that in this scenario, the polymer dominates the reaction and has no significant disruption during the single-step degradation due to the presence of LS. Lastly, in high-biomass composite (LS3P1), the lines were spread out across the conversion, exhibiting nonparallel behavior at higher temperatures. This suggests complex kinetics wherein in the non-parallel lines, there is significant variation in activation energy as the reaction progresses, which confirms occurrence of secondary reactions.

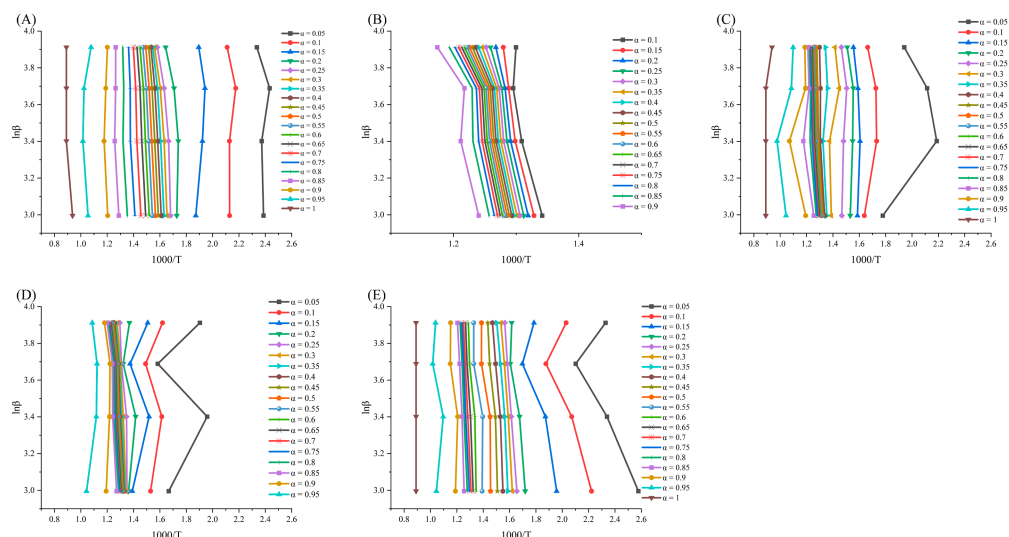


Figure 8. FWO isoconversional plots for (A) LS; (B) WTP; (C) LS1P1; (D) LS1P3; (E) LS3P1.

3.5. Activation Energy Calculation

The tabulated E_a values (Table S8), as calculated using isoconversional methods, clearly show that the LS sample displays an increasing trend in activation energy (E_a) as conversion (α) increases. The E_a value rises steadily from approximately 56 kJ/mol at $\alpha = 0.2$ to a peak of almost 172 kJ/mol at $\alpha = 0.8$, suggesting that the threshold energy requirement for reactions gradually rises as pyrolysis progresses. This can be explained by the presence of different carbohydrate polymers, e.g., cellulose, hemicellulose, lipid and protein in algal biomass. On average, the activation energy for LS hovers around 103.2 kJ/mol. In terms of methodology, the Bosewell method consistently yields the highest values (avg. 104.83 kJ/mol), while the Flynn–Wall–Ozawa (FWO) method provides the lowest estimates (avg. 100.92 kJ/mol). The Tang and Starink methods produce intermediate results and are identical to each other, tracking closely throughout the entire conversion range.

In contrast, the WTP sample exhibits a highly stable with decreasing E_a -versus- α trend, typical of complex solid-state reactions where lower energy pathways become accessible over time. The activation energy starts high at 137–143 kJ/mol for $\alpha = 0.2$ and declines monotonically to between 92 and 100 kJ/mol by $\alpha = 0.9$, with no sudden anomalies. The declining trend in the E_a value of WTP can be explained by the fact that the successive molecular degradation of monomers to lower molecules requires less threshold energy relative to that involved in the initial de-polymerisation reaction. The overall average E_a for WTP is higher than LS, due to the high threshold energy requirement for the initial breakage of the polymer bond relative to those involved in LS. The average values of E_a , determined using different isoconversion methods, are quite distinct: FWO and Bosewell form an “upper tier” yielding higher averages (~123.6 kJ/mol), while Tang and Starink form a “lower tier” with averages around 117.4 kJ/mol.

Based on the E_a values for co-pyrolysis of LS-WTP composites, represented in Table 3, the LS1P1 exhibits drastic fluctuations with the increase in α . The E_a spikes sharply to a peak value of 161.85 kJ/mol followed by a declining trend until a drastic reduction to 43.4285 kJ/mol at $\alpha = 0.85$. In terms of average activation energy, this composite shows the widest disparity between calculation methods: Tang and Starink yield the highest averages (~157 kJ/mol), while the Flynn–Wall–Ozawa (FWO) method provides a much lower estimate (~108 kJ/mol). This erratic behavior suggests a complex, multi-step degradation mechanism where the rate-limiting step changes rapidly or involves significant instability. In contrast, the LS1P3 composite demonstrates much more stable and consistent kinetic

behavior. The activation energy decreases slowly from 103 kJ/mol at $\alpha = 0.35$ to a minimum of 92 kJ/mol at around $\alpha = 0.7$ before rising slightly to 99 kJ/mol towards the end at $\alpha = 0.85$). This stability implies a consistent degradation pathway compared to LS1P1. The average activation energy is moderate, with Tang and Starink again providing the upper bound estimates (~124 kJ/mol) and FWO providing the lower bound (~96 kJ/mol).

Table 3. E_a values calculated for different composites using isoconversional methods.

	LS1P1				LS1P3				LS3P1			
α	FWO	Bosewell	Tang	Starink	FWO	Bosewell	Tang	Starink	FWO	Bosewell	Tang	Starink
0.35	2.759795	26.13539	46.85227	47.47092	103.728	118.8672	127.586	127.7308	84.356	76.8719	66.15579	65.89823
0.4	161.8594	202.7871	231.5376	232.5112	100.3397	116.48	126.2521	126.4277	85.94521	77.91022	66.62662	66.35332
0.45	138.9525	170.4798	191.9433	192.6833	98.10783	114.7177	125.0136	125.2051	86.26547	76.81986	64.26276	63.95179
0.5	128.408	156.6281	175.6468	176.3064	95.99295	112.7569	123.2892	123.4887	71.84038	62.34515	50.43481	50.13259
0.55	122.7764	149.2573	166.9946	167.612	93.90873	110.6824	121.3202	121.5243	70.20359	61.17436	49.75805	49.46935
0.6	120.5169	146.2726	163.4715	164.0711	92.76982	109.6767	120.4867	120.6963	102.5067	90.79969	75.44764	75.06531
0.65	120.1674	146.0954	163.4647	164.0692	92.44429	109.4507	120.365	120.5776	119.342	106.1865	88.73607	88.30352
0.7	120.3331	146.7362	164.5213	165.1383	92.23384	109.41	120.4858	120.703	125.2992	111.6792	93.52903	93.08
0.75	120.7021	148.2172	166.9763	167.6226	92.61665	109.9876	121.2199	121.4409	129.5579	115.9146	97.53968	97.08706
0.8	115.2906	145.4942	166.9106	167.632	94.25935	112.2189	123.9014	124.133	133.4456	119.9367	101.4953	101.0435
0.85	43.4258	66.17135	84.37826	84.95181	99.766	119.6872	132.8685	133.1354	142.2696	129.1094	110.5565	110.1078
Average	108.65	136.75	156.60	157.27	96.015	113.08	123.88	124.096	104.63	93.52	78.59	78.22

Lastly, the LS3P1 composite presents a stepped kinetic trend that sets it apart from the others. The activation energy remains stable and low at 84 kJ/mol during the first half of the conversion ($\alpha = 0.35$ to 0.55) but undergoes a sharp “step up” starting at $\alpha = 0.6$, continuing to rise to 142 kJ/mol until the end of the process. This suggests a clear shift in the reaction mechanism, where the material becomes significantly harder to degrade in the latter stages. From the comparison of the average E_a values of the individual feedstocks and their mixtures, calculated through the FWO method, it is evident that E_a is the least in case of LS1P3, which has already been proven as synergistic. When the starting reactants and the ultimate products are the same, the decrease in E_a usually happens due to the change in the reaction pathway through the formation of highly active intermediates, as observed in the case of catalysis [62]. There is a possibility that the presence of LS in an extremely low proportion can also drastically change the reaction pathway of WTP towards a faster direction requiring less activation energy. As the value of E_a is lower than that of LS, the facilitation of its pyrolysis is also anticipated. This can also happen due to change in reaction mechanism from the phase boundary-controlled contracting cylinder (R2) type for WTP to the P2-type mechanism characterized by the acceleratory reaction rate signifying the spread of decomposition over multiple reaction spots (nuclei) without interfering with each other for LS1P3, as evidenced by Master plot analysis, described under Section 3.6. For other mixtures, E_a lies in between those of LS and WTP.

3.6. Reaction Mechanism

As described under Section 2.8, the Master plot approach has been used to identify the most probable solid-state reaction mechanism governing the pyrolysis of LS and WTP and co-pyrolysis of their mixtures (LS1P1, LS1P3 and LS3P1). Fifteen reaction mechanisms were attempted. The experimental data have been compared with those from each reaction mechanism for each of the integral isoconversional models, namely, Flynn–Wall–Ozawa (FWO), Bosewell, Starink and Tang. Master plots using the activation energy predicted by FWO method and the TG data are presented in Figures 9–13 for LS, WTP, LS1P1, LS1P3 and LS3P1, respectively. In most of the cases, the plots using the E_a values using Bosewell, Starink and Tang methods are presented in the Supplementary Material (Figures S1–S5). The same figures show theoretical values of left hand side of Equation (12), i.e.,

normalized $g(\alpha)$, predicted by those standard reaction mechanisms which generate RMSE values less than 0.5 with respect to the RHS. For each feedstock, such reaction mechanisms ($\text{RMSE} < 0.5$) corresponding to each isoconversion method are presented in the Supplementary Material.

The RMSE value is the minimum ($=0.1251$) for two-dimensional nucleation and the growth (A2) mechanism when E_a values according to Boswell, Starink and Tang models are used. In this mechanism, the decomposition initiates at a localized nucleus and is followed by expansion and overlapping until the complete consumption of the material. The Master plots reveal a complex degradation of material where a dominant mathematical fit and a strong agreement among the majority of methods indicates the Avrami–Erofeev (A2) model as the primary reaction mechanism. A representative figure using the Boswell method is shown in Figure 9. In contrast, the two-dimensional phase boundary-controlled contracting cylinder (R2) mechanism was identified as the best match for LS using the FWO method having a slightly higher RMSE ($=0.1301$). This mechanism visualizes a contracting surface where decomposition begins at the exterior particles and progresses inward at a steady rate.

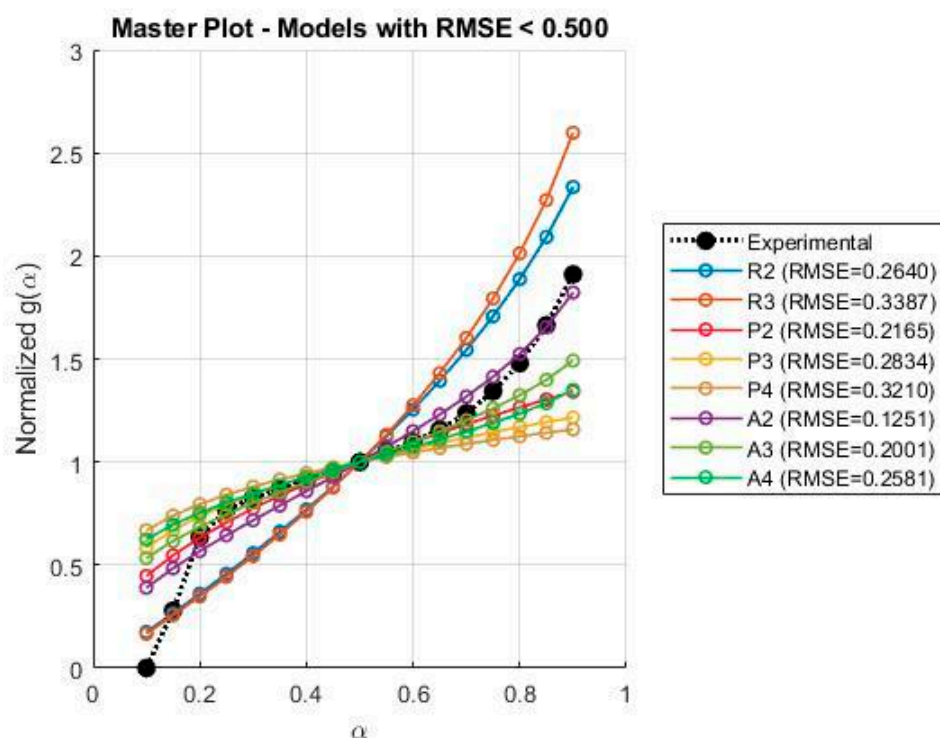


Figure 9. Master plot for thermal decomposition of LS using Boswell method having least RMSE ($=0.1251$).

Using the same methodology as in the case of LS, the two-dimensional phase boundary-controlled contracting cylinder (R2) mechanism gives the minimum RMSE ($=0.1301$) for WTP when Starink-, Tang- and Boswell-type integral models are used. This suggests that the geometry of textile fiber is cylindrical and that the reaction proceeds from two dimensions with a shrinking unreacted core. In contrast, the FWO Master plot suggests that the three-dimensional phase boundary-controlled contracting volume (R3) mechanism gives the closest match with a higher RMSE ($=0.1985$). Due to lower RMSE value and convergence of predictions by the other integral models, it can be inferred that a two-dimensional phase boundary-controlled contracting cylinder (R2) mechanism is the closest fit. It is not just a statistical coincidence. This signifies that the reaction progresses at

the interface of the volatile-char and undecomposed solid whose rate is controlled by interface movement towards the core. A representative Master plot for WTP using the Boswell method is shown in Figure 10.

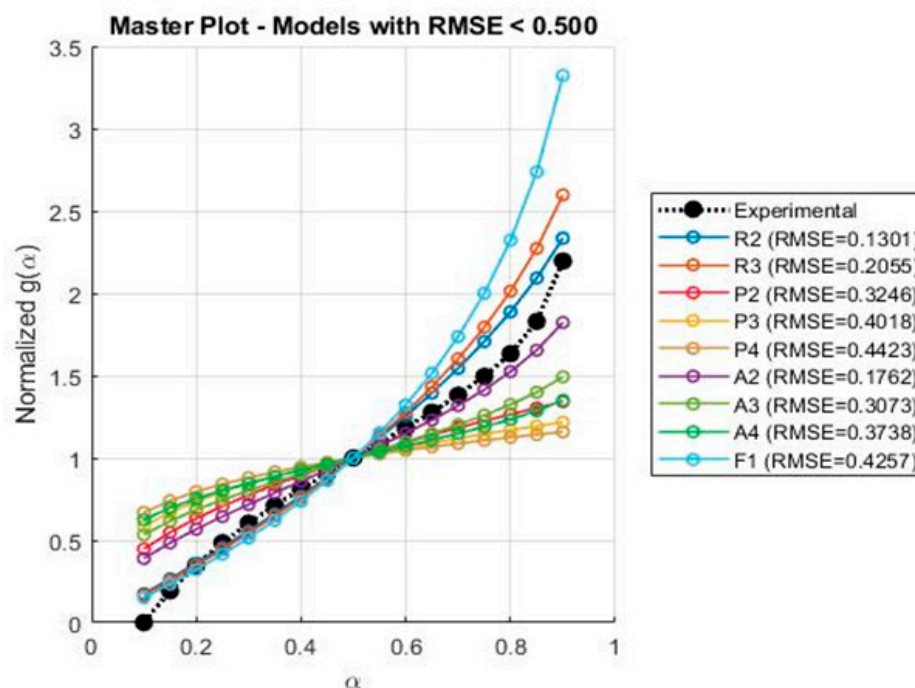


Figure 10. Master plot for thermal decomposition of WTP using Boswell method having least RMSE ($=0.1301$).

Figure 11 shows the Master plot using the activation energy of FWO method for LS1P1. It is clear that the balanced composite (LS1P1) exhibits the minimum RMSE ($=0.1910$) for the power law (P2) model in the context of the kinetic analysis of thermal degradation using the FWO method. This is true for all the other isoconversion methods, i.e., Starink, Tang and Boswell. This suggests that the degradation mechanism, in this specific composition during the reaction, can be best described by a nucleation-controlled process.

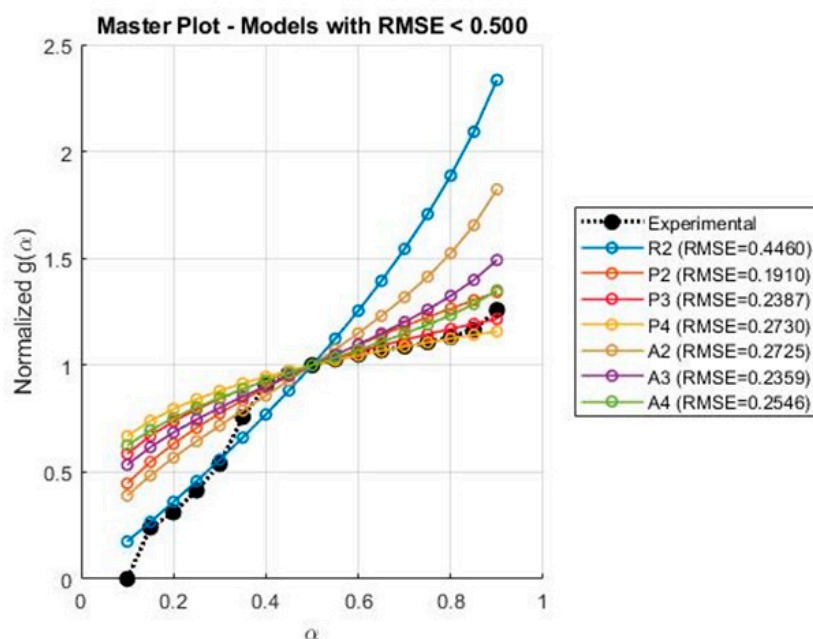


Figure 11. Master plot for thermal decomposition of LS1P1 using FWO method having least RMSE ($=0.1910$).

Similarly, Figure 12 shows the Master plot using the activation energy of FWO method also exhibited this mechanism during the thermal decomposition of the polymer rich composite (LS1P3). The Master plots using the E_a values predicted by the different integral methods have identified P2 mechanism as the best fit, with the least and identical RMSE value ($=0.1333$). This mechanism effectively captures the acceleratory reaction rate where decomposition spreads from multiple reaction spots (nuclei) without interfering with each other. This also signifies the heterogeneous nature of the composite.

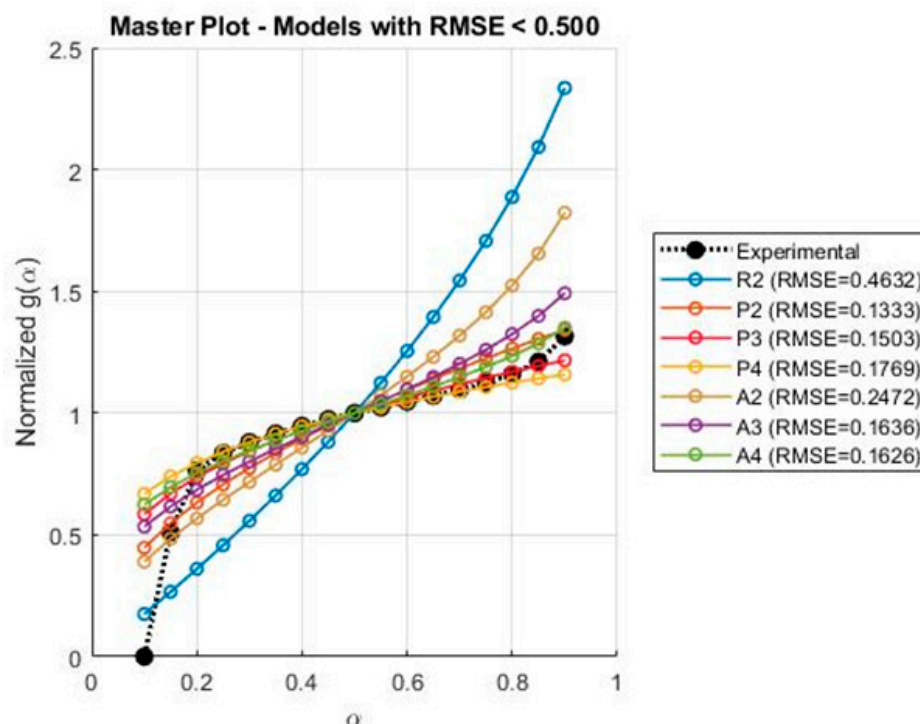


Figure 12. Master plot for thermal decomposition of LS1P3 for FWO method with Least RMSE ($=0.1333$).

However, as evident from Figure 13, the Master plot using the activation energy of FWO method for biomass-rich composite (LS3P1) suggests that the two-dimensional nucleation and growth (A2) mechanism with the least RMSE value ($=0.1411$) seems to be the most accurate mechanism. The chosen isoconversional models converge on this result by having identical Master plots and RMSE values. This mechanism identifies the role of the distributed reaction centers and the progressive spread of thermal breakdown. It can be observed that reaction mechanism of the biomass-rich composite is similar to that of LS. The Master plots for all the samples using other isoconversion methods are presented in the Supplementary Material.

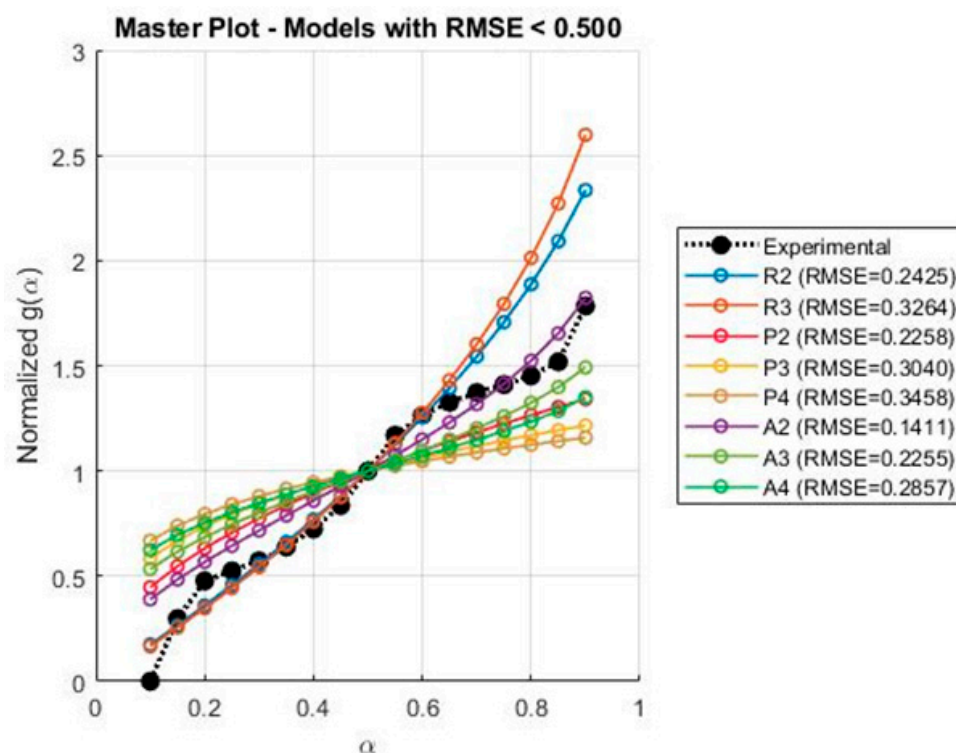


Figure 13. Master plot for thermal decomposition of LS3P1 for FWO method with Least RMSE ($=0.1411$).

3.7. Thermodynamic Analysis

The thermodynamic parameters, the heat of reaction, ΔH , Gibbs free energy change, ΔG , and entropy change, ΔS , are expected to be helpful in identifying the interplay between energy input, reaction spontaneity and the disorder of the system, respectively, in the decomposition process. Table 4 summarizes the values of ΔH , ΔG and ΔS for LS, WTP and LS1P3. In Figure 14, the values of ΔH , ΔG and ΔS for LS, WTP and LS1P3, the most synergistic mixture of LS and WTP, were plotted against conversion level, α , using β (20 °C/min; 30 °C/min; 40 °C/min and 50 °C/min) as a parameter based on FWO method. In the Supplementary Material, Figures S7–S9 depict similar plots of thermodynamic parameters of LS, WTP and LS1P3 based on Bosewell, Tang and Starink models.

Table 4. Comprehensive summary of thermodynamic parameters for LS, WTP and LS1P3.

Sample	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol·K)	Observed Thermal Signature
LS (Algae)	54.0 to 155.0	−69.43 to −203.4	404.8 to 713.9	Multi-stage; linear increase in spontaneity.
WTP (Polyester)	138.7 to 96.2	−115.3 to −139	523.9 to 441.1	Single-stage; peak demand at $\alpha = 0.2$.
LS1P3 (Blend)	101.6 to 95.1	−115.6 to −143.5	435.8 to 425.7	Synergistic; lowest overall energy barrier.

Figure 14A reveals the endothermicity during the multi-stage decomposition of LS. The energy requirement is lower for carbohydrate degradation in comparison to lipid or protein degradation that is more complex. It was also noted that ΔH is independent of the heating rate (β) which is indicative of a consistent product array irrespective of the heating rate. Simultaneously, ΔG becomes increasingly negative with respect to conversion (α) for LS as seen in Figure 14B. While the ΔG values range from a −69 kJ/mol to −93 kJ/mol for second-stage reactions, those for third-stage reactions vary between −94 kJ/mol to −204 kJ/mol. This indicates that the third-stage reactions are more favorable than those of the second-stage ones. Lastly, positive ΔS values for LS indicates to increased randomness due to formation volatiles during thermal degradation as seen in Figure 14C. In contrast

to ΔH and ΔG , ΔS declines with increasing β , which suggests that reduced residence time limits the molecular disorder and furthermore affects the conversion of condensable volatiles into gases having a lower molecular weight.

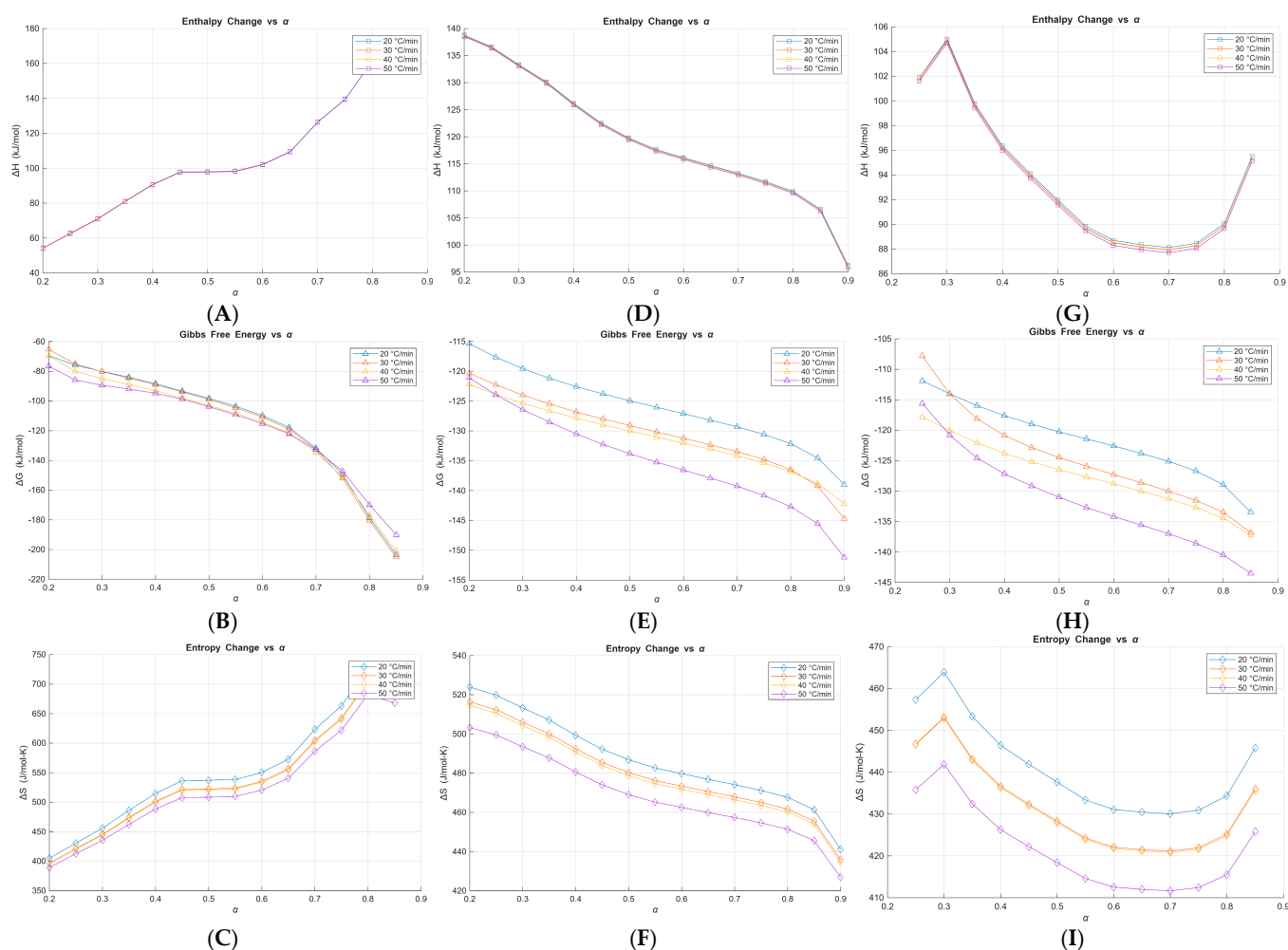


Figure 14. Enthalpy, free energy and entropy for LS (A–C), WTP (D–F) and LS1P3 (G–I), respectively, using FWO method.

The fact that WTP decomposition is a single-stage endothermic process is evident from Figure 14D. Similar to LS, ΔH values remain independent of the heating rate (β). The reaction initiates with a high ΔH at $\alpha = 0.3$, indicating the chain cleavage reaction as the most energy-intensive process which is followed by stabilization. Trends observed in Figure 14E,F corresponding to ΔG and ΔS corroborate to the trajectories observed for ΔH . It confirms a decline in thermodynamic spontaneity and randomness due to volatile formation as the reaction proceeds towards conclusion. The peak disorder at $\alpha = 0.2$ coincides with polymer breakdown. However, unlike LS, the spontaneity of WTP is actually dependent on the heating rate. The absolute peak value increases up to 50 °C/min due to higher temperatures at lower residence times. Similar to LS, the entropy during WTP decomposition decreases with increasing heating rates. Shorter residence time leads to suppressed molecular disorder.

Figure 14G,H show that ΔH and ΔG for LS1P3 peak at $\alpha = 0.3$ in a shift from WTP's peak at $\alpha = 0.2$ which can be attributed to the presence of LS. The reaction for this blend is endothermic and favorable and occurs in the intermediate zone between the individual feedstocks. It was also noted that ΔH for LS1P3 remains more or less the same throughout

the conversion range in comparison to LS and WTP. It is indicative of an energetic advantage in the blend. The polymer dominance of the kinetic fingerprint of LS1P3 is evident from high initial enthalpy, which is associated with the energy-intensive chain cleavage. However, as the reaction progresses, ΔH declines. The smaller fragments and biomass require lesser energy to decompose. Interestingly, enthalpy rises again at the end of the reaction, which may signify that the energy requirement of the composite increases during carbonization of the sample. The enthalpy profile remains an intrinsic property across the heating rates. Entropy, on the other hand, decreases with increasing heating rate, which suggests that shorter residence time arrested the molecular disorder as observed in Figure 14I.

In the Supplementary Material, the values of ΔH , ΔG and ΔS for LS1P1 and LS3P1 are plotted against α in Figures S10 and S11, respectively, for all the isoconversional methods. In the case of balanced composite (LS1P1) of biomass and polymer, decomposition is dominated by the polyester fraction despite both feedstocks being in equal proportions. The process is fundamentally favorable and endothermic in nature requiring initially a higher heat input. However, in the case of biomass-rich composite (LS3P1), the decomposition closely follows the signature of biomass as feedstock. There is a multi-step breakdown of the composite observed through the complex and irregular entropy and energy profiles. In this case, thermodynamic characteristics of biomass fraction dominates over polymer. Similar to the LS profile, the algae-rich composite displays fluctuations, representing the breakdown of different structural fractions of the biomass. The change in entropy shows multiple factions signifying disintegration of ordered composite structures into increasingly disordered volatile fragments. The Gibbs free energy changes for LS1P1 and LS3P1 also remain negative across all the fractional conversion, α , which confirms the intrinsic spontaneity of the reaction process. As the reaction progresses, the value becomes more negative which signifies that the later stages are thermodynamically more favorable. However, the increase in the heating rates makes the process less favorable. The fluctuations map the overlapping breakdown of the organic as well as polymeric structures.

3.8. Product Yields from Pyrolyser Experiments

Figure 15 presents the mean values of triplicate observations of yields of pyro-char, pyro-oil and pyro-gas for LS, WTP and their mixtures, as obtained from the semi-batch reactor, run at 450 °C. The confidence level of the yields of all pyro-products from each feedstocks under the study is 98%, as represented by the error bars. The standard deviations and standard error of mean for the yields of pyro-products for each feed are presented in the Supplementary Material (Table S9). The error bars represent $\pm 2\%$ error, while the thermal decomposition range of LS is from 200–470 °C and that of WTP ranges from 470–545 °C. The co-pyrolysis of composites is expected to be influenced by the thermal degradation of both LS and WTP. Therefore, temperature for isothermal semi batch pyrolysis has been chosen to be 450 °C, deliberately in the overlapping pyrolysis temperature range of both LS and WTP. It is observed that the blends result in distinct yield distribution with respect to their individual constituents, i.e., LS and WTP. Analysis revealed that char yield (41%) of LS is the highest among all. The high rate of formation of char can be attributed to the complex biological structure containing proteins, lipids and carbohydrates which undergo dehydration as well as carbonization at high temperatures [63]. Meanwhile, WTP exhibits the highest oil yield (48%) along with an increased gas yield (23%). This can be attributed to the scission of polymeric long chains [64]. The depolymerisation and thermal cracking resulted in higher proportion of condensable volatiles and non-condensable gases as compared to LS alone.

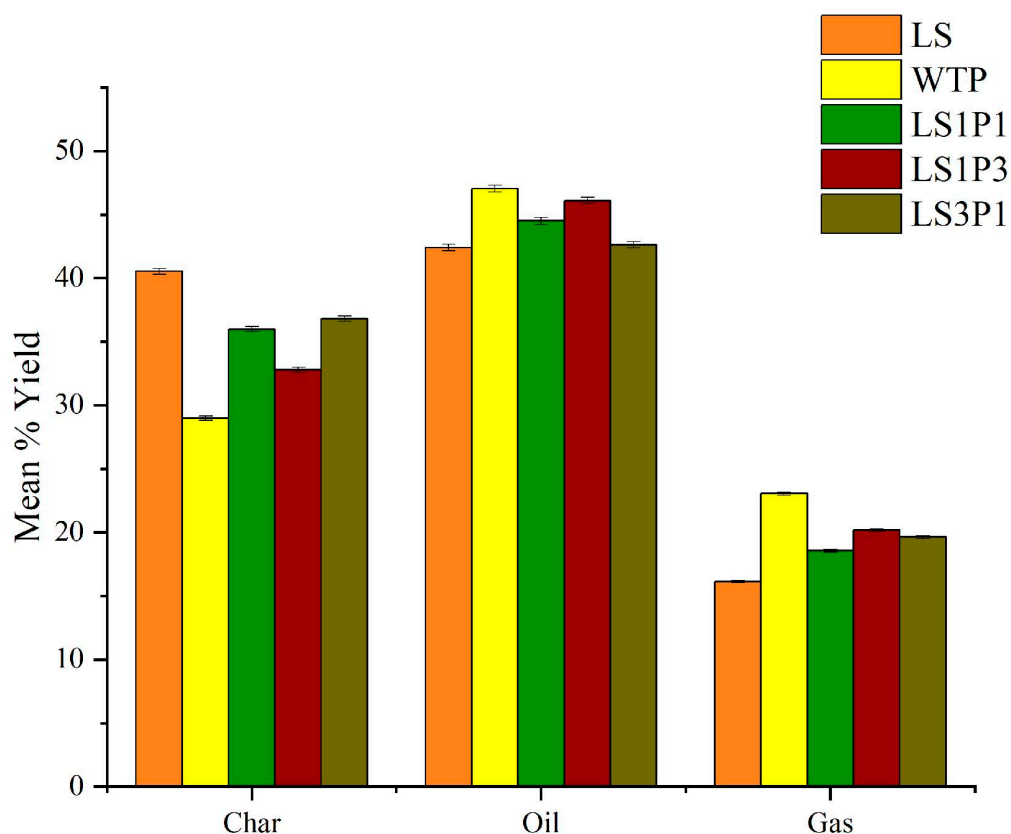
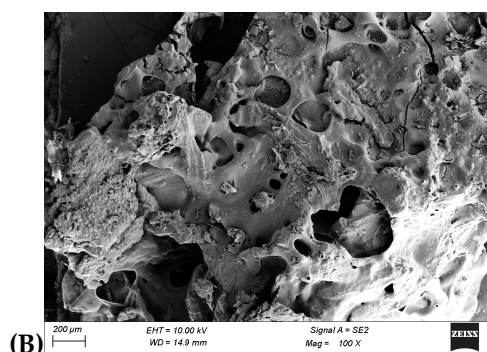
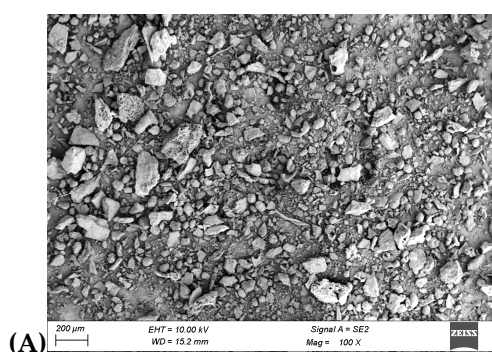


Figure 15. Product yield percentage of the different feedstocks.

It can also be observed that the increase in WTP fraction in the composites shifts the pyrolysis products to yield more oil and gases corresponding to a decrease in char. LS1P3 shows high oil yield (46%) which approaches the oil yield characteristics of WTP. As expected, the yields of char, oil and gas for the 1:1 blend (LS1P1) are in between those of LS and WTP. Conversely, the product distribution of LS3P1 exhibits that though the oil and gas yield remain comparable with that of LS, addition of WTP actually helps in reducing the char fraction from 41% for LS to 37%. Based on the observations, it can be inferred that addition of WTP stabilizes the thermal reaction and enhances oil yield. As evidenced in the reported literature, this can be due to the release of hydrogen during WTP degradation, which can stabilize the oxygenated radicals. This prevents the repolymerisation reaction to form char [20]. Notably, LS1P3 is the most favorable composite that can be employed for maximizing oil production. As per the claims in the literature, other than the enhancement of quality of oil through the decrease in O:C ratio due to the blending with polymer, the quality of char is also improved [65]. In Figure 16, the Field Emission Electron Microscopy images of char, as obtained in the reactor from the pyrolysis of LS, WTP and their composites, are presented.



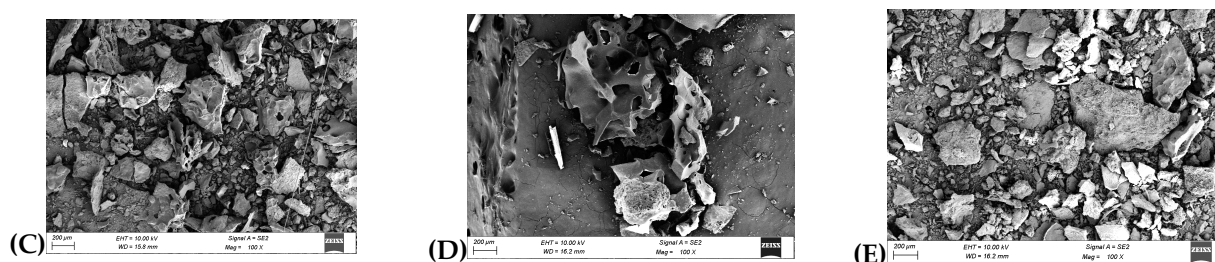


Figure 16. FESEM images of pyro-chars of (A) LS; (B) WTP; (C) LS1P1; (D) LS1P3; (E) LS3P1.

It is observed that due to the presence of polymer, a support layer is developed in all char samples and it is expected to be beneficial in the case of the application of char for water treatment. There is a prospect of using char as an adsorbent and the pyro-oil and pyro-gas as biofuels and also as sources of valuable chemicals [66–71]. Thus, the surface properties of char and the actual composition of pyro-oil and pyro-gas are to be determined. Although out of the scope of the present study, more elucidation about the characterization of pyro-products, namely char through X-Ray Diffraction, Fourier Transfer Infrared Spectroscopy, Brunauer-Emmett-Teller surface area analysis, pH_{pzc} (point of zero charge) analyses, etc., pyro-oil through Gas Chromatography Mass Spectroscopy, FTIR, elemental analysis, O/C ratio, HHV analyses and pyro-gas through GC analysis is, therefore, required for the ultimate application of co-pyrolysis of LS-WTP composites [72–81].

4. Conclusions

The present study could successfully generate information regarding the co-pyrolysis of distinct and contrasting feedstocks like *Leptolyngbya subtilis* (LS) and waste textile polyester (WTP) through the determination of isoconversional kinetics, thermodynamics and reaction mechanisms. The effect of the blending ratio of LS and WTP on their co-pyrolysis performance has been adjudged through the comparison of the Comprehensive Pyrolysis Index (CPI) and testing of synergism. It has been established that LS1P3 composite (25% LS: 75% WTP) exhibits a strong synergistic effect, particularly between 400 °C and 500 °C. The actual mass loss significantly exceeds the theoretical predictions of the summative model applicable for non-interacting feedstock pairs. This indicates a rapid destabilization and enhanced reactivity of the composite compared to that obtainable from non-interacting pairs. In contrast, it has been noted that in the case of blends with higher biomass concentrations, such as LS3P1 (75% LS), only moderate synergism is present. Furthermore, the kinetic assessments also underscore the efficiency of the LS1P3 blend. This blend exhibits the lowest average activation energy (E_a) of 96.015 kJ/mol (via the FWO method) which is lower than both pure LS (100.92 kJ/mol) and pure WTP (123.76 kJ/mol). There is a possibility that the presence of LS in an extremely low proportion can drastically change the reaction pathway of WTP towards a faster direction requiring less activation energy. As it is evident from the determination of reaction mechanisms, this can also happen due to a change in reaction mechanism from phase boundary-controlled contracting cylinder (R2) type for WTP to R2-type mechanism characterized by the acceleratory reaction rate signifying the spread of decomposition over multiple reaction spots (nuclei) without interfering with each other for LS1P3. Thermodynamic analysis divulges that the thermal decomposition for all samples is endothermic ($\Delta H > 0$) and thermodynamically favorable, as evidenced by negative Gibbs free energy ($\Delta G < 0$) values across all conversion levels. The present study also highlights that higher heating rates (up to 50 °C/min) may result in universally boosting reactivity and reactor throughput. However, such a high heating rate reduces molecular disorder (entropy) by shortening the residence

time available for volatile conversion. This study also focuses on the determination of distribution of product yields from the pyrolysis of LS and WTP and co-pyrolysis of LS1-WTP composites conducted at 450 °C in a semi-batch pyrolyser. The results of the research study indicate that co-pyrolysis can contribute potentially towards textile waste valorization simultaneously with utilization of algal biomass, growing on industrial cooling towers, particularly in coal-based power plants having a CO₂-rich environment. Overall, it is expected that the database, generated through the study, will corroborate in utilizing the co-pyrolysis of LS-WTP composites and similar ones to achieve UN-sustainability goals of affordable clean energy generation and implementation of a circular economy. However, more elucidation about the characterization of pyro-products, namely char through XRD, FTIR, BET, pHpzc analyses, etc., pyro-oil through GC-MS analysis and pyro-gas through GC analysis as well as process simulation for large-scale performance and life cycle analysis, are required for the ultimate application of co-pyrolysis of LS-WTP composites.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cleantechnol8040112/s1>: Table S1: Correlations for $g(\alpha)$ for standard reaction mechanisms. Table S2: Standard deviations (SD) and standard error of mean (SEM) for TG data. Table S3: Standard deviations (SD) and standard error of mean (SEM) for DTG data. Table S4: Pyrolysis and thermal degradation of different species of algal biomass. Table S5: Pyrolysis and thermal degradation of different type of polymeric and waste textile. Table S6: Thermal degradation profiles of polymer algae composites. Table S7: Characteristic parameters for each sample at different β . Table S8: E_a (kJ/mol) values calculated for individual feedstocks using isoconversional methods. Table S9: Standard deviation and standard error of mean of the %Yield from the experimental pyrolysis of LS, WTP and their composites at 450 °C. Figure S1: Master plot for thermal decomposition of LS using other isoconversional methods. Figure S2: Master plot for thermal decomposition of WTP using other isoconversional methods. Figure S3: Master plot for thermal decomposition of LS1P1 using other isoconversional methods. Figure S4: Master plot for thermal decomposition of LS1P3 using other isoconversional methods. Figure S5: Master plot for thermal decomposition of LS3P1 using other isoconversional methods. Figure S6: Isoconversional profiles of LS (A–C), WTP (D–F), LS1P1 (G–I), LS1P3 (J–L) and LS3P1 (M–O) for Bosewell, Tang and Starink methods respectively. Figure S7: Thermodynamic parameters namely ΔH , ΔG and ΔS of LS using Bosewell, Tang and Starink isoconversional methods. Figure S8: Thermodynamic parameters namely ΔH , ΔG and ΔS of WTP using Bosewell, Tang and Starink isoconversional methods. Figure S9: Thermodynamic parameters namely ΔH , ΔG and ΔS of LS1P3 using Bosewell, Tang and Starink isoconversional methods. Figure S10: Thermodynamic parameters namely ΔH , ΔG and ΔS of LS1P1 using FWO, Bosewell, Tang and Starink isoconversional methods. Figure S11: Thermodynamic parameters namely ΔH , ΔG and ΔS of LS3P1 using FWO, Bosewell, Tang and Starink isoconversional methods.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

TGA	Thermogravimetric Analysis
DTG	Derivative of Thermogravimetric Analysis
CPI	Comprehensive Pyrolysis Index
α	Degree of Conversion
β	Heating rate
LS	Leptolyngbya subtilis JUCHE1
WTP	Waste Textile Polyester
LS1P1	LS (50%) + WTP (50%)
LS1P3	LS (25%) + WTP (75%)
LS3P1	LS (75%) + WTP (25%)
y_i	Yield %
w_i	weight fraction of ith pyrolysing material (LS or WTP) in the mixture
$(m\%(T))_i$	%m data of ith pyrolysing material in the mixture any temperature, T
SD	Standard deviation
SEM	Standard error of mean
FESEM	Field Emission Scanning Electron Microscopy
RMSE	Root Mean Square Error
ΔH	Enthalpy change
ΔG	Gibbs free energy change
ΔS	Entropy change

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