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# Modelling of Thermal Decomposition Kinetics of Proteins, Carbohydrates and Lipids Using *Scenedesmus microalgae* thermal Data

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In present work, the thermal decomposition behaviour and kinetics of proteins, carbohydrates and lipids is studied by use of models derived from mass-loss data obtained from thermogravimetric analysis of *Scenedesmus microalgae*. The experimental results together with known decomposition temperature range values obtained from various literature were used in a deconvolution technique to model the thermal decomposition of proteins, carbohydrates and lipids. The models fitted well ($R^2 > 0.99$) and revealed that the proteins have the highest reactivity followed by lipids and carbohydrates. Generally, the decomposition kinetics fitted well with the Coats-Redfern first and second order kinetics as evidenced by the high coefficients of determination ($R^2 > 0.9$). For the experimental conditions used in this work (*i.e.* high heating rates), the thermal decomposition of protein follows second order kinetics with an activation energy in the range of 225.3-255.6 kJ/mol. The thermal decomposition of carbohydrate also follows second order kinetics with an activation energy in the range of 87.2-101.1 kJ/mol. The thermal decomposition of lipid follows first order kinetics with an activation energy in the range of 45-64.8 kJ/mol. This work shows that the thermal decomposition kinetics of proteins, carbohydrates and lipids can be performed without the need of experimentally isolating the individual components from the bulk material. Furthermore, it was shown that at high heating rates, the decomposition temperatures of the individual components overlap resulting in some interactions that have a synergistic effect on the thermal reactivity of carbohydrates and lipids.

**Keywords: *Scenedesmus* microalgae, Proteins, Carbohydrates, Lipids, Thermal decomposition, Coats-Redfern, Activation energy.**

## INTRODUCTION

The use of biomass as an alternative energy source is now becoming popular considering the amount of green-house gas (GHG) emissions associated with the use of coal. Plant based biomasses are considered as carbon neutral sources of energy. The reason being that the plant's life-cycle involves the use of carbon dioxide from the atmosphere for growth, which is then released back to the atmosphere via energy generation thermal decomposition processes. McKendry [1] classified biomass into woody plants, grasses, aquatic plants and manure. Microalgae, being an aquatic plant, is regarded as a special type of biomass because of its noticeable differences in core chemical composition compared to woody biomass. Instead of cellulose, microalgae is composed of proteins, lipids and carbohydrate [2]. John *et al.* [3] stated that due to the increased demand of fuel, algal derived fuels such as ethanol are an alternative to those derived from food crops such as cereals. Microalgae are the fastest-growing plants that can be cultivated on a large scale by use of open ponds [2]. Furthermore, microalgae can grow in fresh water with a supply of carbon dioxide from industrial emissions [4].

Because of its potential as a renewable resource, a number of individuals have attempted to study the thermal decomposition (pyrolysis) behaviour and kinetics of microalgae biomass [2,5-7]. Chaiwong *et al.* [8] studied the slow pyrolysis of *Spirulina* sp. microalgae powder of size range 500-1000 μm. The study was performed using thermogravimetric analysis (TGA) methods so as to generate mass-loss curves. The experimental conditions were set to emulate slow pyrolysis by thermally decomposing the samples at non-isothermal conditions. A heating rate of 10 °C/min was used to attain a gradual temper-

ature increase to 900 ºC in the presence of nitrogen. Analysis results revealed that there are three stages in the slow pyrolysis of *Spirulina* sp. The first stage is the dehydration occurring in the temperature range 50-200 ºC which is followed by the devolatilization of the bulk of the material (second stage) at 200-600 ºC. The third stage occurs at 600-900 ºC where the the remaining solid material seemed to decompose slowly. The first stage in the decomposition corresponds to the removal of moisture and light organics contained in the microalgae. The second stage (200-600 ºC) is the important and most studied one because this is the temperature range where proteins, carbohydrates and lipids decompose. Wang *et al*. [5] managed to isolate proteins, carbohydrates and lipids from *Nannochloropsis* sp. microalgae so as to study the pyrolysis behaviour and mechanism of microalgae by focusing on the individual components. Derivative thermogram (DTG) study showed that the thermal decomposition of proteins and lipids had highest reactivity at 310 and 353 ºC, respectively. Furthermore, it was shown that the decomposition occurred *via* decarboxylation, deamination and fragmentation of glycerine (in lipids) peptide bonds (in proteins) to form hydrocarbons, carboxylic acids, amines and esters. The decomposition peak of carbohydrate occurred at 275 ºC *via* dehydrated reactions and further bond fragmentation to form ketones, aldehydes and phenols.

The majority of the studies seem to agree that the thermal decomposition of microalgae occurs *via* the individual decompositions of proteins, carbohydrates and lipids [5,9-12]. However, there is some considerable conflict between researchers with regards to parameters such as the actual decomposition temperatures, reactivity and kinetic parameters such as activation energy and order of reaction. The objective of this work is to contribute to the available large pool of knowledge in the field of thermal decomposition of algal biomass. In this work, we will use the information obtained from Wang *et al*. [5] and others together with this work's experimental data to model the thermal decomposition kinetics of proteins, carbohydrates and lipids using *Scenedesmus* sp. microalgae TGA data.

## EXPERIMENTAL

Dried *Scenedesmus* sp. microalgae (< 8% moisture) was obtained at Innoventon, Downstream Chemicals Technology Station (Nelson Mandela University, South Africa), where it was cultured by use of photo-bioreactors. Proximate analyses of the samples was done using a muffle furnace according to the ASTM standard method E871 and E872 [13-15]. Ultimate analysis of microalgae was performed using an elemental analyzer (Elementar GmbH vario EL Cube). Thermo-gravimetric analysis (TGA) was performed using a high resolution thermogravimetric analyser (Discovery TGA-5500). Each sample underwent a temperature ramp from its initial temperature to a final temperature of 800 ºC, heating rates of 10, 50, 100 and 200 ºC/min under inert nitrogen conditions.

**Modelling of mass loss curves:** The mass-loss data obtained from TGA experiments were decoded into derivative mass-loss (DTG) curves using TA Instruments, Universal Analysis 2000 software. In order to model the thermal decomposition of protein, carbohydrates and lipids, the DTG curve for microalgae must be deconvoluted into element curves that are described by a suitable function, in this case the Gaussian distribution. These element curves represent individual peaks that add up to create the overall DTG plot. Deconvolution of the experimental DTG plots into a series of Gaussian distributions was performed by making use of OriginPro™.

**Coats-Redfern kinetic study:** The decomposition of a solid fuel sample to form volatiles and solid residue can be modelled as a function of conversion as follows;

$$\frac{dX}{dt} = kf(X) \tag{1}$$

If X is the solid conversion, the function can be written as follows:

$$f(X) = (1-X)^n \tag{2}$$

By substituting eqn. 2 and the general form of the Arrhenius equation into eqn. 1, we obtain

$$\frac{dX}{dt} = A_{exp}\left(\frac{-E_a}{RT}\right)(1-X)^n \tag{3}$$

If the heating rate β (ºC/min), given by eqn. 4 is constant, the time delta (dt) can be made to be the subject of formula and substitute it into eqn. 3 to obtain eqn. 5;

$$\beta = \frac{dT}{dt} \tag{4}$$

$$\frac{dX}{dT} = \left(\frac{1}{\beta}\right)A_{exp}\left(\frac{-E_a}{RT}\right)(1-X)^n \tag{5}$$

The Coats-Redfern method is an integral method that requires the integration of eqn. 5 [16]. As a result, the following expressions are obtained in eqns. 6 and 7, for n = 1 and n = 2, respectively.

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\frac{AR}{\beta E_a}\left[1-\frac{2RT}{E}\right] - \frac{E_a}{RT} \tag{6}$$

$$\ln\left[\frac{(1-X)^{-1}-1}{T^2}\right] = \ln\frac{AR}{\beta E_a}\left[1-\frac{2RT}{E}\right] - \frac{E_a}{RT} \tag{7}$$

where T is the absolute temperature (K), X is the conversion ratio and given by eqn. 8, A is the pre-exponent factor in the Arrhenius equation, R is the universal gas constant (0.0083 kJ/mol), β is the heating rate (ºC/min) and $E_a$ is the activation energy (kJ/mol).

$$X = \frac{w_i - w}{w_i - w_f} \tag{8}$$

where $w_i$ and $w_f$ are the initial and final sample mass (mg) respectively, and w being the instantaneous mass.

Generally, pyrolysis activation energies are large, the first term on the right hand side of eqns. 6 and 7 can be regarded as a constant because the value of $2RT/E_a$ is small [17,18]. Therefore, a plot of the term on the left hand side against the reciprocal of the temperature should give a straight line. The pyrolysis kinetic parameters, that is, the activation energy and the pre-exponential factor (A) can then be evaluated from the slope

TABLE-1
MICROALGAE COMPONENTS THERMAL DECOMPOSITION LITERATURE SURVEY

| Species/genome | Protein | | Carbohydrate | | Lipid | | Heating rate (°C/min) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | Range (°C) | Peak (°C) | Range (°C) | Peak (°C) | Range (°C) | Peak (°C) | | |
| *Nannochloropsis* | 200-450 | 310 | 200-450 | 275 | 200-450 | 353 | 10 | [5] |
| *Chlorella* | 150-350 | 290 | 150-350 | 290 | – | – | 10 | [12] |
| *Tetraselmis suecica* | 150-350 | 290 | 150-350 | 290 | – | – | 10 | [12] |
| *C. vulgaris ESP-31* | 210-310 | 290 | 110-420 | 310 | 150-515 | 380 | 10 | [9] |
| *C. vulgaris ESP-31* | 231-309 | 280 | 185-467 | 360 | 200-635 | 450 | 10 | [10] |
| *N. oceanica CY2* | 209-304 | 280 | 164-408 | 320 | 209-540 | 420 | 10 | [10] |
| *C. sp. JSC4* | 209-295 | 270 | 181-449 | 360 | 226-518 | 420 | 10 | [10] |
| *A. platensis* | 250-500 | 340 | – | – | – | – | 10 | [11] |
| *C. reinhardtii* | 200-500 | 355 | – | – | 170-500 | 410 | 100 | [19] |
| *D. tertiolecta* | 200-500 | 300 | 220-400 | 270 | – | 450 | 5-20 | [20] |

and y-intercept of the resultant plot, respectively. Furthermore, the rate constant (k) can be calculated by eqn. 9. In this case, T is taken as the mean experimental temperature [18].

$$k = A.e^{\frac{-E_a}{RT}} \quad (9)$$

Table-1 represent the thermal decomposition temperature ranges of microalgae components deduced from previous works by different authors. In present interpretation of the temperature ranges, conversions of 5% and 95% were used as the start and end of decomposition, respectively. For the given literature survey, it is clear that there is good agreement between researchers with regards to the thermal decomposition temperature ranges of protein, carbohydrate and lipids in microalgae. Furthermore, it is learned that the thermal decomposition of protein and carbohydrate have a short temperature range of 200-500 and 110-450 ºC, whereas that of lipid occurs in a rather long range of 150-635 ºC. This implies that for the decomposition of microalgae, the decomposition of the individual components will overlap and may result in interactions with each other. Furthermore, the interactions between protein and carbohydrate decomposition might be significant because their peak decomposition temperatures are approximately the same as evidenced by the data presented in Table-1.

## RESULTS AND DISCUSSION

**Characteristics of microalgae:** The proximate analysis results of microalgae are presented in Table-2. It is clear that algal biomass has a considerably higher and lower volatile and carbon contents, respectively. Generally, the low O/C and high H/C molar ratios of algal biomass is an indication of large amounts of aliphatic hydrocarbons and low amounts of polar compounds, respectively. Most woody biomass materials have higher O/C ratio indicating that wood has a high proportion of polar compounds. However, the ash content in this microalgae is significantly high, this is attributed to the presence of frustules [21]. Furthermore, algae uses silica from its culture medium for cell wall strength and this manifests as a high ash content [22].

**Model DTG curves for pseudo components:** Fig. 1 shows the DTG curves of microalgae at different heating rates [(a) 10; (b) 50; (c) 100; (d) 200 ºC/min]. Deconvoluted curves representing the individual decomposition of the pseudo components are also included. A summation of the individual contributions of the pseudo components results in an overall DTG model that can be compared with experimental data. The DTG models for the four heating rates fit the experimental curves with high correlation coefficient ($R^2 > 0.99$). Therefore, these deconvoluted DTG curves can be used to precisely describe the pyrolysis behaviours of the components in microalgae. With deconvoluted DTG curves, the precise position of the peaks can be determined. It has been shown that microalgae is composed of proteins, carbohydrates and lipids that decompose in the approximate temperature ranges 200- 450, 180-450 and above 200-600 ºC, respectively [5,11,12,19,20]. The components decomposition temperatures deduced from the models are presented in Table-2.

TABLE-2
PROXIMATE AND ULTIMATE ANALYSIS OF *Scenedesmus* sp. ALGAL BIOMASS

| Proximate (dry basis) | % |
|---|---|
| Volatiles | 78.5 |
| Ash | 10.4 |
| Fixed carbon | 11.1 |
| **Ultimate (dry ash free basis)** | **%** |
| Carbon | 45.6 |
| Hydrogen | 6.50 |
| Nitrogen | 11.1 |
| Sulphur | 0.48 |
| Oxygen | 36.2 |
| O/C molar ratio | 0.60 |
| H/C molar ratio | 1.71 |

**Thermal decomposition behaviour:** Thermal decomposition behaviour of algal biomass can be analyzed using Fig. 1. Generally, it is clear that at high heating rates (> 50 ºC/min), decomposition goes to completion at a lower temperature of 650 ºC compared to 700 ºC at 10 ºC/min. Microalgae shows two distinct decomposition peaks at 210-400 and 500-750 ºC at a heating rate of 10 ºC/min. The first peak with a right hand shoulder corresponds to the combined decomposition of proteins and carbohydrates. The second peak is most likely the decomposition of lipids [23-25]. However at higher heating rates (50, 100 and 200 ºC/min), the second peak appears as a right hand shoulder of the first peak. This observation is evidence that the decomposition behaviour of microalgae changes significantly when the heating rate is increased. Microalgae displays highest reactivity at 283, 333, 339 and 333 ºC for heating rates of 10, 50, 100 and 200 ºC/min, respectively. There is a considerable

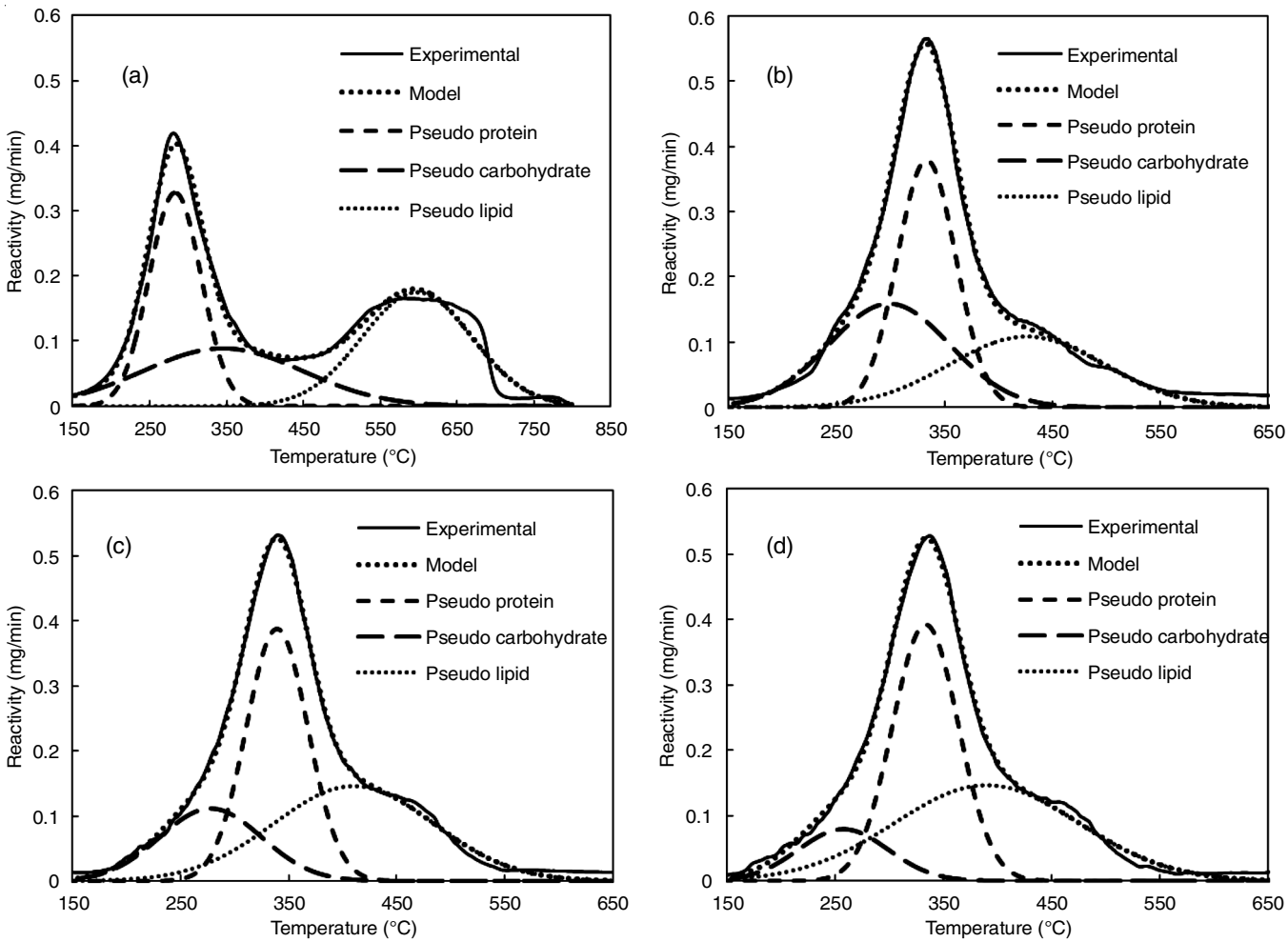


Fig. 1. DTG curves of microalgae at different heating rates

change in the peak temperatures when the heating rate is increased from 10 to 50 ºC/min compared to the change from 50 to 200 ºC/min. Mishra and Mohanty [26] have attributed this observation to heat transfer effects. At low heating rates, the temperature profile is almost the same throughout the structure of the material because of a long residence time. However, at high heating rates, there is a large temperature gradient across the cross section of the material. The inner core of the material will have a lower temperature compared to the surface. Because of this thermal lag, the decomposition peaks will show at higher temperatures.

The deconvoluted curves revealed that the high reactivity of microalgae is due to protein whose peak decomposition temperatures are 283, 333, 339 and 333 ºC, at heating rates of 10, 50, 100 and 200 ºC/min respectively. This observation is consistent with the work of Wang *et al*. [5] and Kassim *et al*. [12] who experimentally isolated the components of microalgae and showed that the reactivity of protein is highest and occurs at the same time with carbohydrates at approximately 287-290 ºC. Furthermore, Wang *et al*. [5] proposed the peak decomposition temperature of protein as 310 ºC which is within the range reported in present work. It is clear that the heating rate has an effect on the thermal decomposition behaviour of the individual components. Table-3 shows the decomposition temperature characteristics of the microalgae components. It can be seen that the peak temperatures of protein shift to the right as the heating rate is increased whilst those of carbohydrate and lipid shift to the left. This implies that the thermal decomposition events for protein tend to occur at higher temperatures when the heating rate is increased. On the other hand, the thermal decomposition events for carbohydrate and lipid occur at a lower temperature when the heating rate is increased. The effect

TABLE-3
TEMPERATURE CHARACTERISTICS OF PROTEINS, CARBOHYDRATES AND LIPIDS

| | Heating rate (°C/min) | Start temp. (°C) | Peak temp. (°C) | End temp. (°C) |
|---|---|---|---|---|
| Protein | 10 | 150 | 283 | 400 |
| Carbohydrate | 10 | 150 | 345 | 650 |
| Lipid | 10 | 350 | 597 | 800 |
| Protein | 50 | 250 | 333 | 450 |
| Carbohydrate | 50 | 150 | 298 | 450 |
| Lipid | 50 | 250 | 426 | 650 |
| Protein | 100 | 250 | 339 | 450 |
| Carbohydrate | 100 | 150 | 278 | 450 |
| Lipid | 100 | 200 | 410 | 650 |
| Protein | 200 | 250 | 333 | 450 |
| Carbohydrate | 200 | 150 | 258 | 400 |
| Lipid | 200 | 150 | 390 | 600 |

is very clear for lipids, considering the disappearance of the single second peak at high heating rates.

Further analysis of the DTG curves presented in Fig. 1 reveals that the thermal reactivity of carbohydrate increases with an increase in heating rate from 10 to 50 ºC/min. On the contrary, the reactivity of protein and lipid decrease when the heating rate is increased from 10 to 50 ºC/min. This observed behaviour can be attributed to the shift and subsequent overlap of the individual decomposition thermal events. The overlap of the individual thermal events at high temperatures may result in interactions that have a synergistic effect on the thermal decomposition of carbohydrates. Similar synergistic effects on lipids decomposition are observed when the heating rate is increased from 50 to 200 ºC/min.

**Coats-Redfern kinetics:** Table-4 shows the Coats-Redfern kinetic parameters evaluated according to eqns. 1-9. Protein and carbohydrate thermal decomposition is fitted to second order kinetics with high coefficients of determination ($R^2 > 0.95$). On the other hand, thermal decomposition of lipid fits to first order kinetics well. Therefore, in the experimental conditions used in the present work (i.e. high heating rates), the thermal decomposition of protein follows second order kinetics with activation energy in the range of 225.3–255.6 kJ/mol, pre-exponential factor range of $1.1 \times 10^{20}$–$7.2 \times 10^{22}$ $min^{-1}$ and rate constant of 14-26.1 $min^{-1}$. The thermal decomposition of carbohydrate also follows second order kinetics with activation energy in the range of 87.2–101.1 kJ/mol, pre-exponential factor range of $2.1 \times 10^{8}$–$9.6 \times 10^{10}$ $min^{-1}$ and rate constant of 2.38–7.72 $min^{-1}$. The thermal decomposition of lipid follows first order kinetics with activation energy in the range of 45–64.8 kJ/mol, pre-exponential factor range of $3.6 \times 10^{3}$–$3.2 \times 10^{4}$ $min^{-1}$ and rate constant of 0.32-1.16 $min^{-1}$. A short literature survey reveals that generally there is conflict in the results presented by different researchers. Debiagi *et al.* [11] reported the activation energy of protein, carbohydrate and lipid to be 15.5, 26 and 49.7 kcal/mol (64.8, 108.8 and 207.9 kJ/mol), respectively. Chen *et al.* [10] reported the first order kinetics activation energy of protein, carbohydrate and lipid to be in the range of 142.6-188.2, 53.2-53.3 and 40.2-59.2 kJ/mol respectively. Bach and Chen [9] in their three reaction models, revealed that the activation energy of protein, carbohydrate and lipid were 208.8, 40.4 and 48.5 kJ/mol, respectively. Kim *et al.* [20] studied the thermal decomposition of a lipid extracted but protein rich microalgae residue and found that the activation energies of carbohydrate and protein were in the ranges of 102.5-124 and 157.1-284 kJ/mol, respectively. Clearly, the results of present study compare well with the works of Bach and Chen [9] for protein and lipid, Kim *et al.* [20] for carbohydrate and protein and Debiagi *et al.* [11] for carbohydrates. However, as expected, there is some conflict with some of the results that have been presented so far. The differences in kinetic parameters presented by present work and other researchers is due to the two main reasons: (i) the method of component isolation *i.e.* experimental isolation or deconvolution of TGA data and (ii) the analysis method used to deduce kinetic data.

## Conclusion

In this work, the use of a suitable software to model the DTG plots for the thermal decomposition of *Scenedesmus* sp. microalgae and its constituent components at high heating rates is demonstrated. The model curves generated predicted the experimental data well, this was evidenced by high coefficients of determination ($R^2 > 0.99$). Further, the Coats-Redfern kinetic analysis method was successfully applied to the modelled data so as to determine each of the component's thermal decomposition kinetic parameters. Present study has revealed that of the three major constituents of *Scenedesmus* sp. microalgae, protein shows highest thermal decomposition reactivity. Furthermore, this work also managed to show that the thermal decomposition kinetics of proteins, carbohydrates and lipids in microalgae can be studied without the need of experimentally isolating the individual components.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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TABLE-4
COATS-REDFERN THERMAL DECOMPOSITION KINETIC PARAMETERS FOR PROTEIN, CARBOHYDRATE AND LIPID

| Component | Heating rate (°C/min) | First-order | | | | Second-order | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $E_a$ (kJ/mol) | A (1/min) | k (1/min) | $R^2$ | $E_a$ (kJ/mol) | A (1/min) | k (1/min) | $R^2$ |
| Protein | 50 | 129.1 | $9.1 \times 10^{10}$ | 1.33 | 0.92 | 255.6 | $7.2 \times 10^{22}$ | 26.1 | 0.95 |
| | 100 | 130.3 | $1.9 \times 10^{11}$ | 2.20 | 0.93 | 229.8 | $4.5 \times 10^{20}$ | 24.2 | 0.97 |
| | 200 | 110.9 | $9.8 \times 10^{9}$ | 4.91 | 0.94 | 225.3 | $1.1 \times 10^{20}$ | 14.0 | 0.95 |
| Carbohydrate | 50 | 56.4 | $6.4 \times 10^{4}$ | 0.47 | 0.96 | 87.2 | $2.1 \times 10^{8}$ | 2.38 | 0.95 |
| | 100 | 65.0 | $1.7 \times 10^{6}$ | 1.07 | 0.96 | 97.7 | $9.8 \times 10^{9}$ | 4.76 | 0.96 |
| | 200 | 70.1 | $2.3 \times 10^{7}$ | 2.28 | 0.96 | 101.1 | $9.6 \times 10^{10}$ | 7.72 | 0.98 |
| Lipid | 50 | 64.8 | $2.3 \times 10^{4}$ | 0.32 | 0.97 | 99.1 | $5.3 \times 10^{7}$ | 2.04 | 0.95 |
| | 100 | 60.9 | $3.2 \times 10^{4}$ | 0.61 | 0.97 | 89.2 | $2.2 \times 10^{7}$ | 2.66 | 0.95 |
| | 200 | 45.0 | $3.6 \times 10^{3}$ | 1.16 | 0.97 | 72.6 | $3.7 \times 10^{6}$ | 8.52 | 0.93 |

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