

## Effects of Algal Biomass Blending on Coal Decomposition Behaviour and Kinetics at Intermediate Pyrolysis Regimes

BOTHWELL NYONI<sup>1</sup>, PHUTI TSIPA<sup>1</sup>, HALEDEN CHIRIRIWA<sup>2,\*</sup> and SHANGANYANE HLANGOTHI<sup>1</sup>

<sup>1</sup>Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa

<sup>2</sup>Department of Chemical Engineering, Vaal University of Technology, P. Bag X021, Vanderbijlpark, 1911, South Africa

\*Corresponding author: Fax:+ 27 16 950 9999; Tel: +27 16 950 9884; E-mail: [harrychiririwa@yahoo.com](mailto:harrychiririwa@yahoo.com)

Received: 16 November 2020;

Accepted: 20 April 2021;

Published online: 5 June 2021;

AJC-20371

Co-pyrolysis of coal with biomass is becoming a popular method of reducing the net carbon dioxide emissions associated with the process. In present work, the pyrolysis of coal and algae was studied using thermogravimetric methods and the kinetics were analyzed using the Coats-Redfern integral method. The kinetics were evaluated for 1<sup>st</sup> and 2<sup>nd</sup> order reaction models. The effect brought by blending coal with algae on kinetics was studied *via* the analysis of pyrolysis of different coal-algae blends. The results revealed that the pyrolysis of coal and algae follows 2<sup>nd</sup> and 1<sup>st</sup> order kinetics with activation energy evaluated in the range 213.4-241.8 and 108.9-122.8 kJ/mol, respectively. It was observed that for coal-algae blending of 20-40% algae, intermediate pyrolysis, typical heating rates of 50-200 °C/min was characterized by two distinct stages (ignoring the drying stage) that correspond to the individual decomposition of algae and coal. However, there was an evidence of coal-algae interactions during co-pyrolysis, which made the kinetics of the two distinct stages not to correspond to the kinetics of the individual materials.

**Keywords:** Algae, Blends, Coal, Coats-Redfern, Pyrolysis, Thermogravimetry.

### INTRODUCTION

Coal is the most abundant solid fuel resource. Countries that have the largest reserves (per region) are South Africa and Zimbabwe (Africa), USA and Canada (North America), Brazil and Colombia (South-Central America), Russia and Germany (Europe), China and Australia (Asia-Pacific) [1]. Coal has been used in large scale pyrolysis processes for the production of a high energy coal char (coke) using a method that was developed in the turn of the 20<sup>th</sup> century [2]. However, the use of coal is associated with the emission of green-house gases (GHG) that are believed to be the major cause of climate change and global warming [3,4]. To reduce the emissions of GHG associated with the pyrolysis of coal, researchers are exploring the route of co-pyrolysis with biomass. Biomass has the major advantage of its carbon neutralness. Biomass can be viewed as a natural carbon capture and a store of solar energy because it is a product of photosynthesis, a process that uses solar energy and carbon dioxide from the atmosphere as inputs [5,6]. Algae is a special type of biomass that is composed of

proteins, lipids and carbohydrates [7]. Furthermore, microalgae can grow in fresh water with a supply of carbon dioxide from industrial emissions [8]. A number of researchers have studied the pyrolysis of coal, biomass, coal-biomass blends and other materials [9-15]. An important aspect in the study of pyrolysis is the kinetics of the process itself. In pyrolysis kinetics research, different methods can be used to analyze mass-loss data generated during thermogravimetric analysis (TGA) [16]. Wang *et al.* [17] used the distributed activation energy model (DAEM) to fit pyrolysis kinetics of a low rank Mongolia Xinghe coal. The results of their study showed that for the type of coal they used, the kinetic parameters, *i.e.* activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were 186.5 kJ/mol and  $3.96 \times 10^{10} \text{ s}^{-1}$ . Other kinetic methods such as the Coats-Redfern, Kissinger-Akahira-Sunose, Ozawa-Flynn-Wall and Friedman methods have been used in the kinetic analysis of the pyrolysis of different types of biomass [8,18]. In co-pyrolysis of coal and algae, Kirtania & Bhattacharya [12] investigated the kinetics of the pyrolysis process using the DAEM method. It was found that the activation energies of coal and algae were 219.9 and 190.0

kJ/mol, respectively, for a heating rate range of 5-20 °C/min. Furthermore, no interactions between the coal and algae were detected. As such, the activation energies of the coal-algae blends were distributed between that of coal and algae. The majority of the research [12,18,19] that has been done with regards to pyrolysis kinetics of coal-biomass blends has explored only the low and narrow heating rates range that correspond to slow pyrolysis processes.

The objective of this study is to explore the pyrolysis kinetics at higher heating rates (intermediate pyrolysis). For example, this work must be able to give an insight as to what happens to the decomposition kinetics at higher heating rates (intermediate pyrolysis) commonly employed by state of the art biomass pyrolysis reactors. It is with this background that the pyrolysis kinetics of coal-algae will be explored at higher heating rates (50-200 °C/min). When exploring this region of heating rates, care must be taken in selecting the kinetic methods for use during analysis. There are two common approaches to pyrolysis kinetics analysis: (i) model fitting and (ii) model free methods [20]. The difference between the approaches is that model fitting techniques require an assumption of the order of reaction before the evaluation of kinetic parameters such as the activation energy, rate constant and half-life. Whereas, model free methods known as iso-conversional methods can predict the kinetic parameters without knowledge of the order of reaction. Model free methods require sets of mass-loss data at different heating rates in order to make a sufficient kinetic analysis. As such, these methods are suitable for a narrow range of heating rates. The methods include the Kissinger-Akahira-Sunose and Ozawa-Flynn-Wall, to name a few. The Coats-Redfern method is a common model fitting technique that can be used to evaluate kinetic parameters from a single mass loss curve, if a reaction order is guessed accurately [21-23]. For this reason, the Coats-Redfern model fitting technique was used for this study because it can allow for the testing of  $n^{\text{th}}$  order kinetics.

A number of studies have been conducted for kinetics of conventional pyrolysis of coal, biomass or their blends. This study is important in the sense that it investigates the effects on pyrolysis behaviour and kinetics of coal when algal biomass is added. Furthermore, the investigation is not only done for conventional pyrolysis but also higher heating rates. The high heating rates employed in this study correspond to intermediate pyrolysis regime. State of the art industrial pyrolysis reactors for the processing of biomass operate in the intermediate pyrolysis regime [24].

## EXPERIMENTAL

Coal was obtained from a commercial supplier based in Port Elizabeth, Eastern Cape province of South Africa. Algal biomass (*Scenedesmus* sp.) was cultivated at Innoventon, Downstream Chemicals Technology Station at Nelson Mandela University, South Africa. The coal-algae blends were made by mixing a known amount of coal with an algae slurry of known solids concentration. The resultant paste was centrifuged and then sun dried for 48 h. Proximate and ultimate analyses of the samples were done according to the following ASTM methods

D3172-07a, E871, E872 and D4239. The calorific value was determined by using a bomb calorimeter (Leco AC 600) following the standard method D5865-10a.

**Thermogravimetric analysis:** Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TA Instruments, Discovery TGA-5500). Each sample was subjected to a temperature increase under an inert nitrogen atmosphere. TGA runs were performed on each sample at different heating rates of 10, 50, 100 and 200 °C/min. The coal-algae blends explored in this study contained 20, 30 and 40% algae content and their samples will be subsequently referred to as CA20, CA30 and CA40, respectively.

**Kinetic study:** For the reasons already mentioned, the Coats-Redfern integral method was used to evaluate the 1<sup>st</sup> and 2<sup>nd</sup> order kinetics. The kinetics of decomposition of a coal-algae sample to form volatiles and solid residue can be modelled as a function of conversion as illustrated in previous works [21-23].

## RESULTS AND DISCUSSION

**Ultimate and proximate analysis:** The ultimate analysis and energy content of coal and algae samples are presented in Table-1. The calorific values for the algae is comparable with that of coal, this indicates that there is a huge potential of using algae as an energy source. Generally, the low O/C and high H/C molar ratios displayed by algae is an indication of large amounts of aliphatic hydrocarbons and low amounts of polar compounds, respectively. This property makes algae a suitable alternative fuel source. The proximate analysis of coal, algae and their blends is shown in Table-2. Compared to coal, it is clear that algae has a considerably higher and lower volatile and carbon content, respectively. Therefore, algal biomass is expected to have higher pyrolysis reactivity. However, currently it is uneconomical to use algae alone instead of coal, therefore there is need to blend coal with small amounts of algae. Table-2 presents the proximate analysis results of coal-algae blends. It is clear that the blending of coal with algae results in a composite that has proximate properties emanating from proportionate individual contributions of coal and algae.

TABLE-1  
ULTIMATE AND ENERGY PROPERTIES OF COAL AND ALGAE

	Coal	Algae
Carbon (%)	63.6	45.6
Hydrogen (%)	3.64	6.50
Nitrogen (%)	1.57	11.1
Sulphur (%)	0.49	0.48
Oxygen (%)	30.7	36.3
O/C molar ratio	0.36	0.60
H/C molar ratio	0.69	1.71
Calorific value (MJ/kg)	27.8	23.4

TABLE-2  
PROXIMATE ANALYSIS OF COAL, ALGAE  
AND THEIR BLENDS (DRY BASIS)

	Coal	Algae	CA20	CA30	CA40
Volatiles (%)	27.5	78.5	36.9	41.9	47.2
Ash (%)	15.7	10.4	14.2	13.7	13.5
Fixed carbon (%)	56.8	11.1	48.9	44.4	39.3

**Thermal decomposition behaviour:** Fig. 1 shows the derivative mass-loss (DTG) curves of coal and algae at increasing heating rates (ignoring the drying stage). The DTG curves for both coal and algae at 10 °C/min display considerable differences from those at higher heating rates. By comparing the peak heights, it can be said that algal biomass has higher pyrolysis reactivity than coal. Specifically at 10 °C/min, algal biomass is approximately three times more reactive than coal. Interestingly, at higher heating rates, the magnitude of the difference in reactivity between algae and coal is reduced. This observation is attributed to coal's sharp change in heat and mass transfer properties at higher heating rates [25]. The DTG curves for 10 °C/min reveal some major decomposition events (in the form of peaks and shoulders) in the pyrolysis temperature range studied. The DTG curve for coal exhibits a broad peak that represents the decomposition of the aliphatic constituents of coal in the temperature range 280-700 °C. Another distinct peak that represents the decomposition of the aromatic and hydro-aromatic structures appears in the temperature range 750-850 °C [21]. As for algal biomass, the three shoulders on the peak correspond to the decomposition of proteins, carbohydrates and lipids [12,13,26]. These decomposition events occur at a narrow temperature range of 200-500 °C. The three shoulders that occur in the approximate temperatures of 270, 320 and 400 °C represent the decomposition of carbohydrates, proteins and lipids, respectively [27,28]. Most of the present observations correspond with other works in literature [12,29-31].

Fig. 1a further shows that at higher heating rates (> 50 °C/min) coal displays a different behaviour, firstly, the two peaks that show at lower heating rates seem to have overlapped to form one which displays higher reactivity. This observation can be attributed to the sudden improvement in mass and heat transfer phenomena that occurs within the crystalline structure of the coal. Increasing the heating rate from 50 to 200 °C/min results in little change on the pyrolysis behaviour of coal. The observed behaviour of coal at high heating rates is also reported by Dwivedi *et al.* [32]. A similar effect is displayed in algae

pyrolysis (Fig. 1b). Three decomposition shoulders combine to form one peak. However, for algae, increasing the heating rate slightly shifts the DTG curves to the right along the horizontal axis. This means that at higher heating rates, the decomposition events occur at higher temperatures.

To understand the pyrolysis behaviour of coal, algae and their blends, TG and DTG curves at a heating rate of 10 °C/min are shown in Fig. 2. The thermogravimetric curves show that the maximum temperature for algae decomposition is 600 °C, any further increase in temperature results in a negligible or no further mass change. Also coal shows a continuing but slow decomposition beyond 800 °C. DTG plots shown in Fig. 2b give us an insight on the pyrolysis reactivity of the materials. Furthermore, as expected, Fig. 2 shows that the TG and DTG curves of the coal-algae blends lie in between those of coal and algae. It is clear that the higher the algae loading the higher the reactivity of the resultant blend.

The DTG plots for coal, algae and their blends at heating rates of 50, 100 and 200 °C/min are shown in Fig. 3. The plots give us an insight on the pyrolysis behaviour of different coal-algae blends at different heating rates. Even though coal and algae display two and three stage decomposition, respectively at low heating rates, it has been revealed that at higher heating rates, their decomposition show one distinct stage (Fig. 1). The coal-algae blends show two distinct stages that occur at temperature ranges of 250-350 and 440-520 °C. These two stages appear to be individual contribution from algae and coal. It is clear that the reactivity of the blends increases with an increase in the algae content, also, there is evidence of an increase of reactivity due to increasing the heating rate. These observations are also consistent with the works of Lu *et al.* [33]. From the TG and DTG curves, the pyrolysis temperature characteristics of coal, algae and their blends are deduced and presented in Table-3. It is clear from Table-3 that at higher heating rates, increasing the heating rate for coal-algae blends results in negligible change in the pyrolysis peak temperatures for the first stage, however, the peak temperatures for the second decomposition stage are

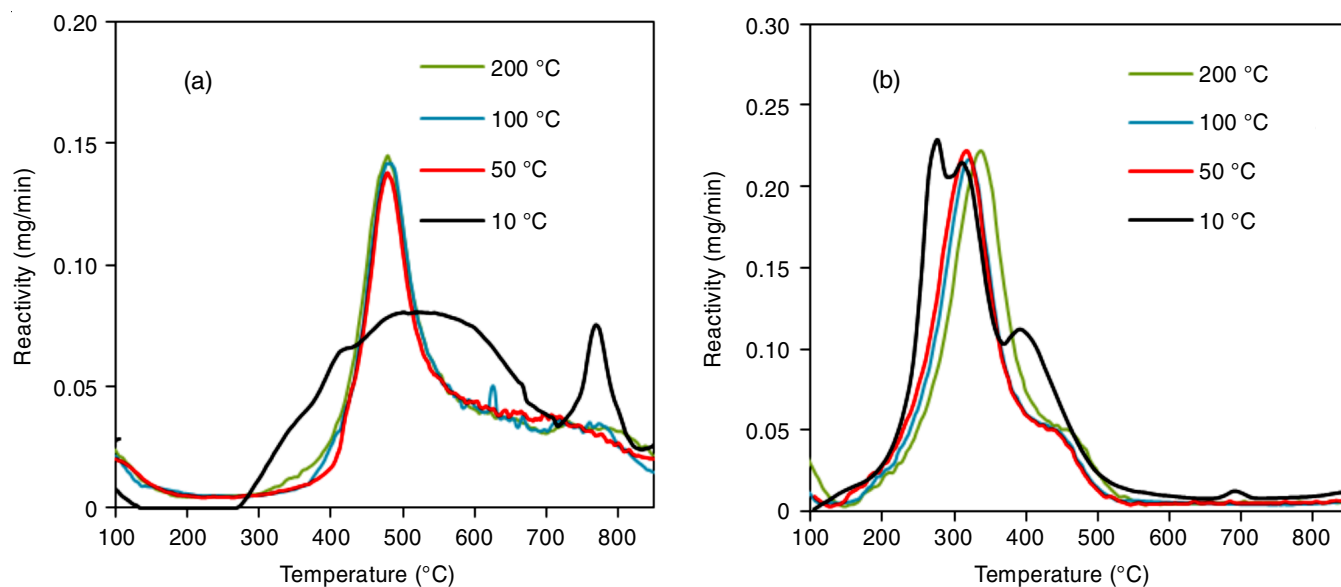


Fig. 1. DTG plots for coal (a) and algae (b) at increasing heating rates

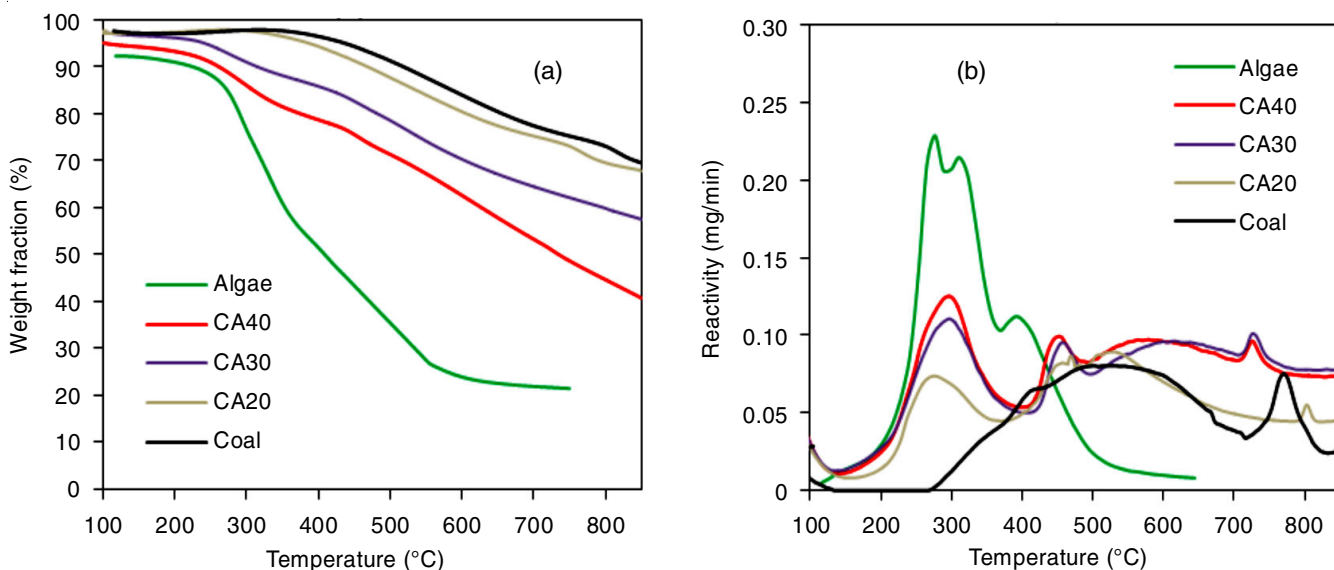


Fig. 2. TGA (a) and DTG (b) plots for coal, algae and blends at a heating rate 10 °C/min

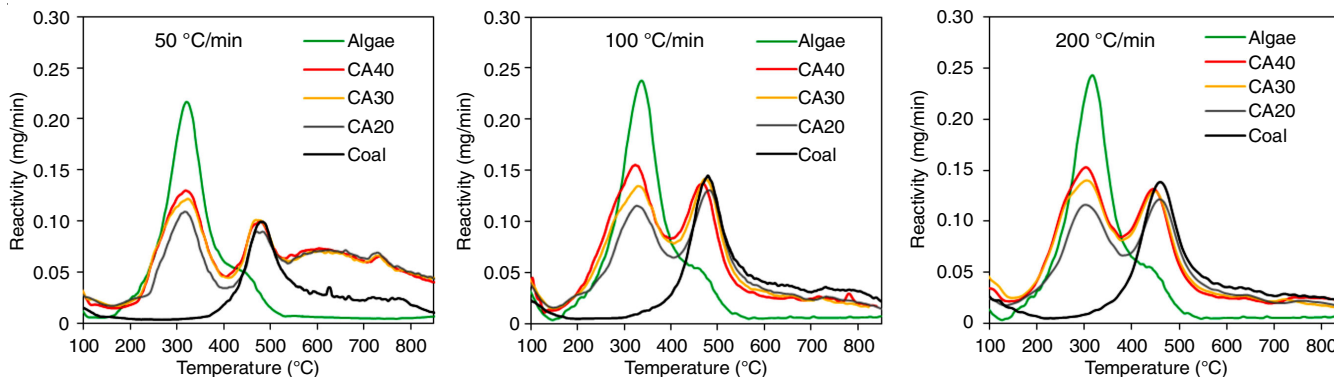


Fig. 3. DTG plots for coal, algae and their blends at different heating rates

TABLE-3  
PYROLYSIS CHARACTERISTICS OF COAL, ALGAE AND THEIR BLENDS AT DIFFERENT HEATING RATES

Sample	Heating rate (°C/min)	Stage 1			Stage 2		
		Start temp. (°C)	Peak temp. (°C)	End temp. (°C)	Start temp. (°C)	Peak temp. (°C)	End temp. (°C)
Algae	10	200	280	380	380	405	700
CA20	10	200	290	380	410	510	750
CA30	10	200	310	390	410	460	500
CA40	10	200	310	390	410	460	500
Coal	10	280	530	700	720	780	820
Algae	50	200	310	550	-	-	-
CA20	50	200	320	390	430	500	800
CA30	50	200	330	390	430	490	800
CA40	50	200	330	390	430	480	800
Coal	50	400	480	800	-	-	-
Algae	100	190	330	550	-	-	-
CA20	100	190	320	390	420	470	650
CA30	100	190	330	400	420	450	650
CA40	100	190	330	400	420	450	650
Coal	100	400	470	700	-	-	-
Algae	200	180	310	530	-	-	-
CA20	200	180	300	380	410	460	650
CA30	200	180	310	380	410	440	650
CA40	200	180	310	380	410	440	650
Coal	200	400	460	700	-	-	-

reduced. Furthermore, increasing the algae ratio increases and decreases the peak temperatures of the first and second decomposition stages, respectively. These observations can be attributed to the heat and mass transfer phenomena that occur within the crystalline structure of the solid fuel. At low heating rates there is a general resistance to heat and mass transfer which is easy to overcome at higher heating rates [25].

**Decomposition kinetics:** Kinetics results generated from linear plots of the Coats-Redfern equation are presented in Table-4. For the evaluation of first stage decomposition kinetics of algae, the linear plots show higher coefficients of determination for 1<sup>st</sup> order compared to 2<sup>nd</sup> order. This implies that the first stage pyrolysis kinetics of algae fits 1<sup>st</sup> order better than 2<sup>nd</sup> order kinetics. Considering the 1<sup>st</sup> order kinetic parameters, algae has a one stage pyrolysis activation energy of 108.9-130.3 kJ/mol and a rate constant of 0.32-4.82 min<sup>-1</sup> for the studied heating rate range of 10-200 °C/min. For the same range of heating rates, coal pyrolysis shows a first stage 2<sup>nd</sup> order decomposition kinetics with activation energy of 213.4-245.7 kJ/mol, rate constant of 0.44-11.4 min<sup>-1</sup>. As for the coal-algae blends, at the same heating rate range, their first stage decomposition follow 1<sup>st</sup> order kinetics. The magnitudes of their activation energies are closer to that of algae indicating that the first stage decomposition in the blends is mainly due to algae. Furthermore, by extrapolation, it seems an increase in algae content may result in the activation energies of the blends becoming lower than that of the parent algae material. However, it was not possible to study coal-algae blends of > 40% algae loading because of the general economic implications if such blends were to be used at a commercial scale. Some of these observations and kinetic results are consistent with the works of Kirtania & Bhattacharya [12] and Bhagavatula *et al.* [34]. The results for the second stage decomposition revealed that

at low heating rates the kinetics generally follow 1<sup>st</sup> order. As expected, the activation energies for the second stage decomposition are almost of the same magnitude as that of coal, twice the amount of energy needed for the first stage. This can be attributed to the breaking of heat resistant aromatic bonds found mostly in coal [31]. It could have been expected that the second stage decomposition kinetics of coal-algae follows 2<sup>nd</sup> order similarly to coal. However, the kinetics follow 1<sup>st</sup> order and this can be attributed to interactions during pyrolysis between algae and coal. These interactions manifest as a change of process parameters obtained experimentally from the expected theoretical (calculated) ones [35]. In this case, it was expected that the second stage decomposition of coal-algae blends will follow 2<sup>nd</sup> order kinetics similarly to coal, however, results point out that the decomposition follows 1<sup>st</sup> order kinetics. The coal-algae interactions can manifest as synergistic or inhibitive. This is a research field that has generated conflicting results amongst different authors. For example, no synergistic effects were observed by some researchers where the pyrolysis behaviours of coal-biomass blends were studied [9,11]. On the contrary, other researchers have pointed out some synergistic effects in their studies of pyrolysis of coal-biomass blends [15,34,36,37].

## Conclusion

This work reported the pyrolysis behaviour and kinetics of coal, algae and their blends at conventional and high heating rates (10 and 50-200 °C/min, respectively). The objective was to explore the effects of blending coal with algal biomass at different heating rates. Firstly, blending coal with algae increases the volatile content and therefore for obvious reasons, coal-algae blends have higher pyrolysis reactivity than coal. Secondly, there is a huge change in the pyrolytic behaviour of coal, algae

TABLE-4  
1<sup>st</sup> AND 2<sup>nd</sup> -ORDER CR KINETIC PARAMETERS FOR THE PYROLYSIS OF COAL, ALGAE AND THEIR BLENDS

Heating rate (°C/min)	1 <sup>st</sup> order						2 <sup>nd</sup> order						
	Stage 1			Stage 2			Stage 1			Stage 2			
	Plot R <sup>2</sup>	E <sub>a</sub> (kJ/mol)	k (min <sup>-1</sup> )	Plot R <sup>2</sup>	E <sub>a</sub> (kJ/mol)	k (min <sup>-1</sup> )	Plot R <sup>2</sup>	E <sub>a</sub> (kJ/mol)	k (min <sup>-1</sup> )	Plot R <sup>2</sup>	E <sub>a</sub> (kJ/mol)	k (min <sup>-1</sup> )	
Coal	10	-	-	0.94	134.7	0.15	-	-	-	0.94	213.4	0.44	
	50	-	-	0.93	143.9	1.02	-	-	-	0.95	237.3	3.76	
	100	-	-	0.93	149.2	2.04	-	-	-	0.96	245.7	7.47	
	200	-	-	0.94	146.7	3.38	-	-	-	0.96	241.8	11.4	
Algae	10	0.95	122.8	0.32	-	-	0.95	184.3	1.05	-	-	-	
	50	0.98	130.3	0.96	-	-	0.95	190.4	2.51	-	-	-	
	100	0.96	114.4	1.93	-	-	0.96	174.9	6.01	-	-	-	
	200	0.95	108.9	4.82	-	-	0.97	183.5	18.4	-	-	-	
CA20	10	0.95	109.9	0.43	0.99	444.5	1.02	0.94	166.6	1.74	0.91	745.1	1.66
	50	0.98	125.3	0.83	0.93	371.8	1.42	0.94	175.6	1.85	0.94	485.5	3.49
	100	0.96	117.6	1.96	0.95	303.9	2.92	0.95	201.9	4.82	0.96	430.5	7.16
	200	0.98	117.6	5.49	0.97	252.0	6.52	0.96	216.2	16.3	0.97	394.3	19.0
CA30	10	0.97	101.5	0.39	0.99	502.5	1.61	0.94	149.4	1.47	0.92	803.3	3.85
	50	0.99	125.2	0.85	0.99	367.5	1.25	0.94	177.9	1.91	0.96	425.7	5.89
	100	0.97	121.5	2.50	0.92	287.1	3.12	0.95	191.4	7.73	0.95	413.8	8.13
	200	0.98	119.5	4.91	0.97	244.6	7.08	0.96	193.2	15.4	0.97	395.9	22.7
CA40	10	0.96	116.2	0.43	0.99	449.5	1.72	0.94	163.1	1.61	0.91	755.6	2.65
	50	0.93	118.9	0.80	0.99	324.4	1.40	0.94	168.3	1.74	0.92	463.6	3.85
	100	0.93	119.9	2.36	0.92	279.6	3.10	0.95	173.1	5.21	0.95	403.6	8.12
	200	0.94	114.9	4.86	0.99	206.7	7.06	0.95	189.2	15.4	0.95	391.9	25.8

and their blends at higher heating rates. Thirdly, there is evidence of interactions between algae and coal during pyrolysis because of deviations in the expected kinetic behaviour. Looking ahead, fast pyrolysis (heating rates > 1 000 °C/min) is gaining popularity, however, state of the art TGA instruments do not have the capability of attaining heating rates higher than 1000 °C/min. In light of this, the study focus must be on the development or improvement of current experimental methods to enable thermogravimetric analyses in the fast pyrolysis regime.

### ACKNOWLEDGEMENTS

The authors acknowledge the financial contribution to this work by the Centre for Rubber Science and Technology, Nelson Mandela University and Department of Chemical Engineering, Vaal University of Technology, South Africa.

### CONFLICT OF INTEREST

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

### REFERENCES

- BP, BP Statistical Review of World Energy (2014).
- L.C. Karrick, US Patent 24128627A (1934).
- B. Gervet, Coal Fire Emission Contributes to Global Warming (2007).
- EIA, International Energy Outlook (2016).
- P. Mckendry, *Bioresour. Technol.*, **83**, 37 (2002); [https://doi.org/10.1016/S0960-8524\(01\)00118-3](https://doi.org/10.1016/S0960-8524(01)00118-3)
- H.B. Goyal, D. Seal and R.C.Å. Saxena, *Renew. Sustain. Energy Rev.*, **12**, 504 (2008); <https://doi.org/10.1016/j.rser.2006.07.014>
- A. Demirbas and M. Fatih Demirbas, *Energy Convers. Manage.*, **52**, 163 (2011); <https://doi.org/10.1016/j.enconman.2010.06.055>
- R. Singh, B.B. Krishna, G. Mishra, J. Kumar and T. Bhaskar, *Renew. Energy*, **98**, 226 (2016); <https://doi.org/10.1016/j.renene.2016.03.023>
- E. Kastanaki, D. Vamvuka, P. Grammelis and E. Kakaras, *Fuel Process. Technol.*, **77-78**, 159 (2002); [https://doi.org/10.1016/S0378-3820\(02\)00049-8](https://doi.org/10.1016/S0378-3820(02)00049-8)
- Y.G. Pan, E. Velo and L. Puigjaner, *Fuel*, **75**, 412 (1995); [https://doi.org/10.1016/0016-2361\(95\)00275-8](https://doi.org/10.1016/0016-2361(95)00275-8)
- H.B. Vuthaluru, *Fuel Process. Technol.*, **85**, 141 (2004); [https://doi.org/10.1016/S0378-3820\(03\)00112-7](https://doi.org/10.1016/S0378-3820(03)00112-7)
- K. Kirtania and S. Bhattacharya, *Biomass Bioenergy*, **55**, 291 (2013); <https://doi.org/10.1016/j.biombioe.2013.02.019>
- K. Azizi, M.K. Moraveji and H.A. Najafabadi, *Bioresour. Technol.*, **243**, 481 (2017); <https://doi.org/10.1016/j.biortech.2017.06.155>
- Y. Zhang, Y. Zhang, P. Geng and R. Liu, *Energy Procedia*, **142**, 1382 (2017); <https://doi.org/10.1016/j.egypro.2017.12.523>
- C. Chen, X. Ma and Y. He, *Bioresour. Technol.*, **117**, 264 (2012); <https://doi.org/10.1016/j.biortech.2012.04.077>
- J. Cai, D. Xu, Z. Dong, X. Yu, Y. Yang, S.W. Banks and A.V. Bridgwater, *Renew. Sustain. Energy Rev.*, **82**, 2705 (2018); <https://doi.org/10.1016/j.rser.2017.09.113>
- J. Wang, W. Lian, P. Li, Z. Zhang, J. Yang, X. Hao, W. Huang and G. Guan, *Fuel*, **207**, 126 (2017); <https://doi.org/10.1016/j.fuel.2017.06.078>
- R.K. Mishra and K. Mohanty, *Bioresour. Technol.*, **251**, 63 (2018); <https://doi.org/10.1016/j.biortech.2017.12.029>
- Z. Wu, Y. Li, B. Zhang, W. Yang and B. Yang, *Bioresour. Technol.*, **271**, 202 (2019); <https://doi.org/10.1016/j.biortech.2018.09.076>
- A.I. Mabuda, N.S. Mamphweli and E.L. Meyer, *Renew. Sustain. Energy Rev.*, **53**, 1656 (2015); <https://doi.org/10.1016/j.rser.2015.07.038>
- B. Nyoni, P. Tsipa, S. Duma, S. Shabangu and S. Hlangothi, *Asian J. Chem.*, **32**, 2921 (2020); <https://doi.org/10.14233/ajchem.2020.22768>
- R. Ebrahimi-Kahrizangi and M.H. Abbasi, *Trans. Nonferr. Met. Soc. China*, **18**, 217 (2008); [https://doi.org/10.1016/S1003-6326\(08\)60039-4](https://doi.org/10.1016/S1003-6326(08)60039-4)
- S. Ramukutty and E. Ramachandran, *J. Cryst. Process. Technol.*, **4**, 71 (2014); <https://doi.org/10.4236/jcpt.2014.42010>
- A. Hornung, eds.: L. Rosendahl, Intermediate Pyrolysis of Biomass, Aston University, Woodhead: Cambridge (UK), pp. 172-186 (2013).
- X. Chen, L. Liu, L. Zhang, Y. Zhao and P. Qiu, *Energy Fuels*, **33**, 1267 (2019); <https://doi.org/10.1021/acs.energyfuels.8b03987>
- K. Keibelmann, A. Hornung, U. Karsten and G. Griffiths, *Biomass Bioenergy*, **49**, 38 (2013); <https://doi.org/10.1016/j.biombioe.2012.12.006>
- B. Nyoni, S. Duma, S.V. Shabangu and S.P. Hlangothi, *Nat. Resour. Res.*, **29**, 3943 (2020); <https://doi.org/10.1007/s11053-020-09687-3>
- Q.V. Bach and W.H. Chen, *Bioresour. Technol.*, **246**, 88 (2017); <https://doi.org/10.1016/j.biortech.2017.06.087>
- S. Qi, Y. Yan, C. Jinhui and Z. Yingying, *Energy Procedia*, **88**, 600 (2016); <https://doi.org/10.1016/j.egypro.2016.06.085>
- Z. Wu, W. Yang, X. Tian and B. Yang, *Energy Convers. Manage.*, **135**, 212 (2017); <https://doi.org/10.1016/j.enconman.2016.12.060>
- H. Baloyi and G. Dugmore, *J. Energy South. Afr.*, **30**, 1 (2019); <https://doi.org/10.17159/2413-3051/2019/v30i1a5452>
- K.K. Dwivedi, M.K. Chatterjee, M.K. Karmakar and A.K. Pramanick, *Int. J. Coal Sci. Technol.*, **6**, 102 (2019); <https://doi.org/10.1007/s40789-019-0236-7>
- K.M. Lu, W.J. Lee, W.H. Chen and T.C. Lin, *Appl. Energy*, **105**, 57 (2013); <https://doi.org/10.1016/j.apenergy.2012.12.050>
- A. Bhagavatula, N. Shah and R. Honaker, *Energy Fuels*, **30**, 10045 (2016); <https://doi.org/10.1021/acs.energyfuels.5b00692>
- C. Quan and N. Gao, *BioMed Res. Int.*, **2016**, 6197867 (2016); <https://doi.org/10.1155/2016/6197867>
- B. Nyoni, S. Duma, L. Bolo, S. Shabangu and S.P. Hlangothi, *Int. J. Coal Sci. Technol.*, **7**, 807 (2020); <https://doi.org/10.1007/s40789-020-00310-7>
- H. Shui, C. Shan, Z. Cai, Z. Wang, Z. Lei, S. Ren, C. Pan and H. Li, *Energy*, **36**, 6645 (2011); <https://doi.org/10.1016/j.energy.2011.08.046>