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Determination of the Activation Energy and Kinetics Properties of Algae (Sargassum Polycystum) via Thermogravimetric Analysis

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Algae is a potential third-generation biofuel sources that can be used to produce high quality liquid fuel. The physio-chemical properties of algae depend on the species type, of which can also vary with climate, geography and environmental conditions. In this study, the pyrolysis behaviour of a brown macroalgae, *Sargassum polycystum (SP)*, obtained along the coast of Desaru, Malaysia is characterised using a thermogravimeter. The thermal decomposition of the selected brown algae was carried out at the heating rate of 5, 10, 20 and 40 °Cmin^{-1}. A model-fitting method, which includes the most common reaction mechanism in solid-state decomposition processes is being used to predict the kinetic parameters for *Sargassum polycystum*. The results showed that the *Sargassum polycystum* macroalgae decomposition process follows the third-order of reaction, F3 with a highest correlation value of 0.94, at 15-70 % of conversion level. The average activation energy from all heating rates is found to be 19.09 kJ/mol with a pre-exponential value of 0.537 s^{-1}. An increase in heating rate results in the increase of activation energy and pre-exponential values.

1. Introduction

Renewable energy is getting attractive due to its clean and sustainable sources; moreover, efforts to reduce the carbon footprint on a worldly basis has drawn the interest in discovering new renewable energy sources. Biomass is a type of abundant yet renewable resource that is available in all parts of the world and in numerous varieties. It originates from plant and animal materials such as forestry wood, agriculture leftover, organic industrial and wastes from living creatures. Algae is a type of aquatic organism with photosynthetic ability, while the most commonly known algae are seaweeds. Algae stand out in comparison with terrestrial lignocellulosic biomass due to it is easily cultivated and is capable of CO_2 sequestration, making it a potential feedstock for bio-fuel production. In fact, algae have also been regarded as the third-generation biofuel source.

The thermochemical conversion process involves the usage of heat to decompose feedstock into simpler chemical compounds/substances within an oxidative or oxygen deficit environment. This process often involves numerous complicated chemical reactions occurring instantaneously, which prohibits the understanding of its reaction mechanism. Therefore, thermogravimetric analysis, TGA is commonly used as a tool to comprehend the solid-state decomposition kinetics that occurs during the thermal decomposition process (Mong et al., 2019). Isothermal and non-isothermal are two methods implemented in TGA. The latter method is more popular as it has better sensitivity towards experimental noise (Gai et al., 2013). Model-fitting and model-free method are two types of analysis methods used to evaluate mass loss curve from TGA, to obtain the kinetic triplets, namely activation energy, pre-exponential factor, and the kinetic model. Both

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methods have their pros and cons in the evaluation of the kinetics parameters and are recorded elsewhere in detailed (Vyazovkin and Wight, 1999).

Sargassum sp. (Brown algae) has been viewed as an invasive algae species that are blooming along the coastal line due to increasing seawater temperature, which might have a negative impact on the pelagic ecosystem and associate regional fisheries (Yamasaki et al., 2014). Thermal decomposition of Sargassum sp. might be an effective way of coping this issue. The previous study investigates two types of brown macroalgae*, L. japonica*, and *S. pallidum*, of which they are reported to follow the Avrami‑Erofeev (n=3) solid-state kinetics function, which might be due to the high concentration of inorganic salts that induce heterogeneous nucleation (Li et al., 2010). Another type of brown algae, *Sargassum* sp. from the Red Sea is reported to have five main components during thermal decomposition, which are water, hemicellulose, cellulose, lignin, and protein (Ali and Bahadar, 2017). Although brown algae belongs to the same Phaeophyta group, however, their composition and properties vary greatly depending on the habitat and environment. In this study, the mass loss behavior of *Sargassum polycystum* is investigated through TGA, then the kinetic properties are analysed through model-fitting method.

2. Methods

2.1 Materials preparation

In this study, SP was collected along the shores at Desaru beach, Johor, Malaysia. The sample was dried in an electric oven at 105 ˚C for 24 h to remove moisture, then ground to a size of < 500 μm. It was then kept in an airtight container for subsequence tests. Elemental composition of SP was determined through an elemental analyzer (varioMICRO) to obtain the percentage distribution of carbon, hydrogen, nitrogen, and sulfur, while oxygen proportion was calculated from difference. The heating value of SP was obtained from a bomb calorimeter (IKA C2000 basic).

2.2 Thermogravimetric analysis – FTIR

A thermogravimetric analyzer (TGA Q500 V20.13 Build 39) coupled with a Fourier transform infrared spectrometer, (FTIR - Nicolet iS10) was used to study the thermal decomposition of biomass (SP algae) and the gaseous product evolved. For each run, a sample mass of 3±1 mg was placed onto a platinum crucible, which was lowered into the reaction chamber. Nitrogen gas (Supplier: Megamount Malaysia, Purity: 99.8 %) was used to purge the air within the setup to create an inert environment for pyrolysis; and the same gas was also used throughout the experiment as the carrier gas. The sample was heated from 298 to 1273 K at a heating rate β of 5, 10, 15 and 20 ˚Cmin-1 with a nitrogen flow of 20 mL /min. The change in mass at elevated temperature was plotted in thermogravimetric (TG) and derivative-thermogravimetric (DTG) format. The gasses released during pyrolysis was transferred to the FTIR instrument through a heated line. FTIR software – OMNIC series was used to record the spectrum range of 4,000-400 cm-1 with 64 number of scan and a resolution of 8.

2.3 Kinetic theory

The thermal decomposition of algae is a complicated process that involves numerous chemical equations taking place in a short period of time. To understand the underlying mechanism, kinetics study is needed. As the sample is being thermally decomposed, the conversional level can be calculated by Eq(1):

$$\alpha = \left(\frac{m - m_i}{m_i - m_f}\right) \tag{1}$$

where m is the instantaneous mass, m_i is the initial mass before experiment and m_f is the final mass leftover. The weight of sample within the thermogravimetric analyzer is continuously recorded as a function of time and temperature. Combining the Arrhenius equation and the reaction rate constant equation, gives Eq(2)

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right) exp\left[-\frac{E_\propto}{RT}\right] f(\alpha) \tag{2}$$

Where *β* is the constant heating rate, *t* represents time, *T* represents temperature, *f(α)* is the reaction model that comes in various forms, *A* and E_α are two of the kinetics triplets known as the pre-exponential factor and the activation energy, while *R* is the universal gas constant, which equals to 8.314 J $(Kmol)^{-1}$. Reaction mechanism of biomass pyrolysis can be obtained through the universal integral method (White et al., 2011). Implementing the universal integral approach and constant heating rate, after integration on both side of the Eq(2) gives Eq(3):

$$G(\alpha) = \frac{A}{\beta}(T - T_0)exp\left(-\frac{E_\propto}{RT}\right) \tag{3}$$

The expression of Coats-Redfern is formed by taking the logarithm of both sides and transposing Eq(3), as shown in Eq(4):

$$ln\left[\frac{G(\alpha)}{T - T_0}\right] = ln\frac{A}{\beta} - \frac{E_\propto}{RT} \tag{4}$$

G(α) is the possible integral reaction model that represents the kinetic behavior of the sample. The common types of solid-state kinetics model with their equations can be found elsewhere (Gai et al., 2013). For a specified reaction model, a straight-line plot between ln[G(α)/(T-T_0)] and 1/T will give a slope represented by -E_α/R with y-intercept ln(A/β). With this, the kinetic parameters of activation energy and pre-exponential factor can be obtained.

3. Results and discussion

3.1 Thermal decomposition behavior

Table 1 records the basic elemental properties of SP. It is observed that SP algae contains a high proportion of oxygen causing it to have a relatively low heating value of 8.35 MJ/kg. Brown algae of different species are also being reported to having low heating value, owing to the low fixed carbon content (Li et al., 2010).

Table 1: Characteristics of Sargassum polycystum sp.

N	C	H	S	C/N	O*	Heating Value (MJ/kg)
1.03	24.63	3.95	0.87	23.95	69.52	8.35

*calculated by difference. Data shown are obtained in a dry, ash-free basis.

Figure 1 shows the TG and DTG curve recorded when SP algae are being thermally decomposed in a nitrogen-filled reactor at a heating rate of 5, 10, 20 and 40 ˚Cmin^{-1}. Thermal decomposition of SP can be divided into three stages. The first mass loss stage occurs in the temperature range of 31.4 and 205.6 ˚C owing to the evaporation of remaining moisture within the sample and probably the evolution of some light volatile substance. The conversional level of SP at this stage is still low as the decomposition process have not fully kicked in due to low energy level. This is confirmed from the data presented in Table 2, where the conversional fraction during the highest reaction rate in stage one is just 3 wt% of the total feedstock.

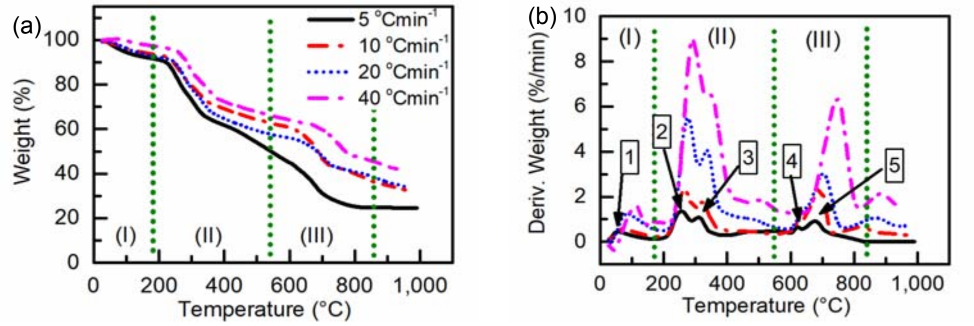

Figure 1: (a) Mass loss and (b) derivative mass loss for Sargassum sp. obtained through thermogravimetric analysis

Second mass loss region, where a huge portion of the feedstock decomposed falls in the temperature range of 186.7 to 459.2 ˚C. In this region, complex chemical reaction such as decarboxylation, depolymerisation and cracking occur that leads to the decomposition of cellulose and hemicellulose components. This phenomena is also reported in the work of (Ali and Bahadar, 2019). The decomposition temperature for cellulose and hemicellulose has been reported in many other researches to be common in the range of 190-400 ˚C (Chong et al., 2019). The two prominent peaks labelled 2 and 3 are attributed to hemicellulose and cellulose, as hemicellulose has a lower decomposition temperature. The third mass loss region is in between the temperature range of 586.4 ˚C to 814.3 ˚C. This reaction zone probably involved the decomposition of inorganics, while partial gasification started due to high energy level. A similar explanation was also recorded at high temperature decomposition during the pyrolysis of T. ornate algae at 600-827 ˚C (Ali and Bahadar, 2019).

Table 2: Thermal degradation properties of SP algae during pyrolysis

	Stage I					Stage II					Stage III				
β	T_i (˚C)	T_f (˚C)	T_p (˚C)	DTG_{max} (%/˚C)	α	T_i (˚C)	T_f (˚C)	T_p (˚C)	DTG_{max} (%/˚C)	α	T_i (˚C)	T_f (˚C)	T_p (˚C)	DTG_{max} (%/˚C)	α
5	31.4	158.2	56.5	0.45	0.03	186.7	378.9	254.1	1.37	0.22	586.4	719.2	677.9	0.94	0.86
10	27.2	163.4	76.7	0.58	0.03	189.0	414.6	259.9	2.25	0.19	598.7	728.6	695.5	2.45	0.78
20	30.4	192.7	86.4	1.24	0.03	195.9	430.9	276.9	5.50	0.24	592.2	765.6	704.1	6.98	0.79
40	43.1	205.6	109.1	1.63	0.01	208.4	459.2	291.5	8.88	0.20	645.2	814.3	746.4	6.32	0.80

*T_i is the initial temperature where decomposition initiate, T_f is the final temperature of decomposition at a particular zone, T_p is the temperature when decomposition rate is the highest in a particular zone

From the effect of heating rate, higher heating rate shifts the mass loss curve towards higher temperature region (Figure 1) and increases the rate of mass loss. It can be observed from Table 2 that as the heating rate increases from 5 to 40 ˚Cmin^{-1}, the temperature for highest mass loss rate increases from 254.1 ˚C to 291.5 ˚C. Besides, the rate of mass loss also increases from 1.368 % /˚C to 8.876 % /˚C, where its decomposition rate was increased by 650 %. However, it is noticeable that although the decomposition rate and temperature peak are shifted to a higher value, the conversional level of feedstock remains almost the same, α = 0.2. This proves that although reaction rate increases with heating rate, the conversional level of the sample is still in the same region due to insufficient energy to decompose the components at higher temperature region. The shifting of mass loss curve towards higher temperature region is caused by heat transfer limitation from the surrounding into the sample that caused thermal lag (Ali and Bahadar, 2019). With a higher heating rate, the temperature is raised rapidly, causing more components within the sample to decompose. As temperature increases, the decomposition process needs to align itself with the temperature rate, inducing a higher reaction rate. On the other hand, a lower heating rate is found to be a better option to visualize the type of main components present within a feedstock. From Figure 1, only one distinct peak is seen on the curve of 40 °Cmin^{-1} in region (III), while for the curve of 5 ˚Cmin^{-1}, two peaks are observed. This is due to the fact when two compounds have a close decomposition temperature range, the concurrent decomposition tends to cause the overlapping of two peaks into one. However, when the heating rate is low, the component with lower activation energy will decompose first, differentiating itself from the second component on the DTG curve.

Figure 2a shows the FTIR spectrum from the gasses evolved during pyrolysis of SP algae at 40 °Cmin^{-1}. During pyrolysis of SP algae, the peak intensity is recorded at 3,900-3,600 cm^{-1}, 2,370-2,300 cm^{-1}, 1,900-1,400 cm^{-1} and 690-650 cm^{-1}. Within these wavelength spectra, H_2O, CO_2, alkyls, aromatics, carbonyls, phenols and acids are reported. The highest portion of CO_2 is being released throughout the pyrolysis experiment, which is in correspondence with others researches that states CO_2, H_2O and CO are the dominant gasses commonly being emitted in pyrolysis (Singh et al., 2012). Carbonyls absorption bands might include aldehydes and ketones (Tang et al., 2017), which are oxygenated hydrocarbons that are suitable to be used as fuel. The presence of aromatics and phenols compounds can be condensed, enabling the collection of bio-liquid that have alternative usage, for example, fuel-typed bio-oil (Thangalazhy-Gopakumar et al., 2012) or resin manufacturing material (Kim, 2015).

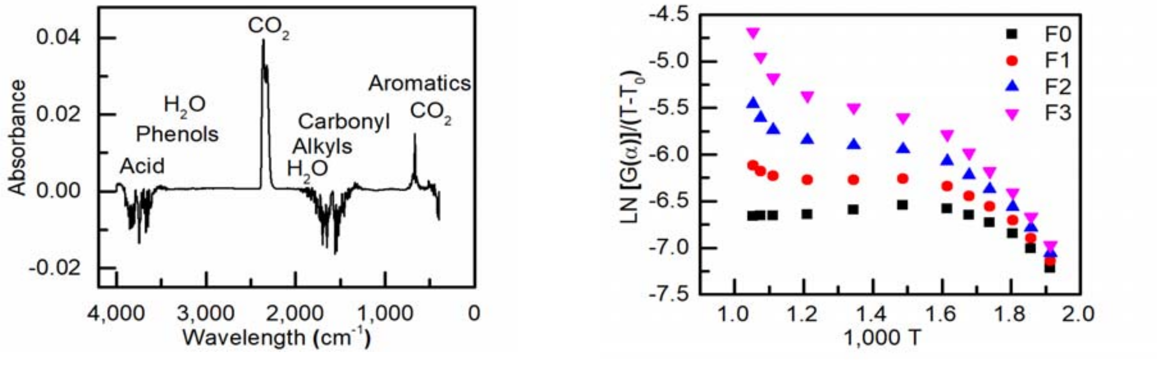

Figure 2: (a) FTIR spectrum of Sargassum Polycystum sp. obtained at TGA 40 ˚Cmin^{-1} and the (b) *regression lines plotted for SP at heating rate of 5 ˚Cmin^{-1} using four types of reaction order models*

3.2 Kinetics properties

A conversional level of 0.15 to 0.7 was used to evaluate the kinetics triplets. The initial and final conversional fractions were excluded for evaluation due to DTG peak tails that will induce errors. Moisture evaporation during the initial reaction zone has been proposed to be ignored, as it will induce errors (Cai et al., 2018).

Four main groups of kinetics models are used for kinetics analysis, while the average value deduced from all different heating rates will be used as the final kinetics properties. The kinetics triplets of the sample can be evaluated and deemed applicable based on the high value of correlation, R^2, which indicates the suitability of the kinetics model in describing the kinetic mechanism.

From Table 3, it can be observed that when implementing model-fitting method, a vast range of kinetics model can be used, leading to a higher possibility in assuming a set of kinetic parameters that does not perfectly describe the reaction mechanism. Among all the models available for solid-state reaction, Reaction order and the Diffusional models seem to suit the thermal decomposition behavior of SP algae better when compared with the Mampel and Nucleation model.

Tabulated in Table 3, the highest correlation of 0.94 using the third-order of reaction (F3) followed by 0.91 for the second-order of reaction, while a correlation of 0.89 is obtained for D2 and D4 Diffusional model during 5 ˚Cmin^{-1}. However, for subsequence heating rate of 10, 20 and 40 ˚Cmin^{-1}, the third-order of reaction turns out to have the highest correlation.

Besides, Figure 2b shows the data plotted through Eq(4) considering all four types of reaction order. It can be observed that the decomposition behavior of SP shows a curve that can be fitted better through linear correlation. Therefore, it is found that the third-order of reaction (F3) best describes the reaction mechanism of SP. The averaged activation energy and pre-exponential factor obtained from all heating rates, using F3 kinetic model are 19.09 kJmol^{-1} and 0.537 s^{-1}.

Table 3: Possible reaction mechanism for the thermal decomposition of Sargassum Polycystum sp.

	5 ˚C/min			10 ˚C/min			20 ˚C/min			40 ˚C/min			Average	
Model	Eα (kJ/mol)	R²	A (s^{-1})	Eα (kJ/mol)	R²	A (s^{-1})	Eα (kJ/mol)	R²	A (s^{-1})	Eα (kJ/mol)	R²	A (s^{-1})	Eα (kJ/mol)	A (s^{-1})
Reaction order														
F0	4.30	0.56	0.014	3.44	0.32	0.009	5.15	0.45	0.015	3.18	0.15	0.011	4.02	0.012
F1	8.14	0.82	0.038	7.20	0.67	0.024	9.36	0.72	0.044	7.77	0.48	0.032	8.12	0.034
F2	12.83	0.91	0.131	11.81	0.84	0.075	14.56	0.86	0.162	13.44	0.72	0.121	13.16	0.122
F3	18.34	0.94	0.548	17.22	0.91	0.286	20.67	0.92	0.745	20.13	0.85	0.570	19.09	0.537
Mampel														
P(2/3)	11.60	0.81	0.034	10.28	0.65	0.019	12.82	0.69	0.039	11.08	0.48	0.026	11.45	0.030
P2	-2.99	0.71	0.005	-3.40	0.64	0.004	-2.53	0.43	0.006	-4.73	0.62	0.004	-3.41	0.005
P3	-5.43	0.95	0.004	-5.69	0.91	0.003	-5.09	0.87	0.004	-7.37	0.90	0.003	-5.89	0.004
P4	-6.64	0.98	0.003	-6.83	0.96	0.003	-6.37	0.95	0.003	-8.68	0.96	0.003	-7.13	0.003
Nucleation														
A1.5	2.00	0.38	0.015	1.39	0.14	0.011	2.84	0.34	0.016	0.97	0.03	0.012	1.80	0.013
A2	-1.08	0.24	0.009	-1.52	0.26	0.007	-0.42	0.02	0.010	-2.44	0.28	0.007	-1.36	0.008
A3	-4.15	0.91	0.006	-4.43	0.87	0.005	-3.68	0.77	0.006	-5.84	0.84	0.005	-4.52	0.005
A4	-5.68	0.97	0.004	-5.89	0.95	0.004	-5.31	0.92	0.005	-7.54	0.94	0.004	-6.10	0.004
Diffusional														
D1	18.89	0.86	0.087	17.13	0.75	0.040	20.50	0.76	0.102	18.99	0.60	0.066	18.88	0.073
D2	21.18	0.89	0.081	19.37	0.79	0.035	23.00	0.80	0.098	21.71	0.65	0.063	21.32	0.069
D3	5.49	0.68	0.012	4.60	0.45	0.008	6.45	0.55	0.014	4.59	0.26	0.010	5.28	0.011
D4	22.06	0.89	0.023	20.22	0.80	0.010	23.97	0.81	0.028	22.76	0.67	0.018	22.25	0.020

On the other hand, an increase in the heating value will also cause a hike in the activation energy and pre-exponential value, where similar phenomena has also been reported in the thermal decomposition of low-lipids microalgae (Gai et al., 2013). The activation energy and pre-exponential factors are inter-correlated, as higher activation energy leads to higher pre-exponential value. This is because the former kinetics parameters indicate the amount of energy needed for the sample to initiate chemical reaction, hence enabling the breakdown of chemical compounds.

On the other hand, the latter parameter indicates the amount of collision required for a certain compound to have the proper orientation for breaking and forming chemicals bonds. A higher value of both parameters indicates a larger obstacle to overcome during thermal decomposition.

4. Conclusion

The marine brown seaweed *Sargassum polycystum* is reported to be a potential biomass source for thermal decomposition through pyrolysis. The possible end-products in liquid and gaseous forms can be derived due to the quality component of volatiles that evolved during pyrolysis. The mass loss behavior of SP has three distinct zones where moisture, volatile, inorganics, and partial gasification occurs simultaneously within the temperature range of 27-1,000 °C. The alga SP is found to follow the thermal degradation of the F3 reaction order model with an average activation energy and per-exponential values of 19.09 $kJmol^{-1}$ and 0.537 s^{-1}.

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