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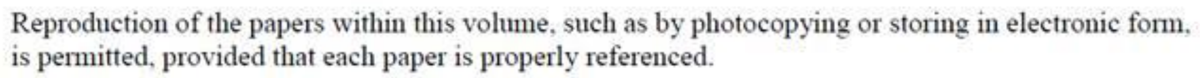

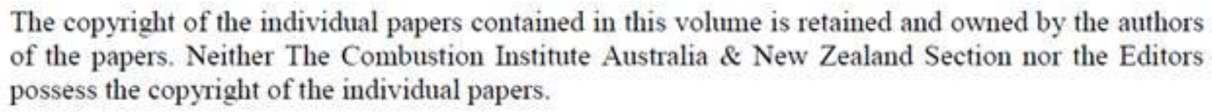

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# Devolatilization characteristics of *Oedogonium* sp., Loy Yang coal and their blends using thermogravimetric analysis

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## Abstract

In order to assess the potential of gasification for the utilisation of algal biomass, the devolatilisation characteristics of a fresh water macroalga (*Oedogonium* sp.), a Victoria brown coal (Loy Yang) and their blends were investigated. The study indicated that *Oedogonium* sp. and Loy Yang coal exhibit quite different pyrolysis characteristics under the same pyrolysis conditions, the devolatization of *Oedogonium* sp. occurs mainly between 180-410 ℃, while for Loy Yang coal pyrolysis occurs over a wider temperature zone. The effect of heating rate on the devolatilization characteristics of these two fuels was also studied; for heating rates of 10-40 ℃ /min it was found that pyrolysis shifts to higher temperatures as the heating rate increases for both fuels. There is no significant change in the residual mass for Loy Yang coal, however, the residual mass of *Oedogonium* sp. decreases slightly as the heating rate increases. The pyrolysis characteristics of blends of these two fuels were also investigated for different blending ratios. No interaction effects were observed to exist for the experimental conditions investigated. Based on this work, successful co-gasification of macroalgae and coal is not expected to be impeded by limitations occurring during the pyrolysis stage.

*Keywords: Macroalgae, Oedogonium* sp*, Loy Yang coal, pyrolysis characteristics, heating rate, biomass/coal blends.*

## 1. Introduction

Co-utilization of coal and biomass has gained increasing attention due to the possibility of decreasing the carbon footprint of conventional fossil fuel plants while at the same time leading to the high-efficiency utilization of relatively small quantities of biomass at large scale. Macroalgae, as one type of aquatic biomass, have a long history of use in the pharmaceutical, chemical and food industries [1]. More recently, new applications of macroalgae for waste-water treatment, $CO_2$ abatement and energy production [1, 2] have received attention due to their short growth cycles, high production yield, and high rates of $CO_2$ fixation, as compared to terrestrial biomass, and because the cultivation of macroalgae can be effective using low-grade water on non-arable land [3].

There are two classes of technology for the conversion of solid fuel to energy: thermo-chemical and bio-chemical [4]. Among the thermo-chemical conversion methods, pyrolysis is important since it is the first step in the processes of combustion and gasification. An understanding of the pyrolysis characteristics of solid fuels is fundamental for reactor design and optimization of these processes. The pyrolysis characteristics of several types of macroalgae have been investigated in recent years. For example, Wang *et al.* [5] conducted pyrolysis experiments using *Enteromorpha clathrata* and investigated the pyrolysis characteristics at different heating rate, with analysis of the resultant gaseous products, using TG-MS. Li *et al.* [6] analyzed the pyrolysis characteristic of three red marine macroalgae and concluded that the pyrolysis process can be divided into three stages, and calculated the kinetic parameters using the Popescu, FWO and KAS methods. Ross *et al.* [7] characterized five types of macroalgae by proximate and ultimate analysis, inorganic content, and calorific value. They concluded that the high ash content of marine macroalgae restricts their use for combustion and gasification, and proposed more suitable conversion methods for macroalgae. However, fresh-water macroalgae are typically much lower in ash content.

One possible strategy to negate the high ash content of algal biomass is to co-fire with low-ash fuels. However, little work has been done to investigate the co-pyrolysis of blends of algae and other fuels. Kirtania and Bhattacharya [8] investigated the pyrolysis reactivity and kinetics of a fresh water alga, *Chlorococcum humicola*, Yallourn coal and their blends, and found no chemical interaction exists during the pyrolysis process. Chen *et al.* [9] studied the co-pyrolysis characteristics of a microalgae, *C. vulgaris*, and a semi-anthracite coal and observed an interaction between these fuels. Thus, there is currently no consensus about whether pyrolysis interaction effects exist during co-utilization processes or indeed, if they do exist, whether these interactions are synergistic or otherwise. Further study of the pyrolysis characteristics of macroalgae, and any interaction effects during co-pyrolysis with other fuels, is necessary to facilitate the design and operation of co-fired pyrolysis, combustion and gasification processes.

A fresh-water green macroalga, *Oedogonium* sp., has been selected for the present study since it is a target species for remediation of industrial pollutants and has previously been assessed for this application[10]. The pyrolysis characteristics of this alga have been investigated and compared with those of Loy Yang coal as a function of heating rate using a thermogravimetic analyzer (TGA). Blends of these two fuels were also

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investigated to verify whether interaction effects exist during co-pyrolysis.

## 2 Experimental

### 2.1 Sample preparation

*Oedogonium* sp. (OD) (hereafter referred to as *Oedogonium*), a fresh water macroalga, was cultured in tanks at James Cook University, Townsville. A detailed description of the cultivation and harvesting of OD is given by Lane *et al.* [11]. Briefly, tanks were stocked with *Oedogonium* at 0.5 g/L in de-chlorinated water with MAF (Microalgae food) culture media and harvested after 7 days. The biomass was divided and a portion air-dried until the moisture content was less than 10 wt%. The dried sample was milled and sieved to <250 µm.

A Victorian brown coal, Loy Yang (LY), was dried in an oven at 40 ℃ for 12h and then stored under ambient conditions until constant weight was achieved (i.e. weight change < 0.1 % per hour). The coal was milled and sieved to less than 250 µm.

Representative samples of coal and algae were obtained using cone-and-quartering and added to an agate mortar before being physically mixed to ensure a homogeneous mixture. Proximate analysis for the coal sample was determined following ASTM standards and using a Setaram Labsys Thermogravimetric analyzer. An ultimate analysis was performed using a LECO TruSpec CHN analyzer and the higher heating value was calculated based on the ultimate analysis following Kirtania and Bhattacharya [8]. The proximate and ultimate analyses for OD are those reported by Lane *et al.* [11] and the reported heating value was also calculated from the ultimate analysis [8]. These analyses are reported in Table 1 for OD and LY.

### 2.2 Experiment methods

Pyrolysis experiments were carried out using a Setaram Labsys Thermogravimetric Analyzer /Differential Scanning Calorimeter (TGA/DSC). Samples (~10 mg) were loaded into an alumina crucible and experiments were conducted under non-isothermal conditions with a $N_2$ (99.999% Purity) flow rate of 60 ml/min as the sweeping gas to provide an inert environment. Samples were heated from ambient temperature to 105 ℃ at a heating rate of 10 ℃/min and held at 105 ℃ for 30 minutes to eliminate most of the free-water. The temperature was then decreased to 50 ℃ and held for 20 minutes to achieve a stable weight signal. Samples were then heated to 900 ℃ at heating rates of 10, 20 or 40 ℃ /min. Prior to each experiment, a baseline run was conducted at the same heating rate and this was used to account for changes in apparent weight due to buoyancy effects [12].

Table 1 Proximate and ultimate analyses and calculated heating values for OD and LY coal. [db = dry basis; daf = dry, ash-free basis]

| | OD | LY |
|---|---|---|
| Proximate analysis (wt% $^{db}$) | | |
| Fixed carbon | 14.7 | 47.3 |
| Volatile | 77.3 | 51.3 |
| Ash | 8 | 1.4 |
| Ultimate analysis (wt% $^{daf}$) | | |
| C | 49.1 | 66.8 |
| H | 6.8 | 4.8 |
| N | 4.5 | 0.4 |
| S | 0.12 | - |
| O (by difference) | 39.2 | 28.0 |
| HHV (MJ/kg)$^{db}$ | 19.4 | 24.5 |

## 3 Results and Discussion

### 3.1 Pyrolysis characteristics

Fig. 1 shows the weight loss (TG) and the derivative of the weight loss (DTG) profiles during the pyrolysis of OD in a $N_2$ atmosphere. It can be seen that three distinct stages occur during the pyrolysis process, as was previously observed by others [13-17]. Stage I can be identified as occurring between the starting temperature and the initial temperature of the main devolatilization event, $T_i$, which is taken as the temperature when the rate of weight loss first exceeds 5% of the maximum weight loss rate. Stage II occurs from $T_i$ to the end temperature of the main devolatilization event, $T_e$, which is taken as the temperature at the inflexion point in the weight loss curve between the largest peak and the shoulder to the right of the largest peak. Stage III occurs from $T_e$ until the final pyrolysis temperature (900 ℃, in this case). Similar data for LY is shown in Fig. 2. The pyrolysis process for LY may also be divided into 3 stages following Ma *et al.* [18].

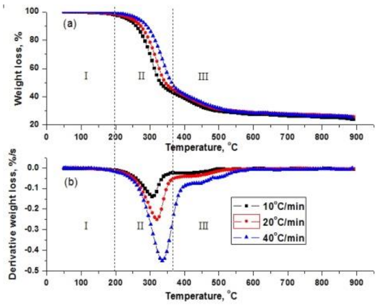

Fig.1 Plot of (a) TG curve and (b) DTG curve for OD at heating rates of 10, 20 and 40 ℃/min (Stages I, II, III are marked based on characteristic temperatures at 20 ℃ /min heating rate ).

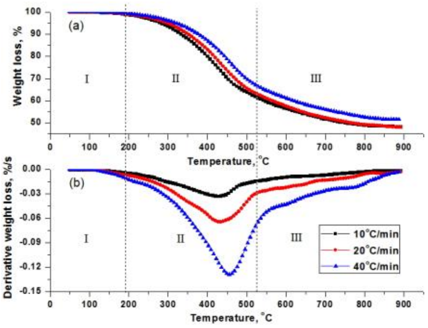

Fig.2 Plot of (a) TG curve and (b) DTG curve for LY at heating rates of 10, 20 and 40 ℃/min (Stages I, II, III are marked based on characteristic temperatures at 20 ℃ /min heating rate)

Table 2 Parameters describing the pyrolysis characteristics of OD and LY coal for different heating rates

| Heating rate | OD | | | | | LY | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (℃) [a] | $T_{max}$ (℃) [b] | $T_e$ (℃) [c] | $(dw/dt)_{max}$ [d] | Residual mass | $T_i$ (℃) | $T_{max}$ (℃) | $T_e$ (℃) | $(dw/dt)_{max}$ | Residual mass |
| 10 ℃ /min | 183 | 304 | 347 | 0.13701 | 25.91 | 180 | 426 | 495 | 0.03262 | 48.32 |
| 20 ℃ /min | 198 | 320 | 365 | 0.24948 | 25.57 | 192 | 433 | 527 | 0.06456 | 48.11 |
| 40 ℃ /min | 210 | 355 | 407 | 0.45079 | 24.26 | 203 | 455 | 582 | 0.12902 | 51.57 |

[a] $T_i$ is the initial temperature of the main devolatilization, °C
[b] $T_e$ is the end temperature of the main devolatilization, °C
[c] $T_{max}$ is the temperature of the maximum reaction rate, °C
[d] $(dw/dt)_{max}$ is the maximum reaction rate, %/s

The temperatures used to define the three stages of pyrolysis, $T_i$, $T_e$ and $T_{max}$, are shown in Table 2 for OD and LY. For OD, during Stage I, since most of the moisture is eliminated before the experiment, there is only a small weight loss which corresponds to the release of the crystalline water and light volatile species. The main volatile components are released during Stage II and the majority of weight loss during pyrolysis occurs during this stage. During Stage III, a shoulder exists at the right of the main peak, it suggests a slow and gradual loss of weight (from $T_e$ to approx. 500-600 ℃) resulting from the decomposition of carbonaceous species in the solid residue [14].

The first stage of LY pyrolysis is also due to the evaporation of remaining water. The second stage corresponds to primary carbonization of the coal with most of the volatile matter released during this stage to form tars and gaseous products. The third stage is due to secondary carbonization and the sample weight decreased progressively until the end of the pyrolysis process during this stage.

Compared with OD, the devolatilization of LY is somewhat slower and occurs over a wider temperature range. It is well known that the pyrolysis characteristic of solid fuel mainly depends on its composition, as macroalgae are composed of many low polymerization polysaccharides and the inorganic species in macroalgae also have a catalytic effect on the thermal decomposition process [16, 19], so the weight loss mainly occurs in a narrow temperature range. The volatile matter in coal is more complex, including mainly alkane, aromatic hydrocarbon and aliphatic hydrocarbons, and these different components are released over a wide range temperature, usually from around 200-900℃, and thus weight loss occurs over a wider temperature zone. The residue mass of LY, shown in Table 2, is much higher than that for OD, which is attributed to its higher fixed carbon content (Table 1).

The effect of heating rate on the TG and DTG curves for the pyrolysis of OD and LY coal is also evident in Fig 1 and Fig 2, respectively. It can be seen from Table 2 that, as the heating rate increases, there was a lateral shift to higher temperature for $T_i$, $T_e$, and $T_{max}$. This lateral shift has been reported for different types of biomass [20, 21] and other types of algae [14, 16, 17] and has been assigned as being due to the combined effects of the heat transfer under different heating rate and the kinetic of decomposition resulting in delayed decomposition [20, 21]. It can also be observed from the DTG curve that $(dw/dt)_{max}$ increases as the heating rate increases. This may due to biomass having a heterogeneous structure with many different constituents, each with their own characteristic peak at certain temperature ranges during the pyrolysis process. Particularly at high heating rates, these different constituents decompose simultaneously and the adjacent peaks overlap to yield broader peaks [22, 23].

In our experiment, there is a slightly decrease in the residue mass of OD as the heating rate increases (Table 2), which may be due to lower heating rates resulting in a longer residence time for the volatiles within the particles and so favoring secondary reactions such as cracking, re-polymerization and re-condensation, which ultimately lead to the formation of the solid char [14].

## 3.2 Co-pyrolysis

Fig. 3 shows the weight loss (TG) and the derivative of the weight loss (DTG) profiles during the pyrolysis of OD and LY with different blending ratios at a heating rate of 20 ℃ /min. It can be seen in Fig. 3(b) that all three blends display two peaks at around 320 ℃ and 430 ℃, respectively, which correspond to the temperature of the maximum devolatilisation rate of OD and LY separately. The peak height at 320 ℃ increases as the percentage of OD increased, while the second peak height increases as the percentage of LY increased. The residual mass for LY (Fig. 3(a)) is higher than OD with the residual mass increasing as the ratio of LY increases.

To investigate whether interaction effects exist during pyrolysis of blends of the two fuels, the amount of volatile species released from the pyrolysis process is plotted in Fig. 4 against the percentage of OD in the blend. It can be seen that there is an approximately linear relationship between the volatile species content and the percentage of OD in the blend, which indicates that no interaction effects exist for these mixtures, under these experimental conditions. To further validate this conclusion, a comparison between experimental weight loss ($W_{exp}$) value and the calculated weight loss value ($W_{cal}$) was conducted.

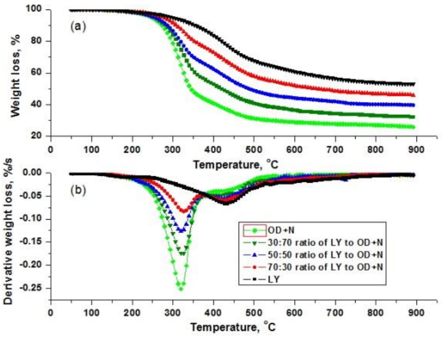

Fig. 3 TG (a) and DTG (b) curve for OD, LY coal and its blend at heating rate of 20 ℃ /min

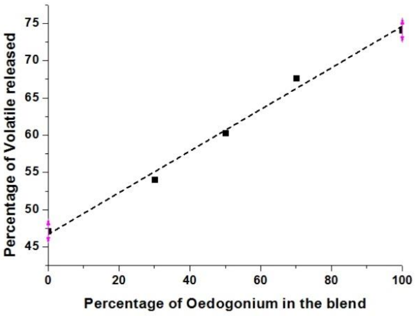

Fig. 4 Percentage of volatile released vs blending ratio of OD

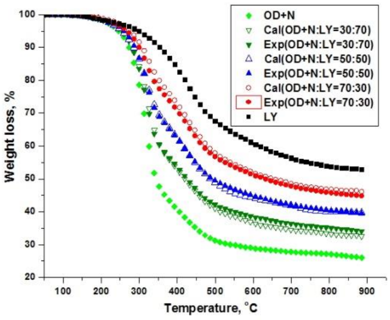

Fig. 5 Comparison of calculated and experimental weight loss curve for OD and LY blends at heating rate of 20 ℃ /min

$W_{cal}$ is calculated using eqn. (1):

$$W_{Cal} = x_{OD}W_{OD} + x_{LY}W_{LY} \tag{1}$$

where $x_{OD}$ and $x_{LY}$ is the percentage of OD and LY in the mixture respectively, and $W_{OD}$ and $W_{LY}$ is the weight loss of OD and LY at the same conditions, respectively. The calculated and experimental weight loss curves, with different blending ratios and for a heating rate of 20 ℃ /min, are presented in Fig 5. Although there is a slight difference, the $W_{cal}$ value agrees well with $W_{exp}$, and similar co-pyrolysis behaviors have been reported previously [24-26], which further demonstrates that no interaction effects exist in the blends.

## 4. Conclusions

(1) *Oedogonium* and Loy Yang exhibit different pyrolysis characteristics for the same conditions. The devolatization of *Oedogonium* mainly occurs between 180-410 ℃, however, the devolatization of Loy Yang coal occurs over a wider temperature. The coal has a higher residual mass as compared with *Oedogonium*.

(2) Pyrolysis curves for both *Oedogonium* and Loy Yang shift to higher temperatures as the heating rate increases, the charcteristic parameters, $T_i$, $T_e$, $T_{max}$ and $(dw/dt)_{max}$ all increase when the heating rate increase. While there is no obvious change in the residual mass for Loy Yang, the residual mass of *Oedogonium* decreases as heating rate increases.

(3) No interaction effects exist during the pyrolysis of *Oedogonium* and Loy Yang coal blends at the current experimental conditions.

(4) Based on this work, successful co-gasification of macroalgae and coal is not expected to be impeded by limitations occurring during the pyrolysis stage.

## 5. Acknowledgments

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