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# Synergistic effects from co-pyrolysis of low-rank coal and model components of microalgae biomass

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ABSTRACT

Synergistic effects from co-pyrolysis microalgae biomass with low-rank coal were investigated in this work. Model compounds of three main component in microalgae algae (glycine, medium chain triglyceride and starch), *spirulina* and simulated *spirulina* were chosen to Shenfu bituminous pyrolysis process. Kinetic parameters were solved through isoconversional method, and scanning electron microscopy with energy dispersive spectroscopy were applied for characterizing the char samples. Results revealed synergistic effects occurred with different forms from co-pyrolysis of microalgae primary compounds and coal. Positive synergistic effects, which were defined as higher volatile yield than calculated value, were found in medium chain triglyceride and coal mixtures at all mass ratio. Whether positive or negative synergistic effects on products yield from glycine or starch blended with coal hinged on the temperature and mixing ratio. Both *spirulina* and simulated *spirulina* show optimal performance on volatile yields under 50 wt.% mass ratio. Non-additivity phenomenon was observed on the distribution of average activation energy. Synergistic effects from co-pyrolysis of coal and microalgae biomass may attributes to the integrative action of the three model compounds.



## 1. Introduction

Low-rank coal accounts for almost half of coal reserve in China, and current utilization of it leads to an adverse influence on the environment [1]. Thus, seeking clean coal transformation technique and low carbon alternative energy are practical solutions for the problem mentioned above. Take low-temperature pyrolysis as the first step, the coal-grading technique can convert coal into clean energy and raw material for chemical industry. However, lower hydrogen-to-carbon atom ratio of low-rank coal results in lower tar yields, which is a high-value-added product obtained from pyrolysis process. As a renewable and carbon-neutral energy, biomass has a higher hydrogen-to-carbon atom ratio, and co-pyrolysis with coal can promote the tar yield and improve the char quality [2–6].

Several researchers have investigated the thermal behavior and kinetic characteristic from co-pyrolysis of coal and terrestrial biomass, such as agricultural residues and forestry residues [2,4,5,7–11]. Microalgae, as a kind of aquatic biomass, has advantages in high fixation rates of $CO_2$, rapid growth rate and no occupation of cultivated land and compared to terrestrial biomass [12–14]. Unlike most of the terrestrial crops, microalgae contain less lignin, which is more suitable for thermo-chemical conversion process and condition of co-pyrolysis with coal is milder than that of terrestrial crops. During pyrolysis of the microalgae, it generates a lot of alkyl radicals, and the gain or loss of hydrogen radicals from alkyl radicals result in normal alkane or $\alpha$-olefin, respectively. Thus, the pyrolytic oil of microalgae has higher hydrocarbon content and lower oxygen content. Therefore, co-pyrolysis of microalgae and coal can promote the yield and quality of tar in milder conditions.

Much attention has been pay to the co-pyrolysis characteristic of algae and coal, but different conclusions on the yield of volatiles were obtained. Yang et al. [15] investigated co-pyrolysis characteristics of *Dunaliella tertiolecta* blended with coal through TGA, and found that synergistic effect existed between algae and coal from 200 °C to 500 °C, which promoted the yields of volatile products. Qian et al. [16] also found the same conclusion. While Chen et al. [17] found that the addition of microalgae during co-pyrolysis inhabited the releasing of volatile products and promoted the formation of char. Furthermore, Kirtania and Bhattacharya [18] pointed out that there is no chemical interaction during co-pyrolysis of *Chlorococcum humicola* and brown coal. Due to the varieties of microalgae biomass, whether synergistic effect existed from co-pyrolysis on the volatile yield and kinetic characteristics is

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still not conclusive, which is not conducive to guide the efficient production and products prediction.

The major organic component of microalgae biomass are lipids, protein, and carbohydrate, and the chemical compositions from different kinds of microalgae are diversity [19,20]. Take *Dunaliella tertiolecta* in Yang's [15] research for example, the mass content of lipids, protein and carbohydrate are 17.80%, 50.30%, and 21.70%, respectively. While for *Chlorococcum humicola* in Kirtania's investigation [18], the three primary organic compositions are 2.51%, 42.70%, and 9.42%, respectively. Thus, the main compounds contents in microalgae may have different influence on the pyrolysis process of coal. However, little attention has been paid to the effect of microalgae biomass individual components on co-pyrolysis thermal behavior.

Furthermore, the mechanism of interactions between coal and algae biomass is still not clear. Kinetic analysis of the co-pyrolysis process can provide detailed information about the rate and degree of reaction, which is beneficial for understanding the co-pyrolysis process [4,5]. Previous research investigated the distribution of kinetic parameters from coal and algae [15,17]. However, all the components of algae involved in the reaction result in the covering of particular effect from the major component. Thus, it is vital to clarify the kinetic characteristics from co-pyrolysis of coal with individual primary compounds of algae.

The aim of this research is to investigate synergistic effects on products yields and reveal the possible mechanism during co-pyrolysis of microalgae biomass and low-rank coal. The pyrolytic behavior of three primary compounds, including lipids, protein, and carbohydrate, blended with a kind of low-rank coal was explored through a thermogravimetric analyzer. Three isoconversional methods were applied for activation energy solving. This paper provides insight on the interaction between coal and microalgae biomass.

## 2. Material and methods

### 2.1. Materials

Microalgae biomass is mainly composed of a complex mixture of biomacromolecules, such as protein, lipids, and carbohydrate [21,22]. Moreover, in previous research, the basic units composing of biomacromolecules mentioned above were chosen as model compounds to understand the behavior of algae during thermal conversion process [23–26]. Changi et al. [24] used amino acid as a model compound of protein in algae biomass, and Biller et al. [23] selected starch as a carbohydrate standard in algae biomass. Palmitic acid and palm-jojoba oils were used as the model compounds of lipids [20,25]. Therefore, in this research glycine (GLE, CAS No. 56-40-6) and starch (STH, CAS No. 9005-84-9) were selected as the model compounds of protein and carbohydrate. Moreover, both of them were purchased from Sigma–Aldrich Co., Ltd. Medium chain triglyceride (MCT, CAS No. 73398-61-5) were investigated as a model compound of lipids and provided by Shanghai OFK Trade Co., Ltd. All the three model compounds are white solid. *Spirulina* (SP) was purchased from Xi'an BaiChuan Biological Technology Co., Ltd. The low-rank coal (LC), a kind of bituminous, was collected from Shenfu coalfield, north of Shaanxi, China.

GLE, MCT, STH and SP with a particle size less than 74 μm were gathered for trial. The low-rank coal was milled into less than 74 μm. The coal sample used in this study had 4.56 wt.% (air-dried based) moisture content, 6.05 wt.% ash content, 36.64 wt.% volatile content, 52.75 wt.% fixed carbon content and a higher heating value of 25.44 MJ·kg$^{-1}$. The carbon, hydrogen, nitrogen, sulphur and oxygen contents (dry ash-free based) of low-rank coal sample were found to be 79.31%, 4.72%, 1.03%, 0.7% and 13.98%, respectively. *Spirulina* (SP) was purchased from Xi'an BaiChuan Biological Technology Co., Ltd. The protein and lipid contents in *Spirulina* were determined via Kjeldahl method and solvent extraction method respectively, and the carbohydrate content was obtained by the mass balance [27]. Therefore, the protein, lipid and carbohydrate contents of *Spirulina* in this research were 62 wt.%, 3 wt.% and 25 wt.%. Thus, the simulated *Spirulina* (SSP) was prepared based on the equal proportion. And the name of the mixture from coal and glycine were "LCGLE3-1", "LCGLE1-1" and "LCGLE1-3", which represented the mixing ratio of GLE was 25%, 50% and 75% based on mass. The definition methods of LC and MCT/STH/SP/SSP were in the same way.

### 2.2. Apparatus and methods

Thermogravimetric analysis was performed via an HCT-2 thermogravimetric analyzer (Beijing HENVEN Instrument). Approximately 10 mg of the sample was measured in each trial for mitigating the heat and mass transfer effects and was heated from 25 °C to 850 °C with three heating rates (10, 20, 40 °C·min$^{-1}$) under

**Table 1**
Pyrolysis parameters of LC, microalgae biomass model components and their mixtures under a *heating rate of* 20 °C·min$^{-1}$.

| Parameters | | LC | 25% GLE | 50% GLE | 75% GLE | GLE | 25% MCT | 50% MCT | 75% MCT | MCT | 25% STH | 50% STH | 75% STH | STH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_{in}$ (°C) | Initial devolatilization temperature | 355 | 193 | 222 | 236 | 252 | 208 | 213 | 216 | 214 | 132 | 121 | 219 | 197 |
| $T_1$ (°C) | Temperature of the first DTG peak | 461 | 251 | 265 | 275 | 266 | 324 | 344 | 352 | 348 | 323 | 320 | 350 | 291 |
| $R_1$ (%·min$^{-1}$) | Decomposition rate of the first DTG peak | 0.08 | 0.66 | 1.62 | 3.96 | 6.22 | 0.7 | 1.36 | 1.77 | 1.44 | 0.83 | 1.42 | 1.77 | 2.2 |
| $T_2$ (°C) | Temperatures of the second DTG peak | – | – | – | – | – | 232 | 218 | 225 | 222 | 460 | 468 | 470 | – |
| $R_2$ (%·min$^{-1}$) | Decomposition rate of the second DTG peak | – | – | – | – | – | 0.16 | 0.21 | 0.29 | 0.64 | 0.21 | 0.16 | 0.14 | – |
| $R_{max}$ (%·min$^{-1}$) | Maximum decomposition rate | 0.08 | 0.66 | 1.62 | 3.96 | 6.22 | 0.7 | 1.36 | 1.77 | 1.44 | 0.83 | 1.42 | 1.77 | 2.2 |
| $T_{max}$ (°C) | Temperature of maximum decomposition rate | 461 | 251 | 265 | 275 | 266 | 324 | 344 | 352 | 225 | 323 | 320 | 350 | 291 |
| $\Delta T_{1/2}$ (°C) | Temperature interval when $R_d/R_{max} = 1/2$ | 116 | 39 | 32 | 23 | 19 | 48 | 58 | 57 | 65 | 45 | 43 | 59 | 32 |
| $D_i$ ($10^{-8}$%·min$^{-1}$·°C$^{-3}$) | Devolatilization index of the sample | 0.42 | 34.93 | 86.05 | 265.29 | 488.38 | 21.64 | 32.00 | 40.84 | 46.01 | 43.26 | 85.29 | 39.14 | 119.93 |
| Char yield (%) | – | 71.18 | 57.00 | 47.26 | 32.49 | 14.02 | 52.39 | 37.16 | 21.64 | 10.39 | 50.45 | 38.84 | 26.67 | 23.59 |