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Planktonic Algae Biomass Catalytic Pyrolysis Dynamics Analysis†

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To follow the law of planktonic algae pyrolytic, using thermogravimetric analysis method of planktonic algae biomass catalytic pyrolysis dynamics behaviour was studied. Results show that after the HZSM-5 catalyst of rare earth modification of planktonic algae biomass pyrolysis, activation energy decreased obviously, which La/HZSM-5 effect is most obvious, pyrolysis activation energy can be reduced to 48.83 kJ mol⁻¹. The results of the study will provide useful reference for planktonic algae pyrolytic liquefaction.

Keywords: Planktonic algae, Biomass, Catalytic pyrolysis, Dynamics.

INTRODUCTION

The algae is an important source of biomass, the human use of algae biomass for energy has a history of more than 50 years. In recent years, with the depletion of fossil fuels and environmental requirements, using algae biomass to produce liquid fuel research get the attention of people more and more. Planktonic algae to produce biofuels has good economical and environmental protection. Extracting liquid fuel from the earliest planktonic algae began at the 1980' s. At first people use edible food (such as soybean, corn) for making the first generation of liquid biofuels (soybean biodiesel, corn ethanol). Due to causes the fuel "competing for food with people", has caused controversy. In contrast, the second generation of biofuels is using non-staple raw materials production, such as wood fiber plant and jatropha oil, the final product is the same as the first generation product (ethanol, biodiesel), but this kind of raw material still exists "to reclaim land with food" problem. The third generation of biofuels is also obtained from raw materials nothing to do with the food and solved the problem of the "with food for land". That is expected to replace traditional fossil fuels¹.

Planktonic algae are the most potential to become one of the raw materials of the third generation biofuels, because they compared with terrestrial plants, have a higher photosynthetic efficiency, faster growth rate and higher yields per unit area. Planktonic algae can be grown in fresh water or high salinity of the water and unsuitable for farming land, so they have no

conflict with traditional farming land. Algae preparation of bio-oil, compared to the second generation of biofuels, algal oil has higher yield, per hectare of algae oil is 30-100 times of the output of land plants. In addition, the planktonic algae biomass can extract many kinds of fuel, including fuel ethanol, vegetable oil, biodiesel, biological oil, biological synthesis, biological hydrogen. The production process of these biofuels can also reduce carbon dioxide emissions², the sewage treatment and still can collect high value-added compounds.

Traditional making fuel from biomass thermal chemical process (such as gasification, fast pyrolysis liquefaction) requirements of raw material is dry, or in the process, drying the damp raw material will consume large amounts of energy. Planktonic algae have high moisture, therefore, from the angle of energy, adopting the traditional thermal chemical conversion method is not practical. Biomass raw materials developed in recent years the hydrothermal transformation has the very good development potential, hydrothermal liquefaction can transform biomass to tar oil or liquid³. The hot liquid water embodied with the nature is different from the liquid at room temperature reflecting the nature. This is because, in contrast, hot liquid water has a lower conductivity, weaker hydrogen bonds, higher hydrogen ion polymerization degree which would be helpful to the reaction of catalyst and higher solubility of small molecule organic compounds, thus has remarkable effect on the pyrolysis behaviour of biomass.

Although liquefaction of algae has many reports, fresh-water pelagic algae pyrolytic behaviour has not been reported,

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especially in the presence of some new type catalyst, pyrolysis characteristics is how affected by the factors such as catalyst and the heating process is not yet clear, planktonic algae catalytic pyrolysis dynamics analysis of the process will help to promote directional catalytic liquefaction of planktonic algae.

EXPERIMENTAL

Planktonic algae materials collected in Hefei University of Technology campus Anhui Hubin pond, as shown in Fig. 1. Ce/catalyst HZSM-5, La/HZSM-5 preparation, method of preparation of reference⁴ the HZSM-5 (silicon aluminum than 28) purchased from nankai university catalyst factory; $\text{Ce}_2(\text{CO}_3)_3$, $\text{La}_2(\text{CO}_3)_3$ bought from Inner Mongolia Space Jin Xia chemical co., Ltd.

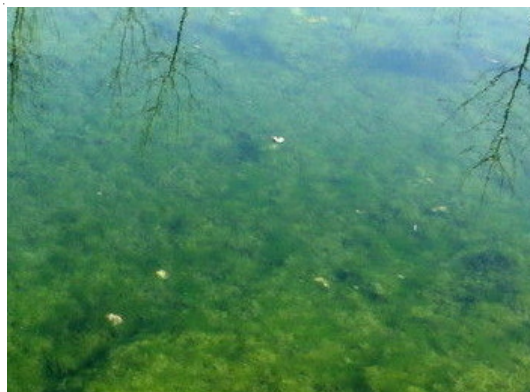


Fig. 1. Planktonic algae

Catalytic pyrolysis experiments: Dry planktonic algae powder by algae water and solid-liquid ratio of 1:10 mL^{-1} were added to the 6 sets containing deionized water in the beaker, then, respectively to join in the beaker biomass weight HZSM-5 of 5 wt %, Ce/HZSM-5, La/HZSM-5 and mix, airtight let stand for 24 h, form planktonic algae paste containing catalysts. Take a suitable amount of planktonic algae paste into the TGA (TG 209 F3, NETZSCH Analyzing and Testing Co.) analysis tray, N_2 as carrier gas, purging flow 10 mL min^{-1} , heating rate 10 $^\circ\text{C min}^{-1}$, temperature range 20-400 $^\circ\text{C}$, through instrument collecting experiment thermogravimetric (TG) and differential thermogravimetric curve (DTG).

RESULTS AND DISCUSSION

Planktonic algae catalytic pyrolysis dynamics analysis:

Fig. 2 is a planktonic algae in the presence of different catalysts in the TG/DTG curves, the figure can be seen that the floating algae can be roughly divided into four stages after heating. The first stage of 20-150 $^\circ\text{C}$, this stage is mainly moisture volatilizing weightlessness stage of planktonic algae paste and corresponding DTG curves on the first peak, thereinto the weightlessness of planktonic algae paste is the most obvious after Ce/HZSM-5's entry into, more than 70 %, the weightlessness of planktonic algae paste under the action of La/HZSM-5 is more than 50 %. And under the action of HZSM-5 the weightlessness of planktonic algae paste is only 20 % or so. That indicates catalyst of rare earth modification to planktonic algae water absorption swelling effect is significantly increased. The

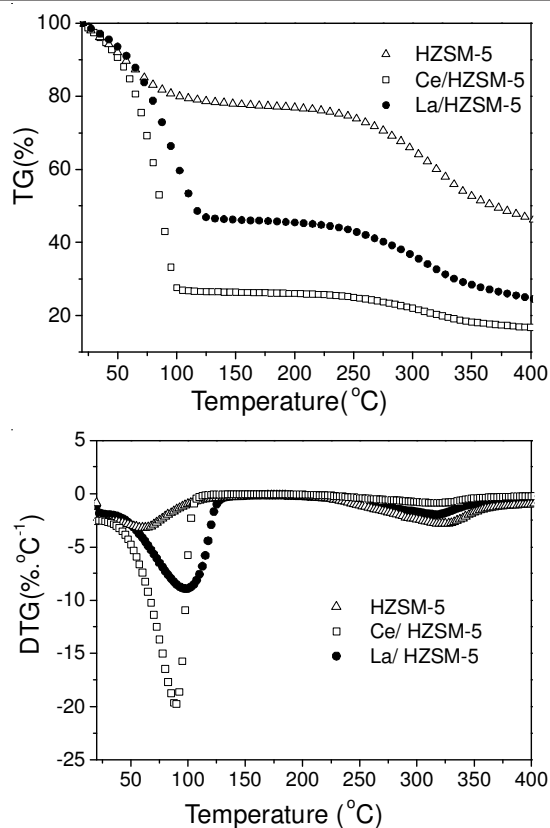


Fig. 2. TG/DTG curves of planktonic algae in presence of different catalysts

second phase is 150-250 $^\circ\text{C}$, this stage as the transitional phase, mainly for the depolymerization of planktonic algae began to appear and similar with a slow process of rice husk “glass transition” “phenomenon⁵. Planktonic algae appear trace weightlessness, that is from of the volatile weightlessness of a small amount of volatile components, TG/DTG curves tend to be more smooth. The third stage is 250-350 $^\circ\text{C}$, DTG appear obvious peak, this phase is the main stages in the pyrolysis of planktonic algae and the stage presents linear downtrend basically, showing that the pyrolysis process is smooth. The fourth stage for more than 350 $^\circ\text{C}$ and this stage is the carbonization process of planktonic algae basically, residues decompose slowly, DTG tend to be more smooth.

Planktonic algae catalytic pyrolysis dynamics analysis:

In order to further analysis of atmospheric pyrolysis process of planktonic algae biomass in the presence of catalyst, dynamic model is proposed for describing the catalytic pyrolysis process. Due to the planktonic algae composition is very complicated and thus the thermogravimetric analysis result is not a single compound information of pyrolysis reaction, but a result of the combined action of multiple components, so it is often difficult to use to describe the dynamics of a single pure component model. Studies have shown that using first order kinetics reaction to describe the process of biomass pyrolysis under nitrogen is simple and has relatively good effect⁶. As a result, the following analysis is based on the following assumptions: the quality loss of sample is only related to reaction temperature, the remaining quality of the sample; reaction temperature and the surplus quality of samples are independent mutually; apparent activation energy is not affected by temperature^{7,8}.

TABLE-1
PLANKTONIC ALGAE PYROLYTIC PROCESS DYNAMICS ANALYSIS RESULT

Catalyst	Fitting equation	Temperature (°C)	E _a (kJ mol ⁻¹)	A (min ⁻¹)	Correlation coefficient
Ce/HZSM-5	y = -6110.94x + 7.37	185-320	50.81	1590.75	0.9809
La/HZSM-5	y = -5873.87x + 7.22	165-320	48.83	1369.47	0.9859
HZSM-5	y = -6286.44x + 7.66	175-320	52.27	2131.77	0.9857

According to the law of mass action, planktonic algae biomass thermal weightlessness reaction rate equation can be represented as:

$$\frac{dx}{dt} = k(1-x)^n \quad (1)$$

In this chemical formula x wt % is conversion rate of planktonic algae, t is reaction time (min), n is reaction series; $x = (w_0 - w)/w_0$, of which w_0 is quality for the original sample, w is the quality of the sample at a certain moment; the Arrhenius equation is:

$$k = Ae^{-E_a/RT} \quad (2)$$

In this chemical formula k is reaction rate K min⁻¹, E_a is activation energy (J/mol), A is pre-exponential factor min⁻¹, T is pyrolysis temperature (K).

The type (2) into type (1) available:

$$\frac{dx}{dt} = Ae^{-E_a/RT} (1-x)^n \quad (3)$$

In the thermogravimetric experiment, a constant heating rate is used, thus heating rate $\beta = dT/dt$ is constant, so type (3) can be represented as:

$$\beta \frac{dx}{dT} = Ae^{-E_a/RT} (1-x)^n \quad (4)$$

According to Sharp differential method, the logarithm to type (4) is:

$$\ln\left(\beta \frac{dx}{dT}\right) - n \ln(1-x) = \ln A - \frac{E_a}{RT} \quad (5)$$

Assuming $f(x) = \ln(\beta dx/dT) - n \ln(1-x)$, we know variable $f(x)$ is a linear relationship with $1/T$ according to the type above. As described above, the process of biomass thermal weightlessness is usually described using first order reaction and it has relatively simple effect. Therefore, $n = 1$, plot $f(x)$

to $1/T$, if it is A straight line, the first order reaction hypothesis is true, thus reaction activation energy E_a and pre-exponential factor A can be calculated from straight line slope and intercept.

Table-1 summarizes result of planktonic algae pyrolysis dynamics analysis, from the table we find that the correlation coefficient of the fitting curve is 0.98 above, the fitting effect is remarkable, the catalytic relative effect of catalyst can be reflected basically. Catalyst HZSM-5 after the load comparing to it before the load, catalytic pyrolysis activation energy appears a downward trend. It indicates rare earth metals after the load is advantageous to the planktonic algae pyrolytic indeed, including La/HZSM-5 catalytic pyrolysis effect is best to catalytic effect of planktonic algae, because the activation energy of pyrolysis can be maximum minimized.

Conclusions

- Rare earth modified HZSM-5 catalyst on the planktonic algae water swelling effect is increased significantly, the Ce/HZSM-5 promotion effect is more obvious.

- Rare earth modified catalyst significantly the pyrolysis performance on planktonic algae increased significantly, can significantly reduce the thermal decomposition activation energy. In which La/HZSM-5 has the most obvious effect and pyrolysis activation energy can be reduced to 48.83 kJ mol⁻¹.

REFERENCES

1. K. Anastasakis and A.B. Ross, *Bioresour. Technol.*, **102**, 4876 (2011). (J).
2. A. Demirbas, *Energy Convers. Manage.*, **51**, 2738 (2010). (J).
3. P. Duan and P.E. Savage, *Ind. Eng. Chem. Res.*, **50**, 52 (2011).
4. W. Xiaoning, Z. Zhen, X. Chunming, D. Aijun, Z. Li and J. Guiyuan, *J. Rare Earths*, **25**, 321 (2007).
5. D.Y. Chen, D. Zhang and X.F. Zhu, *J. Solar Energy*, **10**, 1230 (2010).
6. H.P. Yang, Oil Palm Waste Pyrolysis Experiments and Mechanism Research, Huazhong University of Science and Technology (2005).
7. M.V. Kok and C. Keskin, *Thermochim. Acta*, **369**, 143 (2001).
8. M.C. Torrente and M.A. Galán, *Fuel*, **80**, 327 (2001).