



## Investigation on the co-pyrolysis mechanism of seaweed and rice husk with multi-method comprehensive study



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### ABSTRACT

This study aims to investigate the co-pyrolysis mechanism of *Enteromorpha* (EN) and rice husk (HU) through thermogravimetry coupled with mass spectrometry (TG-MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and fixed-bed experiments. Significant synergetic effects have been observed during the co-thermochemical conversion process, which not only improved the pyrolytic behaviors but also influenced the products compositions. Thermal analysis results showed that the experimental weight loss rate was always higher than that of the theoretical value at the temperature range of 200–300 °C. The release temperature of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> gases products shifted to 291 °C, higher than the single EN and it was in accordance with the derivative thermogravimetric (DTG) curves. This suggests that synergistic effect has a significant influence on the dehydration, the decarboxylation reactions, and fracture, restructuring of methoxy groups and carbon-carbon bonds. The bio-oil yields from the co-pyrolysis of EN and HU mixture reduced, and with addition of HU the bio-oil yield decreased from 30.95% to 29.16% and then increased to 34.12%. The difference of Py-GC/MS and gas chromatography-mass spectrometry (GC-MS) results of bio-oil revealed that the secondary reaction could reduce furans and saccharides but increase carboxylic acids and hydrocarbons. Moreover, the possible reaction path of co-pyrolysis has been given.

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## 1. Introduction

Biomass is the fourth largest energy system after coal, oil and gas, supplying approximately 14% of the world annual energy consumption. Therefore the development and utilization of biomass have attracted worldwide attention [1,2]. In China, there are abundant biomass resources, and the theoretical value of biomass is about 5 billion tons. The Chinese government also pays much attention to biomass energy utilization, which has been listed as a key scientific research project in four national five-year plans consecutively. Due to its strong photosynthesis, fast growth and suitability for large-scale artificial cultivation [3], seaweed biomass has become the promising third generation source for biofuels, and

has a high potential to replace petrochemical fuel resources [4].

Seaweed biomass, which is mainly composed of protein, lipid and carbohydrates (sulfated polysaccharides, such as glucuronide-sulfate-rhamnose; some monosaccharides, such as glucose, xylan, mannan), is one kind of abundant renewable energy resource. Seaweed biomass can be converted into biofuel through thermochemical, biochemical and physical methods, such as pyrolysis, esterification, alcoholysis, direct extraction. Among these methods, pyrolysis is considered as one of the most promising routes for biomass. Methods other than pyrolysis could only convert lipid, protein, etc [5–7]. In fact, every component in seaweed can be converted into bio-oil, biochar and biogas through pyrolysis technique [8–10]. In order to make full use of seaweed biomass (including protein, lipid and carbohydrates), many researchers have employed pyrolysis methods to convert seaweed into biofuels [11,12]. Besides, bio-oil is known as a promising alternative for crude oil to produce transportation fuels and extract valuable chemicals [13]. However, seaweed bio-oil has some undesirable

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**Table 1**  
Proximate and ultimate analysis of samples (GB476-91, GB212-91, GB/T213-1996).

Material	Proximate analysis (Wt. %) (ad)				ultimate analysis (Wt. %) (ad)					LHV $_{Q_{net, ar}}$ (MJ/kg)
	A	V	FC	M	C	H	O	N	S	
EN	28.56	53.95	10.69	6.80	29.42	3.96	21.76	7.05	2.45	14.01
HU	11.41	61.99	16.00	10.60	40.20	4.68	31.77	1.20	0.14	17.67

Note: A means ash; V means volatiles; FC means fixed carbon; M means moisture;  $Q_{net, ar}$  means lower heating value as received basis; LHV means low heating value.

properties, such as high viscosity, high corrosiveness, and low heating value, which restrict its direct application as liquid fuel. Besides, Agricultural residues, such as rice husk, are usually regarded as raw materials to produce bio-oil [15,16], but there are yet to be a commercial process that is economical. It is necessary to upgrade the quality of bio-oil and the technology of extracting valuable chemicals. There are several ways including catalytic pyrolysis and co-pyrolysis to improve the quality of bio-oil [14]. Co-pyrolysis shows synergistic effect and is considered more economical. Hence, it is regarded as an effective technique for bio-oil upgrading [17,18].

There are many complex chemical reactions during the pyrolytic process to produce bio-oil, including primary reaction, various secondary reactions and a condensation process [19]. Especially for co-pyrolysis, it also involves the interaction of many different components and synergistic effect. In order to illustrate the co-pyrolysis process mechanism and the interaction between different materials, some effective technologies should be adopted. TG-MS method is one of the most common techniques to investigate thermal events and analysis the evolved gas from the pyrolysis [20,21]. Py-GC/MS was also applied as a model of fast pyrolysis to gather the information of pyrolysis products and generating mechanisms [22]. However, Py-GC/MS mainly investigates the preliminary reaction, so there exists certain limitation in clarifying

the integrated pyrolysis mechanism [23,24]. Fixed-bed pyrolysis experiment to produce bio-oil is a good supplement to understand the co-pyrolysis mechanism [25]. This study aims to investigate the thermal behavior and the products distributions of co-pyrolysis of seaweed and rice husk and to explore the possibility of upgrading the bio-oil quality through co-pyrolysis conversion. The pyrolytic behavior and gases evolution of single EN, single HU and their different mass ratio of EN and HU mixtures were investigated via in a thermogravimetric analyzer coupled with mass spectrometry. The co-pyrolysis experiments through Py-GC/MS and in a fixed bed were also carried out in this study, while GC-MS technique was also used to identify the components of bio-oil. This paper provides a further understanding of the interaction between seaweed (EN) and lignocellulosic biomass (HU) and offers some theoretical data for the large-scale utilization of seaweed biomass.

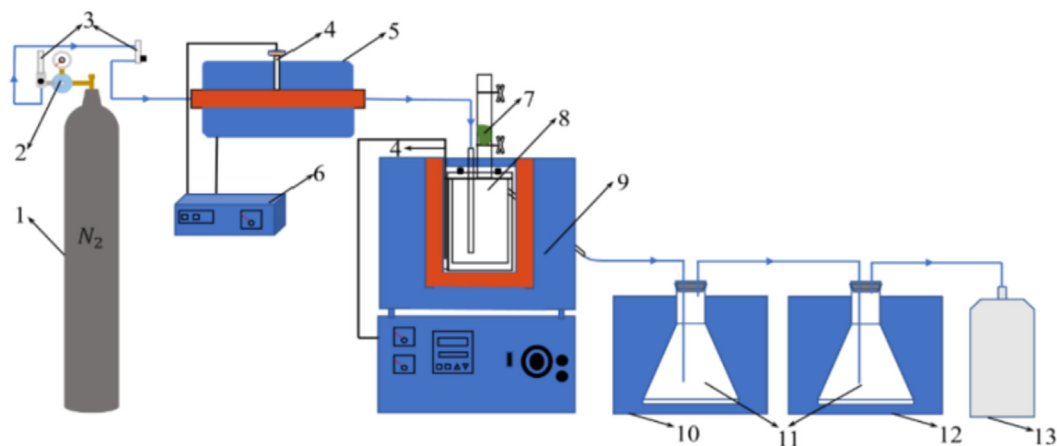
## 2. Experimental

### 2.1. Material

EN, a typical green seaweed and macro algae, and HU, a terrestrial biomass and common residues, were used as raw materials in this study. These samples were dried and stored in a cool, dry environment. Then the dried materials were ground by a pulverizer into particle (0.18–0.45 mm). The proximate and ultimate analysis results of the samples are shown in Table 1. Table 2 shows that there are high level of metal components in EN, and also there are some metal ions in HU, which may affect the co-pyrolysis process. For co-pyrolysis, EN and HU powder were well-mixed mechanically at the mass ratio of 1:1.

**Table 2**  
The ICP analysis of raw EN and HU.

Material	CONTENT (%) [K]	[Ca]	[Na]	[Mg]	[Fe]
EN	5.270	0.370	9.610	0.670	0.131
HU	1.019	0.189	0.016	0.179	0.063



1- Nitrogen cylinder, 2-Gas-pressure gauge, 3-Flowmeter, 4-Thermocouple, 5-N<sub>2</sub> preheating equipment, 6-Controller; 7-Algae sample, 8-Fixed bed reactor, 9-Furnace, 10-Condenser (I), 11-Bio-oil storage, 12-Condenser (II), 13. Gas bag

**Fig. 1.** Experimental setup for Pyrolysis runs.

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