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Co-pyrolysis of microalgae and waste rubber tire in supercritical ethanol

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HIGHLIGHTS

- Temperature and R/M ratio significantly affected yield and quality of the bio-oil.
- Microalgae allows the conversion of WRT under milder conditions than WRT alone.
- A positive synergistic effect was observed between the WRT and the microalgae.
- ZnO and carbon black in the WRT improved the quality of the bio-oil.
- HHVs of bio-oils were found to be in the range of 35.80–42.03 MJ/kg.

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ABSTRACT

Co-pyrolysis of microalgae and waste rubber tire (WRT) in supercritical ethanol was examined to investigate the effects of reaction temperature (290–370 °C), time (10–120 min), WRT/microalgae mass ratio (R/M, 5/0–0:5), and ethanol/feedstock ratio (EtOH/(R + M), 5:5–30:5). Temperature and mass ratio are two factors that significantly affect the yield and quality of bio-oil. Under optimal reaction conditions, the highest bio-oil yield achieved was 65.4 wt%. The presence of microalgae allows the conversion of WRT to occur under milder conditions than WRT alone. The temperature needed for adequate conversion of WRT and microalgae in supercritical ethanol (330 °C) is much lower than the co-pyrolysis temperature without a solvent. ZnO and carbon black in the WRT played catalytic roles in the conversion of the WRT and microalgae as well as the in situ denitrogenation and deoxygenation of the bio-oil. A positive synergistic effect between the WRT and the microalgae was observed. The highest value for the synergistic effect (37.8%) was observed at an R/M mass ratio of 1:1. The interaction of microalgae and WRT during co-pyrolysis also favored denitrogenation and deoxygenation, thus improving the quality of the bio-oil. The heating values of the bio-oils produced from the co-pyrolysis of WRT and microalgae were found to be in the range of 35.80–42.03 MJ/kg. The main components in the gas phase are typically CO_2, H_2, and CH_4. However, methods for improving the quality of bio-oil via co-pyrolysis will require further study.

1. Introduction

It is becoming increasingly obvious that today's reliance on fossil fuels is causing problems (e.g., the energy crisis and environmental pollution) that must be addressed [1]. Therefore, it is urgent for researchers to develop alternative energy sources that can be effective substitutes for fossil fuels. Among the alternatives, biomass shows considerable promise because it is abundant, clean, renewable, and carbon neutral [2,3]. Biomass also represents an important energy resource, both at present and as a potential energy contributor in the future. To date, a wide variety of biomass types such as wood, grass, agricultural crops and their residue, animal waste, and aquatic plants have been examined to determine their efficacy for the production of biofuels. As one of the most important aquatic plants, microalgae have long been recognized as promising sources of biofuel because of their high oil content and rapid biomass production [4].

Thermochemical conversion (e.g., pyrolysis) is among the most common methods for converting microalgae into gasoline-compatible liquid fuels [5–8]. These liquid fuels have a higher energy density than microalgae feedstock, which allows the liquid fuels to be transported more economically and stored more easily. However, liquid fuels have undesirable properties such as a high oxygen

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content and elevated acidity (i.e., high acid number). Thus, H_2 or hydrogen donors are usually employed to improve the properties of the bio-oil during the thermochemical conversion of biomass [9,10]. For a commercial biomass conversion plant, a plentiful and cost-effective supply of hydrogen must be available, which will significantly increase the processing cost. Thus, it is necessary to search for inexpensive and abundant alternative hydrogen sources for the production of high-quality bio-oils.

Waste synthetic polymers, which have a high hydrogen content, could be an alternative source of hydrogen that could, in principle, be transferred from the waste materials to the biomass during the pyrolysis process. Utilizing waste materials in this way has the added advantage of reducing the amount of waste that must be incinerated or disposed of in landfills. Therefore, co-processing of biomass and synthetic polymers shows much promise for the production of high-quality bio-oils.

As an important type of synthetic polymer, waste rubber tire (WRT), which contains a high concentration of hydrogen, could be a potential hydrogen source for the conversion of biomass. WRTs have a high level of volatile organics and a high heating value (33–35 MJ/kg); thus, WRTs are also an excellent material for energy recovery [11]. WRTs contain a certain amount of zinc oxide, which could play a catalytic role during the conversion process. In addition, one billion WRTs are generated annually worldwide [12]. In 2010, China alone produced over 300 million WRTs [13]. Therefore, co-processing of biomass and WRT shows significant promise in terms of energy recovery and the recycling of waste materials.

To date, co-pyrolysis is one of the most commonly used methods to simultaneously convert biomass and WRT into liquid fuel [14–19]. The addition of WRT to the biomass feedstock remarkably improved the bio-oil properties due to the transfer of hydrogen from the WRT to the biomass. A positive synergistic effect was observed during the co-pyrolysis process that enhanced both the yield and quality of the liquid product. However, problems were encountered in the co-pyrolysis of these materials because the reactions were performed under severe conditions (e.g., 450–600 °C). Extremely high temperatures would promote re-polymerization and condensation reactions of the liquid products, which accelerates char formation, especially at a low biomass/WRT mass ratios. Therefore, a solvent was employed to decrease the reaction temperature during the co-pyrolysis of synthetic polymers and biomass. Previous work examined plastics as feedstock for co-pyrolysis with biomass in water and ethanol [20–22]. These investigations suggested that the solvents served as a medium in which the decomposition of biomass and the WRT occurred. The decomposition of plastics occurs at moderate temperatures (380–420 °C), and the solvent allows immediate dissolution and incorporation of the liquids into the oils during processing. Additionally, solvents prevent further aromatization of the liquids and produce a lighter, upgraded oil compared to pyrolyzed tire oil produced without solvents. The presence of water or ethanol can suppress coke formation and is involved in H-donation between the pyrolysis network of biomass and plastics, which improves the quality of the liquid products. The addition of biomass to plastics allows for milder reaction conditions compared with the conditions used for plastic alone. Synergistic effects were observed during co-pyrolysis. Taking into account these experimental results, it may be concluded that the co-pyrolysis of microalgae with WRT in a solvent is a promising way to produce stable liquid products with improved properties. To the best of our knowledge, the co-pyrolysis of microalgae and WRT in a solvent has not been previously examined. The chemical compositions of WRT and plastics are very different. Thus, it would be insightful to study the co-pyrolysis of microalgae and WRT in a solvent environment.

In the present work, microalgae were selected for co-pyrolysis with WRT in ethanol to investigate the synergistic effect on bio-oil yield and composition and to understand the chemical transformations that take place during the co-pyrolysis process. The influences of the co-processing parameters, such as temperature, time, WRT/microalgae mass ratio (R/M), and the ethanol/(rubber + microalgae) (EtOH/(R + M)) ratio, on the yields of the product fractions and the properties of the bio-oil were examined. Finally, the bio-oil derived from the co-pyrolysis of microalgae and WRT was fully characterized to understand the chemical interaction(s) between WRT and microalgae during the co-pyrolysis process and to determine the feasibility of this system as a potential energy source and chemical feedstock. The present study breaks new ground on two fronts: first, we used microalgae and WRT as the co-processing feedstock, and second, we used ethanol as the co-processing solvent.

2. Experimental procedures

2.1. Materials

Chlorella pyrenoidosa, a marine microalga with a lipid content of 19 wt%, was selected and obtained from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (North China). Its proximate and ultimate analyses are included in Table 1.

The WRT was obtained from a local recycling station. The WRT material was mechanically ground into small particles (0.3–0.5 mm) using a file. The WRT powder was composed of rubber without the steel and textile netting. The results of the proximate and ultimate analyses of the WRT powder are included in Table 1. Inorganic compositions of the microalgae and WRT were measured by X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF spectrometer, and the results are listed in Table 1. All other chemical reagents used for the experiments were of analytical grade.

All the experiments were performed in a custom-made autoclave with a total volume of 57.4 mL. A schematic of the apparatus used in the study is shown in Fig. 1. The reactor was seasoned using water at 350 °C for 4 h prior to its use to eliminate the possibility of interference from residual organic material on its surface. A molten-salt bath, consisting of KNO_3 and $NaNO_3$ at a mass ratio of 5:4, was used to heat the reactor.

Table 1
(a) Characteristics of microalgae and WRT. (b) Inorganic composition (wt%, dry basis) of microalgae. (c) Inorganic composition (wt%, dry basis) of WRT.

	Proximate analysis (wt%, dry basis)					Ultimate analysis (wt%, dry basis)				
	VM	CS	FC	A	M	C	H	N	S	O
(a)										
Microalgae	64	19	17	9	10	46.83	6.87	8.44	0.86	25.83
WRT	72	12	19	9	0	78.70	7.47	1.40	1.90	1.63

(b)

Na	Mg	Al	Si	P	Cl
1.165	0.396	0.168	0.893	0.509	2.757
K	Ca	Mn	Fe	Sr	Mo
0.428	4.439	0.082	0.073	0.205	0.017

(c)

Al	Si	P	Cl	K	Ca
0.015	0.201	0.008	0.042	0.108	0.622
Ti	Fe	Cu	Co	Zn	Br
0.038	0.442	0.050	0.031	6.545	0.072

VM: volatile matter; CS: CH_2Cl_2 soluble material; FC: fixed carbon; A: ash; M: moisture.