

Co-Pyrolysis of Waste Polystyrene Foam and Microalgae at Low Temperatures [†]

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Abstract: Fossil fuel reserves have depleted. Therefore, renewable and sustainable energy forms an important issue. Microalgae as a third-generation biomass can be an alternative carbon-neutral fuel source. However, its fuel quality is low. Co-pyrolysis is an important technique to upgrade the fuel quality of microalgae. In this study, we aimed to carry out the pyrolysis of polystyrene and *Spirulina* sp. microalgae at low temperatures (350, 400, and 450 °C). The experiments were conducted using a semi-batch reactor setup. Co-pyrolytic product yields were calculated. The composition of liquid products was enlightened by using GC-MS. As a result of the analysis, aromatic compounds like styrene and toluene were detected in the co-pyrolytic liquid. Moreover, it was observed that co-pyrolysis increased the solid residue yield while it decreased the liquid and gas product yield.

Keywords: polystyrene; plastic wastes; microalgae; biomass; pyrolysis

1. Introduction

Global warming causes environmental changes. It is known that the reason for global warming is human activities. Humans affect global warming by using fossil fuels in huge amounts [1]. While anthropogenic activities cause fossil fuel depletion, the wasted materials, which are called municipal solid waste (MSW), can be used as energy feedstock. These energy sources can be transformed into fuel via thermochemical conversion technologies such as pyrolysis, gasification, carbonization, and incineration. These technologies also make it possible to meet electricity needs [2].

The pyrolysis process is carried out at 300–1200 °C in the absence of oxygen. In this aspect, pyrolysis differs from combustion. Nowadays, pyrolysis is used to produce catalysis, hydrogen, and chemicals [2]. Furthermore, pyrolysis has more advantages than other thermochemical routes. Firstly, low energy consumption occurs in the pyrolysis process compared to gasification. Secondly, harmful gases are produced in relatively low amounts. Lastly, the process can be formed and moved to another place easily [3].

Based on data which were obtained in 2020, nearly 3 million tons of plastic packaging materials are collected in landfills in Europe [4]. There are many research studies in the scientific literature about plastic waste such as polystyrene (PS) [5], polypropylene (PP) [6], and low-density polyethylene (PE) [7] pyrolysis.

Carbon-neutral fuels have a huge importance on sustainability. Microalgae as a non-edible feedstock occurs as an alternative to first-generation biomass sources [8]. However, it is known that the fuel obtained from microalgae pyrolysis has some disadvantages like high humidity and protein content. Therefore, co-pyrolysis with several materials like tires, plastics, and bamboo waste seems to be a good way to obtain high-quality fuel [9]. In this study, we aimed to determine the effect of blending PS with SP feed on liquid yield



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and composition compared to PS pyrolysis. The experiments were conducted at several temperatures, which were selected as low as possible.

2. Material and Methods

The plastic waste source, polystyrene (PS) foam, was supplied as an electronic device package. Before the pyrolysis, it was divided into small pieces in a rectangular prism shape and dried in an oven. The aim of this drying was to fit the PS in the glass reactor. Because expanded PS was used, it was known that over 90 percent of the volume of the expanded PS was air [10]. The microalgae source, *Spirulina* (SP), was bought in powder form commercially. The properties of SP are shown in Table 1. The amount of oxygen in the SP was decided by the difference. The pyrolysis setup was a ceramic furnace, a nitrogen bottle, a PID temperature controller, thermocouples, a glass reactor, and condensers. The setup is shown in Figure 1. For experiments, firstly, the feedstock was weighted. Additionally, then, the feedstock was put in the glass reactor whose weight was known. Then, the reactor was settled in the vertical furnace. The glass equipment components were combined with each other. The circulator was arranged at 0 °C and worked. The temperature in the reactor was shown by using a digital thermocouple. The temperature in the furnace was arranged by utilizing a PID controller. Before the experiments, the setup was purged with nitrogen. Then, the experiment was carried out at the desired temperature. After the experiment, product yields were calculated with respect to the amount of the occurring products. Liquid products were analyzed via GC-MS. The co-pyrolysis of SP and PS was conducted by adding equal amounts of feedstock to the reactor. For comparing the results, pristine PS pyrolysis was performed at the same temperatures. The effect of temperature (350, 400, and 450 °C) on the liquid yield and composition was investigated. Apart from that, other product yields (solid, gas) and total conversion (gas and liquid) values were computed.

Table 1. Elemental composition of SP feedstock (ash-free and dry basis). Reprinted with permission from Ref. [12]. 2020, Dergipark.

Elements	Amount (% , wt./wt.)
C	46.69
H	6.22
N	10.76
S	1.55
O	34.78



Figure 1. Pyrolysis setup. Reprinted with permission from Ref. [11]. 2018, Ankara University.

3. Results and Discussion

As shown in Figure 2, compared to the individual pyrolysis of PS, the co-pyrolysis decreased the liquid yield at all temperatures. For the co-pyrolysis of SP and PS, the maximum liquid yield was observed at 450 °C. It was determined that the SP and PS co-pyrolytic liquid included mainly styrene and styrene-derivative methyl styrene. It was estimated that the observed phenol in the co-pyrolytic liquid originated from the SP's thermal degradation [8]. In Figure 3, the chromatogram of the co-pyrolytic liquid and virgin polystyrene is shown.

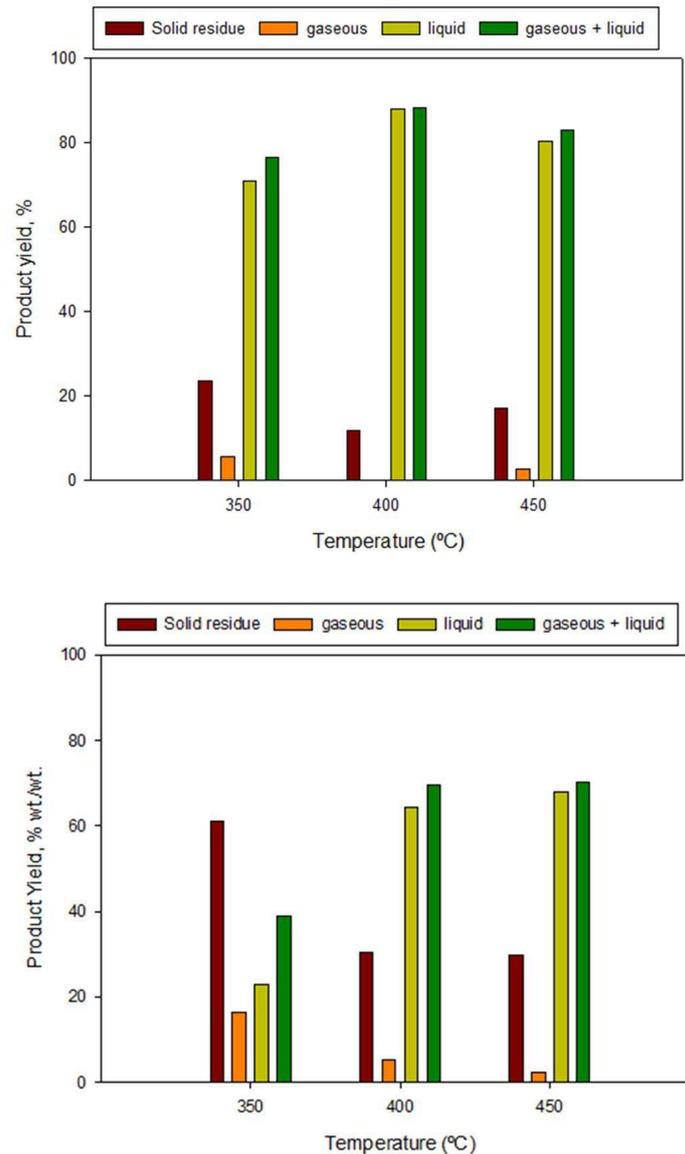


Figure 2. Pyrolytic product distribution by weight for PS (**up**) and PS–algae (1:1) (**down**).

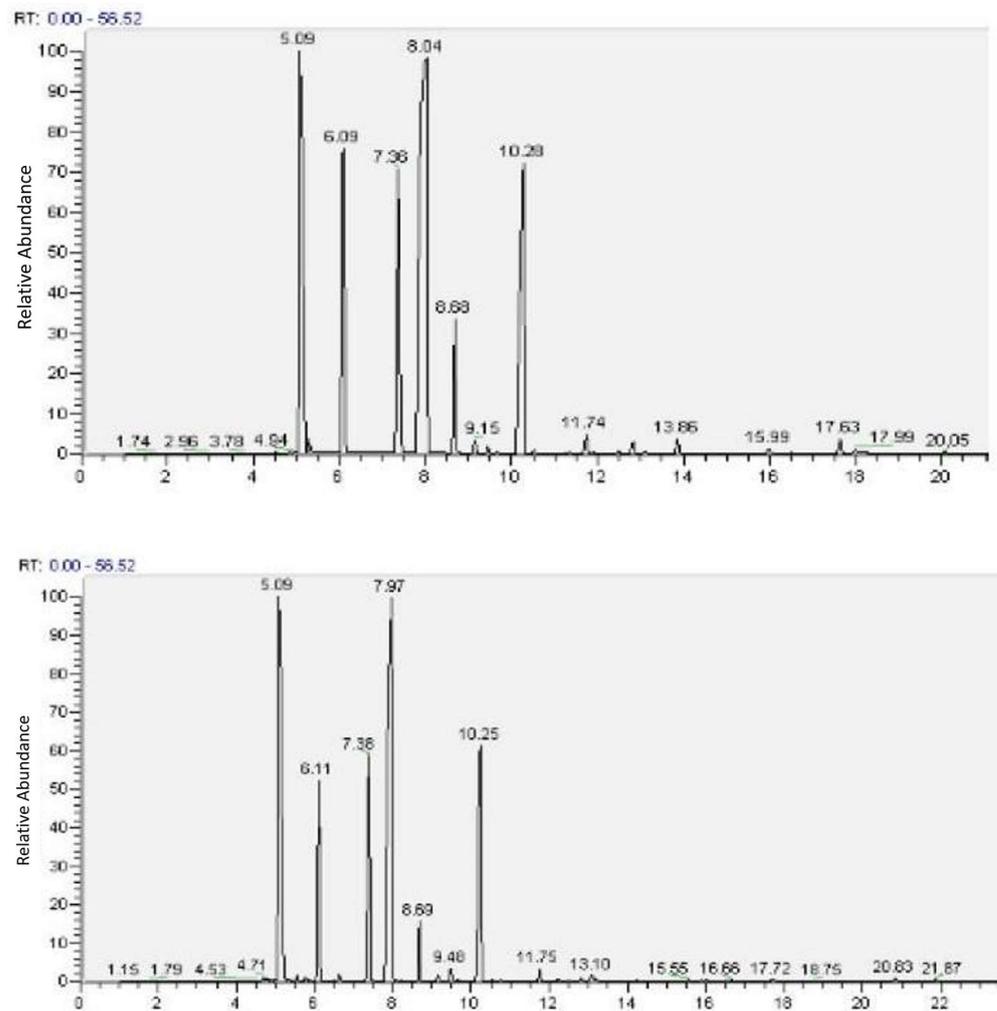


Figure 3. GC-MS chromatogram for the liquid product obtained from and PS pyrolysis (**up**) and PS-algae co-pyrolysis (**down**) at 450 °C.

In Table 2, the component distribution of polystyrene as a result of thermal cracking is shown. The liquid is mainly composed of aromatic hydrocarbons. It was observed that the styrene and its derivative alpha-methyl styrene affected the temperature significantly. Additionally, as expected, styrene was the main component.

Table 2. Detecting main components in the pyrolytic liquid of PS using GC-MS.

Compound	Peak Area (%)		
	350 °C	400 °C	450 °C
benzene	0.5	0.85	0
toluene	9.25	3.5	6.6
ethyl benzene	8.75	4.7	7.92
styrene	46.7	16.05	29
methyl styrene	24.15	9.5	10.6

In Table 3, compounds detected in the co-pyrolytic liquid of SP and PS are shown. Phenol, which was not observed in the PS liquid, was obtained in the bio-oil. Interestingly, at 400 °C, the styrene and alpha-methyl styrene amounts were found higher than pristine PS liquid. This could originate from the synergistic effects between PS and SP.

Table 3. Detecting main components in the pyrolytic liquid of PS–algae using GC-MS.

Compound	Peak Area (%)		
	350 °C	400 °C	450 °C
toluene	5.5	6.62	5.9
ethyl benzene	7.25	9.66	7.85
styrene	24.8	26.89	26.7
phenol	0	1.2	0.9
methyl styrene	9.45	14	10.65

4. Conclusions

The co-pyrolysis of PS and SP was conducted at 350–450 °C. In this temperature range, the liquid product compositions were determined by using GC-MS. As a result of the co-pyrolysis, it was observed phenol which was an oxygenated compound. The synergistic effects between the feedstocks enabled an increase in the toluene, ethyl benzene, styrene, and alpha-methyl styrene amounts at 400 °C.

Supplementary Materials: The presentation materials can be downloaded at: <https://www.mdpi.com/xxx>.

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