Production of Biofuels Through Co-Pyrolysis of Blends of Biomass and Waste Plastics

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In 2021, more than 40 million tons of plastic waste was produced in the United States of America. 34 million tons of which was not recycled or reused and was deposited into landfills or exported out of the country (EPA, 2022). This marks a massive loss of money, energy, and valuable resources from our society. The innate value stored in waste plastics can be reclaimed through either recycling or through various thermochemical processes, such as pyrolysis, which splits plastic polymers into smaller hydrocarbon molecules (Nagarjuna and Shrikanth, 2018). These molecules can then be used as ingredients or reagents for the manufacturing of various value-added products, used for energy production, or refined to produce fuels, lubricants, and asphalt among other products (EIA, 2022). Although some research has been conducted to determine the effectiveness of plastic pyrolysis, little research has been conducted regarding the possible synergistic or antagonistic effects of blending plastics with biomass, which is presently a common feedstock for pyrolysis.

If pyrolysis is to become a widespread waste management solution throughout the United States, it is inherently necessary that it be a cost-effective process. As such, performing co-pyrolysis of blended feedstocks is appealing because municipal waste streams contain various organic and inorganic waste products, and it is both time consuming and expensive to separate these various materials from each other (Burnley, 2007). Co-pyrolysis is the process of performing pyrolysis on mixed feedstocks. It has the potential to produce oil of higher quality than if either feedstock was pyrolyzed individually due to various synergic effects that can occur. If value-added products of sufficient quality and quantity can be achieved at a reasonable cost and energy expenditure through co-pyrolysis of the entire municipal waste stream, the need for landfills and non-renewable petroleum products will simultaneously decrease.petroleum products will simultaneously decrease.

This study investigated the effectiveness of co-pyrolysis of a simplified municipal waste stream modeled by longleaf pine (Pinus palustris) to represent organic waste and polystyrene to represent inorganic plastic wastes. In addition to varying the composition of the blended feedstock, various pyrolysis temperatures, and catalysts were also investigated to determine their respective effects on the yield and energy content of the pyrolysis oil produced.

Three different blends of feedstocks: 100% polystyrene, 100% pine, and 50% polystyrene and 50% pine blend were investigated. Additionally, pyrolysis was performed at three different temperatures: 450°C, 500°C, and 550°C; and with three different catalytic conditions: no catalyst, 10% bauxite residue (red mud) by mass blended with the feedstock, and 10% Zeolite Socony Mobil-5 (ZSM-5) by mass blended with the feedstock.

Polystyrene was purchased from Amazon in the form of clear disposable cutlery and ground into uniformly sized particles using a plastic granulator with a 1/8" screen. Pine was obtained from Auburn University forest tracts and dried, chipped, and ground into uniformly sized particles using a hammer mill with a 1/8" screen. The 50% polystyrene and 50% pine blend was blended on a by-mass basis and blended using an orbital shaker to form a homogeneous mixture.

Red mud was not reduced or calcined and was crushed and sieved through a No. 140 mesh sieve. ZSM-5 was ground into a fine powder using a planetary ball mill and passed through a No. 140 sieve. The catalyst feedstock blends were prepared as a 90% feedstock and 10% catalyst blend on a by-mass basis and blended using an orbital shaker to form a homogeneous mixture.

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A total of 27 experimental trials were performed to allow for each feedstock to be pyrolyzed at each combination of temperature and catalytic activity. Pyrolysis experiments were Auburn University Journal of Undergraduate Scholarship performed in a small-scale fixed-bed pyrolysis reactor at a heating rate of 50°C per minute up to the pyrolysis temperature and with Nitrogen purge gas flowing at 0.75 liters per minute through the reactor tube. The pyrolysis gases leaving the reactor tube passed through a four-unit condenser train sitting in an ice bath and through an electrostatic precipitator operating at 20 kV before being discharged to the atmosphere as seen in Figure 1.

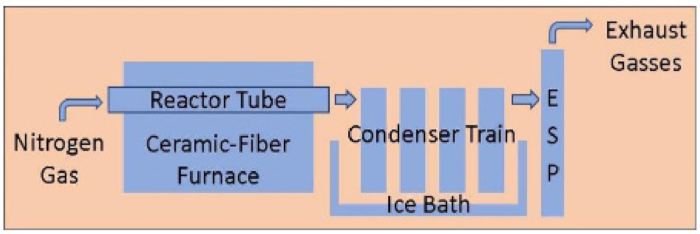

Fig. 1 Model of fixed-bed pyrolysis reactor used in this study.

In each trial without a catalyst, 40.0g of feedstock was loaded into the reactor tube. For each trial containing a catalyst, 44.5g of feedstock blend was used to ensure that 40.0g of the desired feedstock was present at a 90% feedstock to 10% catalyst ratio on a per mass basis. Each trial was run for three hours after reaching the desired pyrolysis temperature to fully pyrolyze all the feedstock in its entirety.

After the reactor had cooled down the percent mass of pyrolysis oil collected and char remaining in the reactor tube were measured and the percent mass of syngas was obtained by the difference. The pyrolysis oil collected was analyzed via Karl Fischer titration to determine the water content, through bomb calorimetry to determine the higher heating value and via gas chromatography-mass spectrometry to determine the chemical composition and hydrocarbon chain sizes of the pyrolysis oil produced.

The summarized results of the 27 trials performed over the course of the experiment are presented in Figure 2. Additionally, from the data collected via gas chromatography mass spectrometry it was determined that the polystyrene containing blends consisted of heavier atoms frequently containing 16 or more carbon atoms and the pine containing blends were composed of lighter aromatic compounds with oxygenated groups. Furthermore, it was observed that oil obtained from pyrolysis performed at higher temperatures and in the presence of catalysts contained more frequent occurrences of smaller and lighter hydrocarbons.

It was concluded that polystyrene pyrolysis produced both the largest oil yield and the pyrolysis oil with the highest energy content. Furthermore, it was observed that higher temperatures led to a higher oil and gas yield in polystyrene containing feedstocks and that 500°C was the optimal temperature for pyrolysis oil production from pure pine feedstocks. When pyrolyzed at temperatures lower than 500°C the pine produced more char and when pyrolyzed at temperatures higher than 500°C the pine feedstock produced larger amounts of gas.

Variation of % Fractions by Temperature

Feedstock	450C Oil	500C Oil	550C Oil	450C Gas	500C Gas	550C Gas	450C Char	500C Char	550C Char
PS_none	88	83.75	84	0	8.75	8	12	7.5	8
PS_RM	80	93.75	96.25	12.5	3.75	1.25	7.5	2.5	2.5
PS_ZSM-5	82.5	80	86.25	6.25	11.25	10	11.25	8.75	3.75
50/50_none	56.25	57.5	65	20	21.25	13.75	23.75	21.25	21.25
50/50_RM	53.75	67.5	73.75	23.75	17.5	15	22.5	15	11.25
50/50_ZSM-5	61.25	61.25	67.5	18.75	12.5	18.75	20	26.25	13.75
Pine_none	48.75	52.5	47.5	15	15	21.25	36.25	32.5	31.25
Pine_RM	48.75	51.25	50	13.75	15	20	37.5	33.75	30
Pine_ZSM-5	46.25	48.75	50	15	150.75	20	38.75	33.75	30

Water Content		Heating Value	
Feedstock	Average % of all trials	Feedstock	Average of all Trials
PS	0%	PS	41.78 (MJ/kg)
50/50	27.59%	50/50	30.83 (MJ/kg)
Pine	45.84%	Pine	10.93 (MJ/kg)

Fig. 2 Summarized results of the percent mass fractions of oil, char, and gas (calculated by difference) as well as the water content and heating value of the pyrolysis oils produced.

Red mud increased the oil yield and decreased the char yield of polystyrene containing feedstocks. ZSM-5 increased the gas yield of polystyrene containing feedstocks and decreased the char yield. Red mud had little effect on the pure pine feedstock and ZSM-5 increased the gas yield of pine and decreased the char yield.

Most importantly, it was concluded that blending polystyrene and pine in a 50% and 50% ratio had an antagonistic effect on both the quantity of oil produced and the energy content of that oil. It is likely that some of the high energy content molecules produced by the pyrolysis of the polystyrene was either absorbed by the pine char or further cracked by the catalytic effects of the char into non-condensable gasses. Further study will be required to determine with certainty the exact cause of the decreased yield of the blended feedstocks.

Statement of Research Advisor

Ayden's research was conducted as part of the overall focus of the Center for Bioenergy and Bioproducts at Auburn University. We aim to produce renewable energy, biofuels, and other value-added products from biomass and various waste materials. Ayden's research on the co-pyrolysis of biomass and plastic wastes can be applied at a larger scale to blended waste streams to produce pyrolysis oil from municipal and industrial wastes. This oil could be upgraded or refined into various biofuel or biolubricant products.

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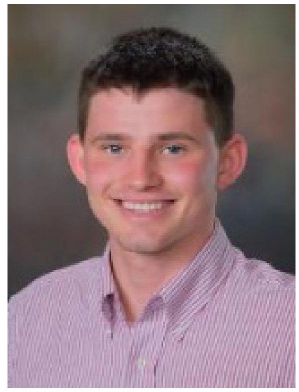
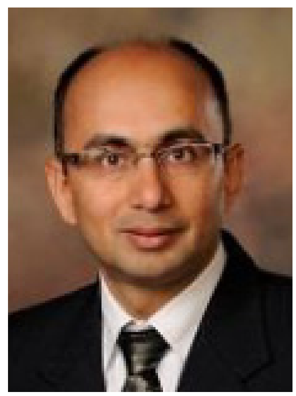
Authors Biography



Ayden Kemp is a junior pursuing a B.S. degree in Biosystems Engineering and a B.S. degree in Aerospace Engineering at Auburn University. His research focuses on pyrolysis of various feedstocks and on catalytic pyrolysis to improve yields and oil quality.



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