

Co-Pyrolysis of Southern Pine and Micronized Rubber Powder with Nickel Oxide and Sodium Carbonate Catalysts

Cody Wainscott, Austin C. Edwards, Jason Street,* Brian Mitchell, Islam Elsayed, El Barbary Hassan, and Todd E. Mlsna



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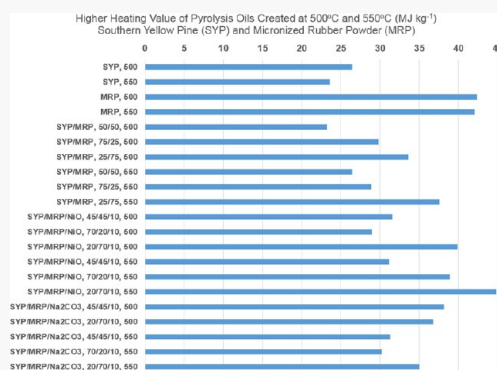


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ABSTRACT: Bio-oil created from biomass sources does not have desirable fuel qualities because of high water and oxygenate concentrations. In an attempt to improve these properties without having to undergo expensive upgrading techniques after production, micronized rubber powder (MRP) was co-fed at various ratios with southern yellow pine (SYP) inside an auger reactor to produce upgraded pyrolysis oil. The MRP proved useful in increasing the calorific value of the pyrolysis oil by lowering the water content and the amount of oxygenates in the oil. To improve the pyrolysis oil properties further, nickel oxide and sodium carbonate were added to the feedstock. Fischer titration revealed a reduction in the water content. Sodium carbonate reduced the formation of acids. Both catalysts caused an increase in the formation of unsaturated hydrocarbons and phenolic compounds. Nickel oxide outperformed sodium carbonate in terms of producing pyrolysis oil with an increased calorific value.



INTRODUCTION

Because of a growing interest in energy independence and climate change concerns, biomass has become an energy source of interest in order to both reduce fossil fuel carbon dioxide emissions and move away from depleting fossil fuel resources. Approximately 70% of biomass produced in the United States comes from forest lands, which encompass 33% of the entire United States landmass. This has the potential to produce approximately 29 billion cubic feet of feedstock per year.¹ Because of the increasing demand for transportation fuel, biomass to fuel and gaseous product technology was developed around pyrolysis, gasification, and liquefaction. Pyrolysis and liquefaction technology can convert biomass to a crude liquid product called bio-oil. Bio-oil is a highly oxygenated liquid composed of a complex mixture of water (15–35%), carboxylic acids (10–25%), aldehydes (10–15%), ketones (1–5%), alcohols (2–5%), sugars (5–15%), phenols (5–10%), and furans and pyrans (1–5%) and also includes approximately 10% other miscellaneous compounds, which must be further upgraded before use as a traditional hydrocarbon fuel.²

Waste tires contribute to about 2–3% of the total waste in the world, with an annual disposal of 1.5 billion tires worldwide.³ There are treatment methods available through energy recovery options, including waste-derived fuel in power stations, cement kilns, co-incineration, and material recycling. However, most tires are either openly dumped in the environment or dumped in landfills because waste tires are difficult to manage because of their complex chemical characteristics.^{4–6} Waste tires contribute to environmental and economic issues because they resist

degradation because of the vulcanization process during their production, which can give them a lifespan of 80–100 years. This process consists of long-chain polymers of isoprene, butadiene, and styrene-butadiene being cross-linked with sulfur bonds, which provides resistance to antioxidants and anti-ozonants. Major components in tires include natural rubber, styrene butadiene rubber, polybutadiene, and butyl rubber with other additives.⁷

Studies involving the pyrolysis of biomass and rubber are limited in the literature; however, a few studies have shown that when rubber undergoes pyrolysis with biomass, the quality of the oil can be upgraded with an increase in the heating value, quality, and overall yield of the oil produced as compared to only using biomass. Pyrolysis of biomass/rubber showed an increase in liquid yield at 90/10 and 80/20 ratios, resulting in an increase of up to 27% and 70%, respectively.⁸ The biomass/rubber mixtures led to an upgraded liquid with a lower acid number, higher calorific value, and lower oxygen content.⁸ Martinez et al.⁹ used wood chips containing bark and blended them with waste tires at 10% and 20% rubber, followed by heating at a rate of 80 °C/min to a maximum of 500 °C in a fixed bed and auger reactor separately. Oil collected

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Table 1. SYP Particle Size Distribution

particle size (mm)	proportion by weight (%)
≥ 2.80	0.4
2.00–2.80	19.4
1.40–2.00	30.7
1.00–1.40	16.6
0.50–1.00	22.0
0.25–0.50	7.0
< 0.25	4.0

Table 2. MRP Particle Size Distribution

particle size (mm)	proportion by weight (%)
≥ 0.250	0.0
0.178–0.250	39.7
0.150–0.178	20.6
0.104–0.150	23.2
0.074–0.104	14.1
< 0.074	2.4

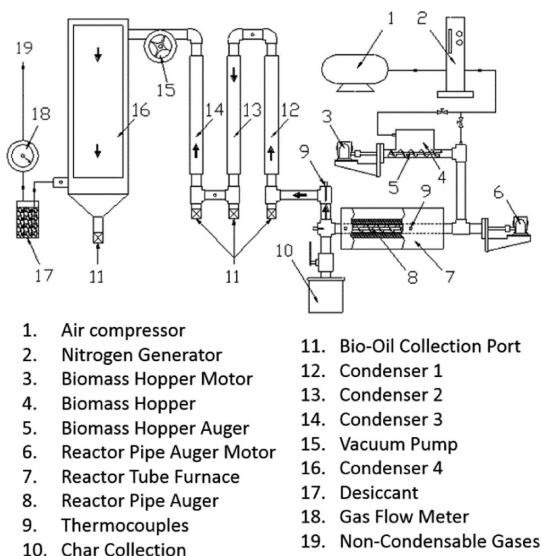


Figure 1. Diagram of the pyrolysis auger system

from both reactors showed a decrease in the water content and acid content, which increased both the pH and heating values. The research found that rubber blends released radicals, which encouraged the formation of higher molecular compounds and increased the viscosity slightly when compared to the liquid produced from the biomass control. It was also observed that an increase of rubber in the feedstock increased the heating value.

Other researchers have introduced catalysts with rubber or biomass with interesting results. Nickel catalysts have been shown to increase hydrogen yield at temperatures of 350 °C and higher. The available hydrogen can be used to deoxygenate the bio-oil and increase the pH value. Williams¹⁰ discussed pyrolysis of waste tire rubber at 300 °C–500 °C with a nickel catalyst. An increase in the yield of hydrogen was observed, which decreased the oxygenated compounds in the oil.

Demirbas et al.¹¹ used a tube reactor to pyrolyze fine rubber particles with 2%, 5%, and 10% sodium carbonate at temperatures of 400 °C–500 °C. A 10% sodium carbonate mixture produced the largest pyrolysis oil yield and lowered the sulfur content. The liquid product from their study, which exhibited the best characteristics, was produced using an inclusion of 5%

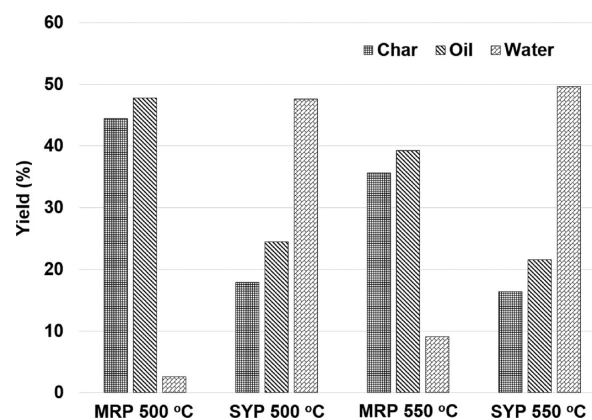


Figure 2. Pyrolysis of pure SYP or MRP (100% SYP or 100% MRP) yields at 500 °C and 550 °C. SYP = southern yellow pine, MRP = micronized rubber powder

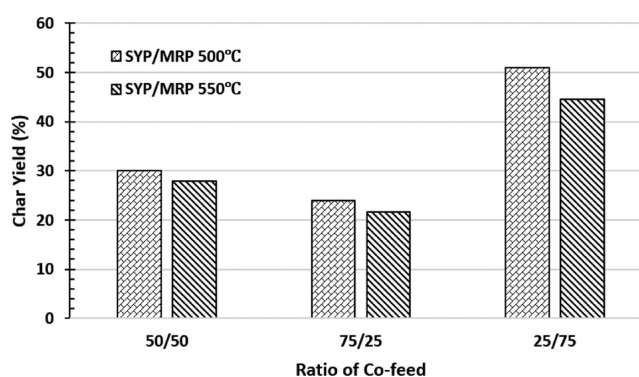


Figure 3. Pyrolysis of co-fed SYP and MRP feedstock char yield. SYP = southern yellow pine, MRP = micronized rubber powder

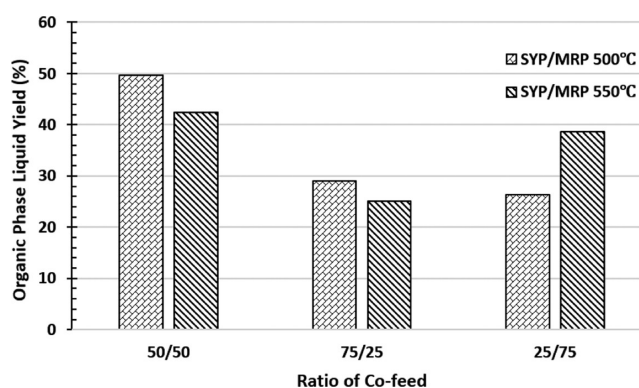


Figure 4. Pyrolysis of co-fed SYP and MRP feedstock oil yield. SYP = southern yellow pine, MRP = micronized rubber powder

sodium carbonate with their feedstock. The raw oil was similar to diesel concerning the characteristics of higher heating value (HHV), water content, viscosity, and density, but their liquid product had a higher sulfur content. Imran et al.¹² used a fixed bed reactor to pyrolyze biomass mixed with sodium carbonate over an alumina-supported sodium carbonate catalyst in separate experiments. A downstream catalyst exhibited the best performance for improving the pyrolysis oil. The HHV increased, water content decreased, and nearly all sugars and acids were eliminated. The pH value increased from 2.5 to 6.3 when comparing the results to the raw pyrolysis oil measurement. Therefore, this greatly improved the handling and storage capability of the oil. The

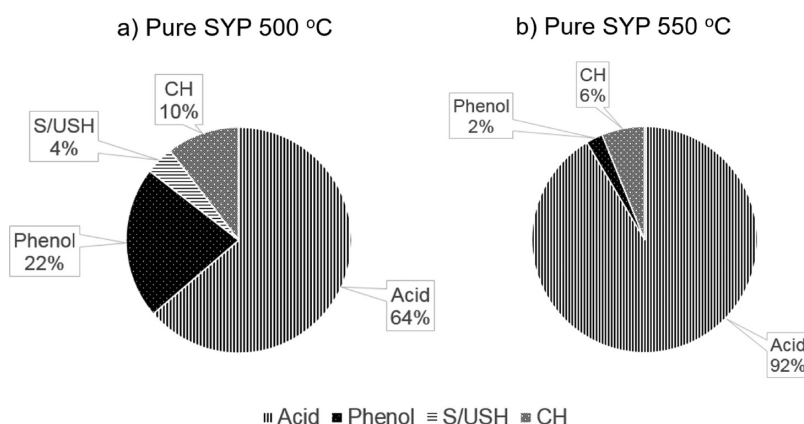


Figure 5. Pure SYP organic phase distribution (GC-MS area %). Pure SYP at 500 °C and pure SYP at 550 °C. Highest 70% of the GC-MS area listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

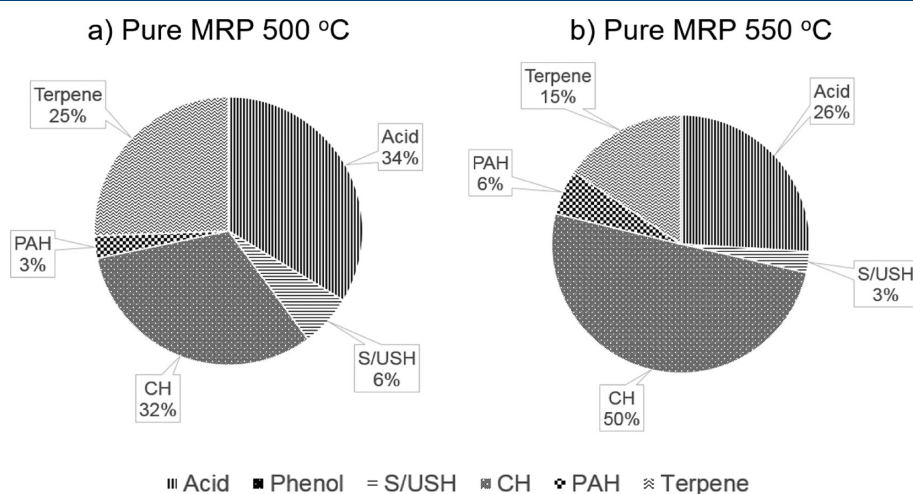


Figure 6. Pure MRP organic phase distribution (GC-MS area %). a) Pure MRP at 500 °C, b) pure MRP at 550 °C. Highest 70% of the GC-MS area listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

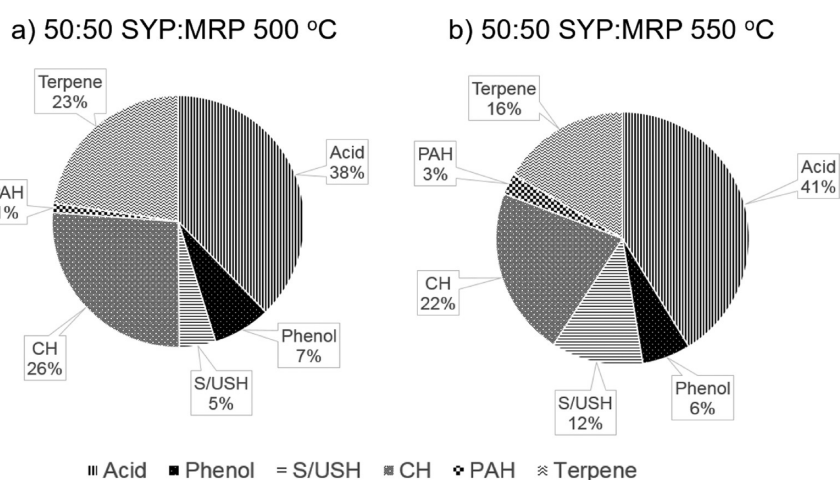


Figure 7. 50:50 SYP:MRP organic phase distribution (GC-MS area %). a) Ratio of 50:50 SYP: MRP at 500 °C, b) ratio of 50:50 SYP: MRP at 550 °C. Highest 70% of the GC-MS area listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

method involving catalyst co-fed with the feedstock (in situ) exhibited a lower organic fraction yield and lower oil HHV than the method using a downstream catalyst (post treatment), but both methods successfully deoxygenated the pyrolysis oil.

This study involved using the elevated temperature of pyrolysis with the various available chemical components in both the rubber

and pine in an attempt to cross-link the materials to prepare pyrolysis oil with a HHV when compared to pure pine bio-oil. This study showed that various rates of inclusion of micronized rubber at high pyrolysis temperatures (500 °C and 550 °C) can improve the characteristics of southern pine pyrolysis oil with the co-fed catalysts nickel oxide and sodium carbonate in an auger reactor.

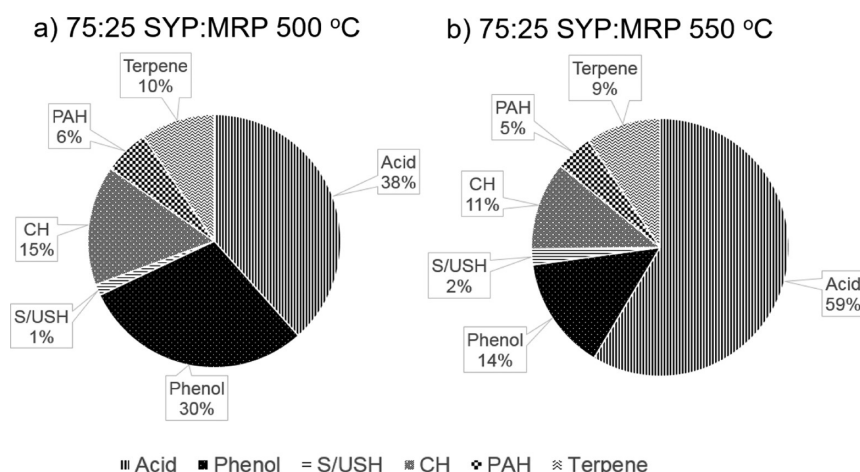


Figure 8. 75:25 SYP:MRP organic phase distribution (GC-MS area %). a) Ratio of 75:25 SYP: MRP at 500 °C; b) ratio of 75:25 SYP: MRP at 550 °C. Highest 70% of the GC-MS area listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

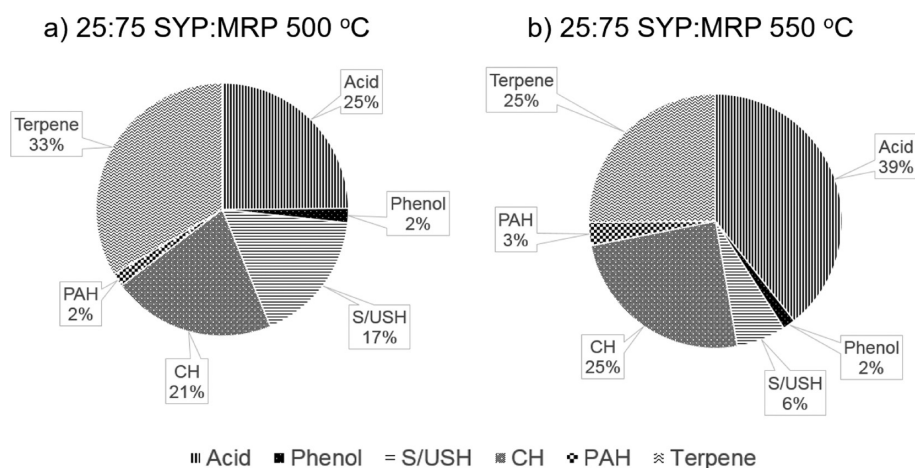


Figure 9. 25:75 SYP:MRP organic phase distribution (GC-MS area %). a) Ratio of 25:75 SYP: MRP at 500 °C; b) ratio of 25:75 SYP: MRP at 550 °C. Highest 70% of the GC-MS area listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

Table 3. Pure SYP, Pure MRP, and Co-Fed Feedstock Pyrolysis Oil Water Content

	wp (%) 500 °C	wp (%) 550 °C
pure SYP	47.6	49.7
pure MRP	2.6	9.0
SYP/MRP: 50/50	12.5	10.1
SYP/MRP: 75/25	50.4	43.5
SYP/MRP: 25/75	22.0	6.2

Wp = Percentage of water content prior to water extraction

METHODS

Materials. Southern yellow pine (SYP) (*Pinus* spp.) and micronized rubber powder (MRP) were the main components pyrolyzed in this experiment. The wood was acquired from Southeastern Timber Products (Ackerman, MS) as planar shavings and milled using a Bauer Model 248 refiner (1700 RPM, Springfield, OH, USA). The milled SYP was dried in an oven at 103 °C to lower its moisture content to approximately 4%. Moisture was measured using a moisture analyzer (DSC 500, Delta Support Company, Panorama City, CA, USA). The MRP was obtained from Lehigh Technologies of Tucker, GA, USA. The product part number was MicroDyne™ MD-188-TR.

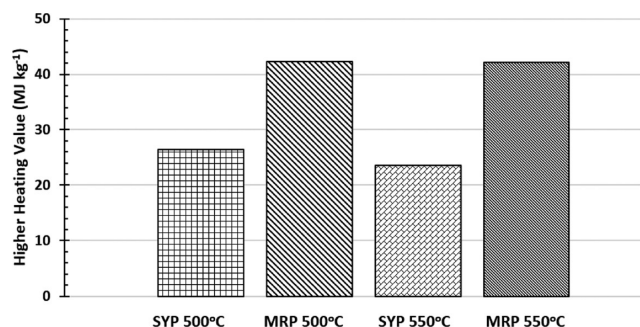


Figure 10. Pure SYP and MRP pyrolysis oil HHVs. SYP = southern yellow pine, MRP = micronized rubber powder

Feedstock particle sizes for the pine feedstock and MRP can be seen in Table 1 and Table 2, respectively.

The proximate and ultimate analysis of the southern pine feedstock used in this study has been previously reported.¹³ The elemental analysis and thermo-gravimetric analysis (TGA) has also been previously reported.¹⁴ The TGA of southern pine has been reported in a previous study conducted by Owen et al.¹⁵

Reactor System. An auger reactor with an auger fed hopper, which introduced the feedstock materials into the heating zone, was used in this experiment, and a schematic of

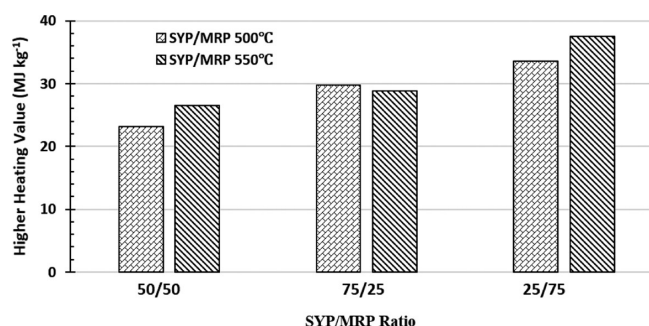


Figure 11. SYP/MRP co-fed pyrolysis oil HHVs. SYP = southern yellow pine, MRP = micronized rubber powder

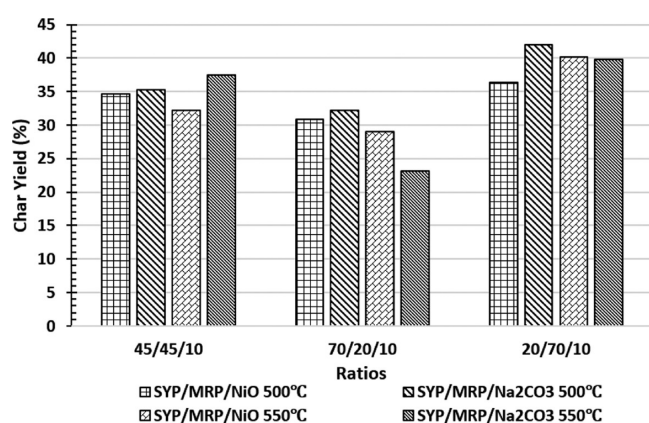


Figure 12. Char yields of SYP/MRP co-fed with the catalyst. SYP = southern yellow pine, MRP = micronized rubber powder.

the system can be seen in Figure 1. The feedstock was placed inside the hopper and sealed. An air compressor moved air through a nitrogen generator system (model N2-14, Parker Hannifin Corp. Haverhill, MA, USA) and allowed for there to be a blanket of inert gas inside the system before the pyrolysis process began.

Feedstock totaling 500 g of material exited the hopper and entered the main reactor auger. The main reactor auger was kept at a constant speed of 0.5 rpm. As the material entered the auger, it was pushed through a furnace (model XST-3-0-36-3 V, Thermcraft Inc., NC, USA). The residence time of the feedstock moving through the reactor was 1 min. As the material was pyrolyzed and entered the end of the auger, the solid product (biochar) was collected in a vessel, while the effluent vapor moved through a separate pipe. Additional heating elements were located throughout the system to maintain the desired temperature of the pyrolysis gases consistent by utilizing temperature controllers, heating tape, and thermocouples.

The effluent vapor flowed into three condensers that were maintained at a temperature of 35 °C with the assistance of a vacuum pump (Leeson model C4D17VK1D, Leeson Electric Corporation, Grafton, WI, USA), which allowed the effluent vapor to condense into a liquid (pyrolysis oil). The liquid products were collected from all condensers for later analysis. The entire system can be seen in Figure 1.

Analysis. Feedstock consisting of 500 g of pure SYP and pure MRP was pyrolyzed separately first as pure controls. The feedstock was then co-fed at different ratios. SYP/MRP was mixed at ratios (50/50, 75/25, and 25/75). Each run took approximately 12 min to complete. The feedstock was weighed before being input into the system. The solid and liquid

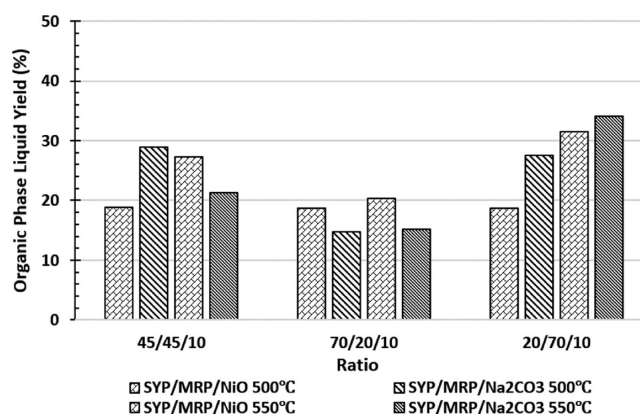


Figure 13. Pyrolysis oil yields of co-fed feedstock and the catalyst. SYP = southern yellow pine, MRP = micronized rubber powder

product yields were weighed after pyrolysis. The pyrolysis oil liquid was collected at the bottom of each condenser. The biochar was collected in a separate container. Solid and liquid yields were calculated using eqs 1 and 2, respectively.

$$C_Y = (M_C/M_F) \times 100\% \quad (1)$$

$$L_Y = (M_L/M_F) \times 100\% \quad (2)$$

where C_Y is the char yield (%), M_C is the mass of char collected, M_F is the mass of feedstock input into the system, M_L is the mass of liquid collected, and L_Y is the liquid yield.

Gas Chromatography–Mass Spectrometry. Pyrolysis oil collected from the system was combined from all four condensers, as shown in Figure 1, into one container. The volatile and nonvolatile components in the organic layer were analyzed using a Hewlett-Packard 5971 series gas chromatography–mass spectrometry (GC–MS) system with a fused silica capillary column (VF-Xms, Agilent technologies, Inc., Santa Clara, CA, USA) with dimensions of 30 m × 0.25 mm ID × 0.25 μm film thickness. The auto sampler injected methylene chloride (DCM) prior to the sample cycle with a solvent delay of 3.70 min. The initial column temperature was set to 40 °C for 1 min, and then, heating was initiated at a rate of 5 °C/min to a final temperature of 270 °C. The injector and detector temperatures were set to 270 °C and 250 °C, respectively. The carrier gas was helium with 99.99% purity (Airgas, Columbus, MS, USA) at a flow rate of 1.25 mL/min. Peak identification was accomplished by comparing mass spectra to that mentioned in the National Institute of Standards and Technology (NIST) 2005 mass spectral library (NIST, Gaithersburg, MD).

Water Analysis. The water concentration of the pyrolysis oil was measured by Karl Fischer titration with Hanna Instruments, HI 903 (Woonsocket, RI, USA) using ASTM E203.

Calorimetry. Raw pyrolysis oil prepared in this study exhibited a high water content and could not be used in a bomb calorimeter, so the pyrolysis oil underwent vacuum distillation prior to obtaining the calorific values. Once most of the water was extracted, the HHV was obtained using a Parr 6200 oxygen bomb calorimeter (Parr Instrument Co., Moline, IL) according to the ASTM D240 standard.

RESULTS

Pyrolysis of Pure SYP or MRP. The 100% MRP feedstock used in the pyrolysis process led to the highest char creation

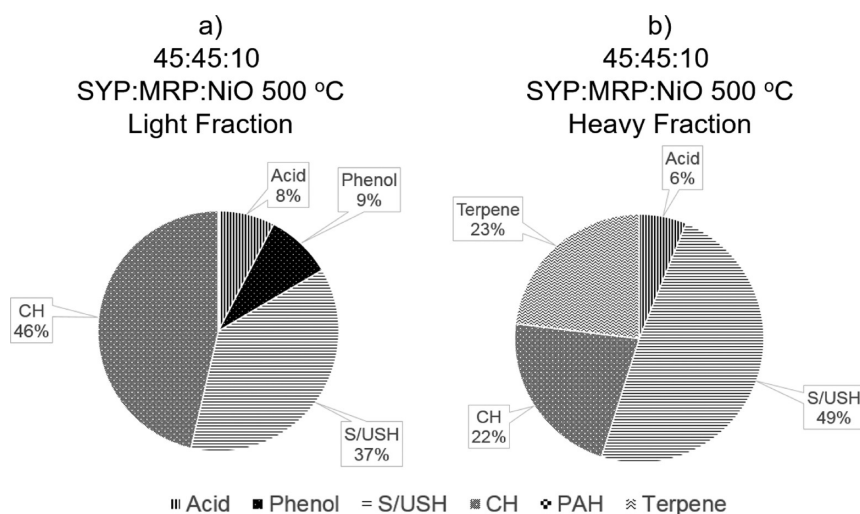


Figure 14. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 45:45:10. a) Light fraction at 500 °C; b) heavy fraction at 500 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

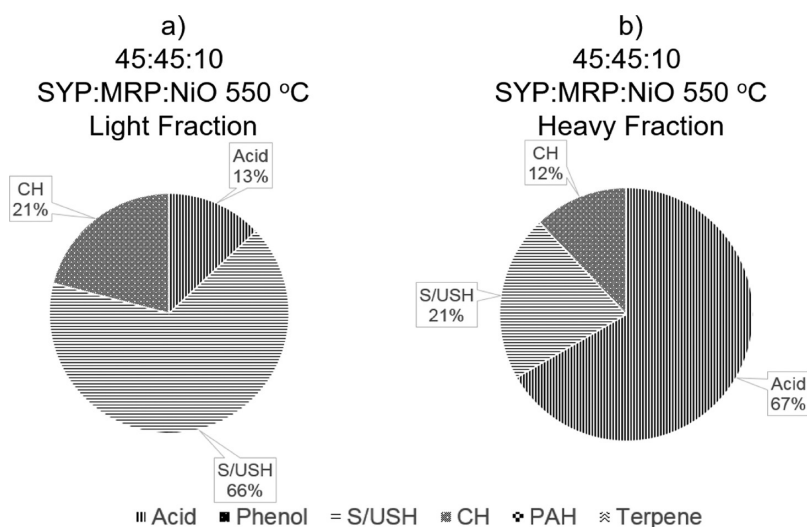


Figure 15. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 45:45:10. a) Light Fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

when compared to the 100% SYP, as can be seen in Figure 2. To best represent the organic phase oil yield, eq 3 was used to calculate the result.

$$O_Y = (R_L \times (100\% - w))/100\% \quad (3)$$

where O_Y is the organic-phase oil yield (%), R_L is the raw liquid yield (%), and w is the water content of the pyrolysis oil (%). MRP produced the largest yield of pyrolysis oil at both creation temperatures of 500 °C and 550 °C. Figure 2 shows that at higher temperatures, oil yields decreased for both feedstock. SYP produced the most water at 550 °C.

Pyrolysis of co-Fed SYP and MRP. When more MRP was present in the feedstock, the char creation increased nearing or exceeding the 100% MRP values. The 25/75 ratio of SYP/MRP exhibited the highest yields of char at both creation temperatures of 500 °C and 550 °C (Figure 3). The 50/50 ratio of SYP/MRP produced high oil yields with a similar amount of oil produced when compared to the pure MRP at both temperatures. Higher

temperatures decreased oil yields except in the SYP/MRP ratio of 25/75 (Figure 4).

Liquid Characterization—Pyrolysis of Pure SYP or MRP.

The reported chemical characterization using the GC/MS area percentage in each pyrolysis oil sample for the pure southern pine and pure MRP feedstock is displayed in Figures 5 and 6, respectively. Each chemical component in the pyrolysis oil was classified as follows: acids, cyclic hydrocarbons (CH), phenols, polycyclic aromatic hydrocarbons (PAH), saturated/unsaturated hydrocarbons (S/USH), and terpenes. Each component was displayed by the GC–MS area percentage for each feedstock and mixture ratio at 500 °C and 550 °C. A more detailed characterization of the liquid analysis can be found in the Supporting Information.

The SYP feedstock at a concentration of 100% produced large amounts of phenols in the pyrolysis oil, while the pure MRP produced none that could be distinguished from the library. The pure SYP feedstock created the highest amount of acids. The pyrolysis of the 100% MRP created terpenes and the highest amount of cyclic aromatic compounds when

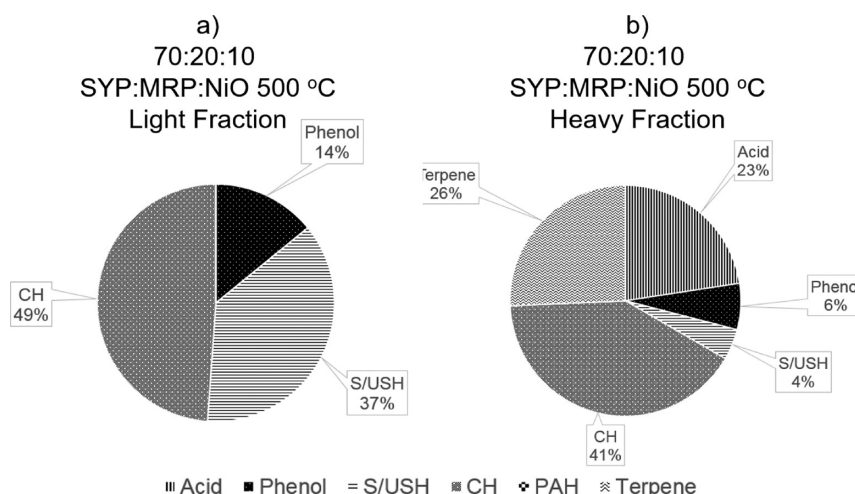


Figure 16. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 70:20:10. a) Light fraction at 500 °C; b) heavy fraction at 500 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

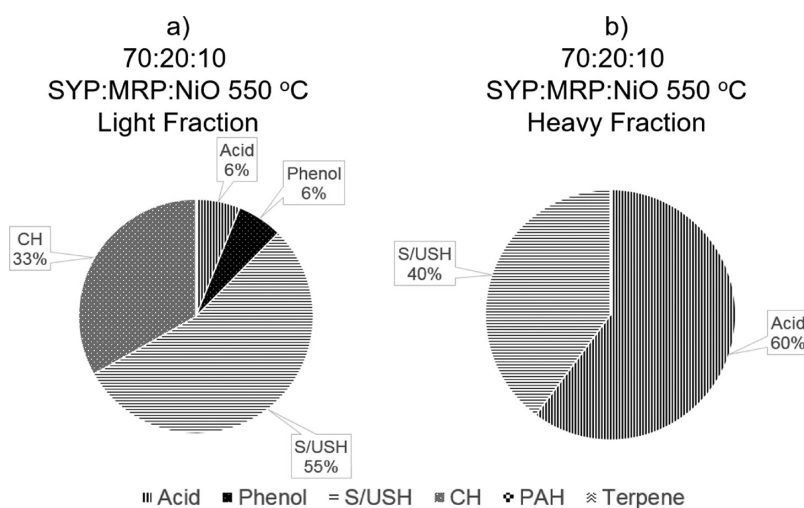


Figure 17. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 70:20:10. a) Light fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

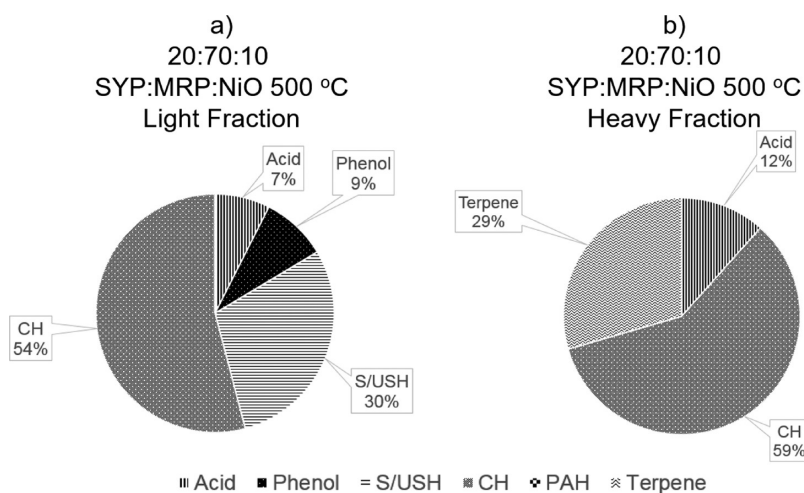


Figure 18. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 20:70:10. a) Light fraction at 500 °C; b) heavy fraction at 500 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

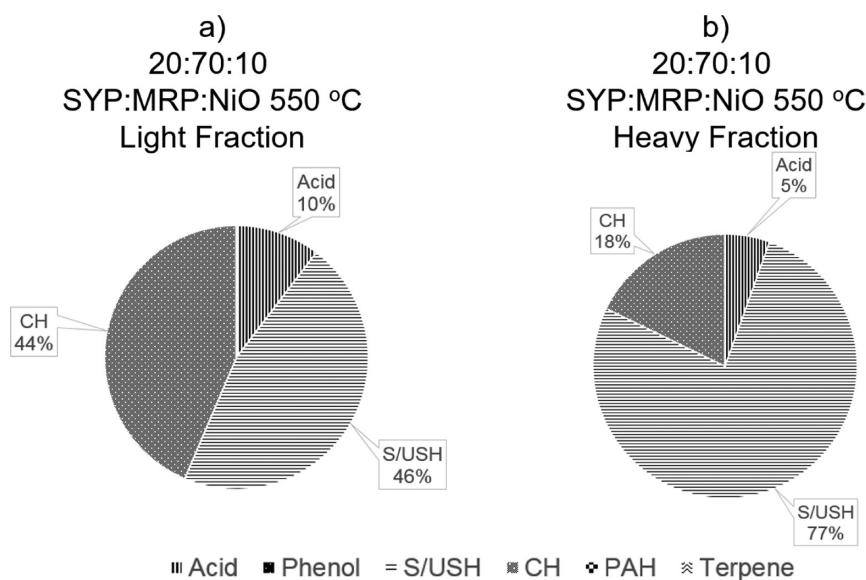


Figure 19. Catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 20:70:10. a) Light fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP:NiO. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

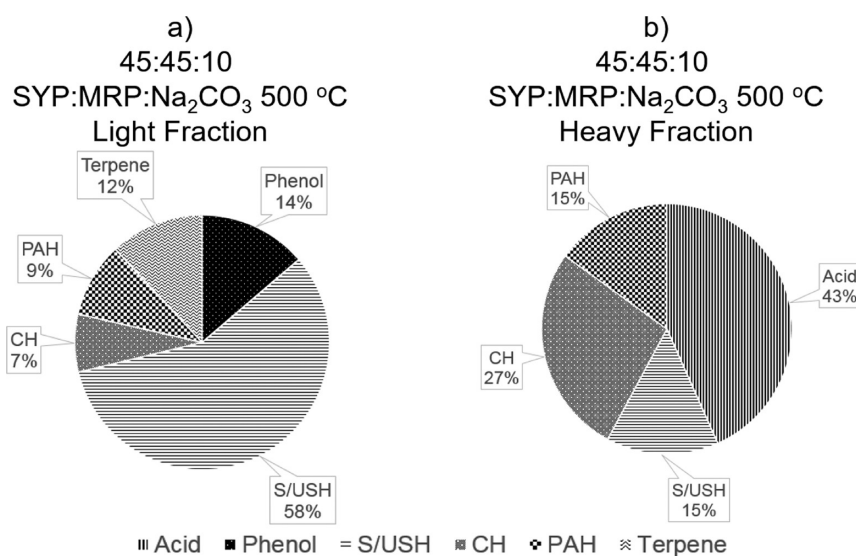


Figure 20. Catalytic chemical distribution of bio-oil using SYP:MRP:Na₂CO₃ at a ratio of 45:45:10. a) Light fraction at 500 °C; b) heavy Fraction at 500 °C of SYP:MRP:Na₂CO₃. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

compared to the pure SYP feedstock. At a creation temperature of 550 °C, the CH compound concentrations increased for the MRP; however, the CH compounds decreased for the SYP feedstock. Pure SYP and MRP feedstock both produced USH-type compounds, but the pure MRP feedstock produced a larger area percentage overall when compared to the pure SYP feedstock.

Liquid Characterization—Pyrolysis of Co-Fed SYP and MRP. Figures 7–9 show the liquid characterization of the pyrolysis oil created from co-fed pine and MRP at different ratios. When the MRP mass was equal to or higher than the mass of SYP contained in the SYP/MRP mixture, more CH compounds formed. CH formation was more prevalent at 500 °C than at 550 °C. As the amount of SYP increased in the feedstock, the amount of CH compounds created at 550 °C decreased. As the ratio of MRP increased in the feedstock, the

CH formation increased. Terpenes were created at higher concentrations as MRP was more prevalent in the feedstock mixture. Higher temperatures decreased terpene concentrations. The highest GC–MS area percentage of PAH formed from the SYP/MRP ratio of 75/25 and decreased as the SYP decreased in the mixture. Acids were created in high concentrations for all ratios of SYP/MRP, especially at the 550 °C creation temperature. S/USH compounds were created at low concentrations overall; however, the levels were higher for the 50/50 and 75/25 ratios at the creation temperature of 550 °C.

Liquid Characterization—Water Content and Calorific Value of SYP and MRP Pyrolysis Oil. Pure MRP pyrolysis oil exhibited a lower water content compared to pure SYP pyrolysis oil. When the two feedstock were combined, higher amounts of SYP in the co-feed produced a larger amount of water. An increase in the amount of MRP decreased the

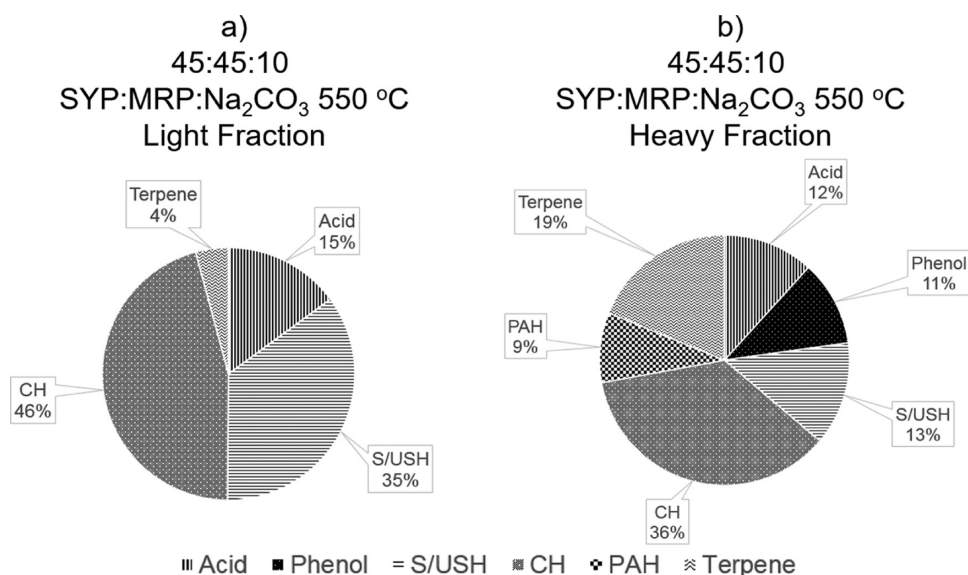


Figure 21. Catalytic chemical distribution of bio-oil using SYP:MRP:Na₂CO₃ at a ratio of 45:45:10. a) Light fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP:Na₂CO₃. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

amount of water in the pyrolysis oil. Although an increase in temperature decreased the amount of water, a higher MRP weight in the feedstock reduced the water content further. Table 3 shows the water content of the pyrolysis oil. The pyrolysis oil samples were treated to remove their water content so they would ignite in the oxygen bomb calorimeter.

Figure 10 shows the pyrolysis oil dry basis HHV from the pure feedstock. Pure MRP pyrolysis oil exhibited the highest heating value at both creation temperatures. An increase in the creation temperature at 550 °C increased the pure SYP bio-oil heating value. Figure 11 shows that when the feedstock underwent co-pyrolysis together, the SYP/MRP ratio of 25/75 produced the oil with an HHV of over 30 MJ kg^{−1} at both temperatures.

Catalyst Influence on SYP/MRP Pyrolysis. The same co-fed mixture was used but with 10% catalyst added by weight. This modified the SYP/MRP mixture ratio to 45/45/10, 75/15/10, and 15/75/10, where the last number shown is the percentage of catalyst used (10%). The catalysts used in the experiments included nickel(II) oxide (NiO) and sodium carbonate (Na₂CO₃). Each catalyst was added to the feedstock mixtures separately.

Figure 12 shows the results of char creation with the added catalyst to comparable SYP/MRP mixtures from the previous section. Char creation was highest when using the 20/70 ratio with the catalyst, but this did not exceed yields of only using the co-fed SYP/MRP at a similar ratio from the previous section. The SYP/MRP/catalyst mixture substantially decreased the liquid yield shown in Figure 13 in comparison to using only the co-fed material outlined in Figure 4. All organic phase liquid yields were below 40% across all ratios for both catalysts. The 70/20/10 ratio of the SYP/MRP/catalyst exhibited the highest yields for both catalysts and temperatures. The use of catalysts caused the liquid product to fractionate into two liquid phases as it cooled, which are denoted as the light and heavy fractions, respectively, and shown in Figures 14–25.

Liquid Characterization—Water Content and Calorific Value of SYP and MRP Pyrolysis Oil Produced with Catalysts. Comparing the water content of oils stated

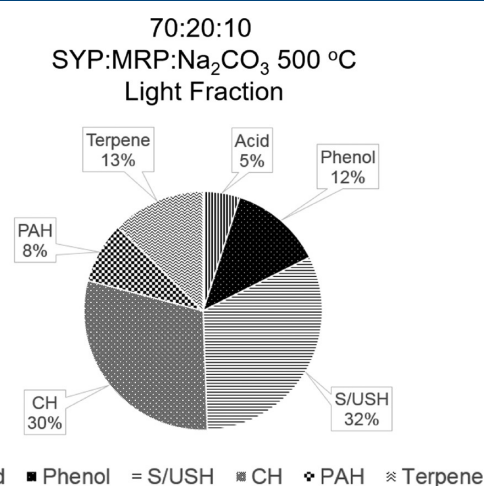


Figure 22. Catalytic chemical distribution of bio-oil using SYP:MRP:Na₂CO₃ at a ratio of 70:20:10. Light fraction at 500 °C. SYP = southern yellow pine, MRP = micronized rubber powder. No heavy fraction was formed. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

previously in Table 3 to that of the oils produced with catalysts presented in Table 4, the SYP/MRP/Na₂CO₃ mixture did not lower the water concentration when compared with the co-feed results shown in Table 3, except at the 20/70/10 ratio at 550 °C temperature. Figure 26 shows the effect that each catalyst had on the HHV of the oil while being pyrolyzed with the SYP/MRP co-feed. The addition of a catalyst greatly increased the heating values over the co-feed overall (compared to Figure 11), except with Na₂CO₃ in unequal ratios at the creation temperature of 550 °C. The feedstock containing MRP at a higher mass ratio with NiO produced the highest HHV value at the 20/70 SYP/MRP ratio, with values of 40 MJ kg^{−1} and 43 MJ kg^{−1} from creation temperatures of 500 °C and 550 °C, respectively. Sodium carbonate only outperformed NiO at the 45/45/10 ratio at 500 °C creation temperature.

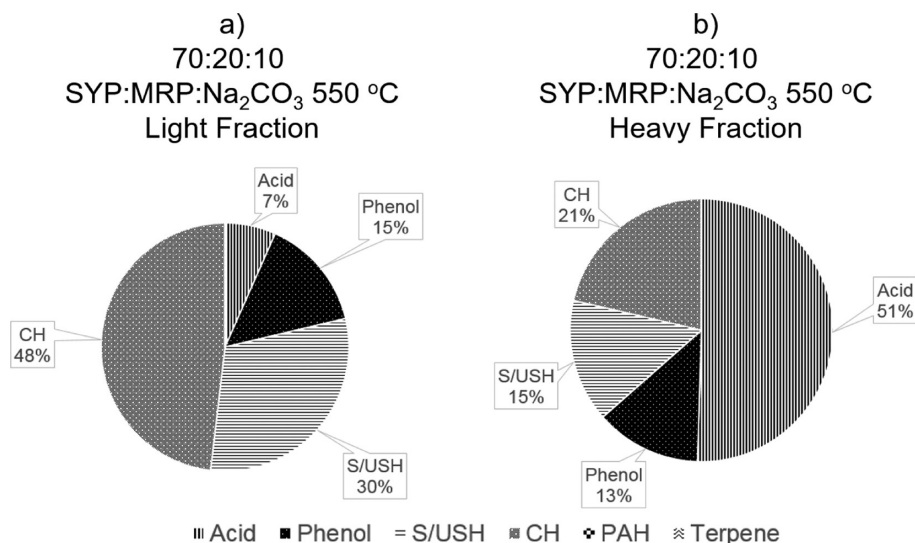


Figure 23. Catalytic chemical distribution of bio-oil using SYP:MRP: Na₂CO₃ at a ratio of 70:20:10. a) Light fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP:Na₂CO₃. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

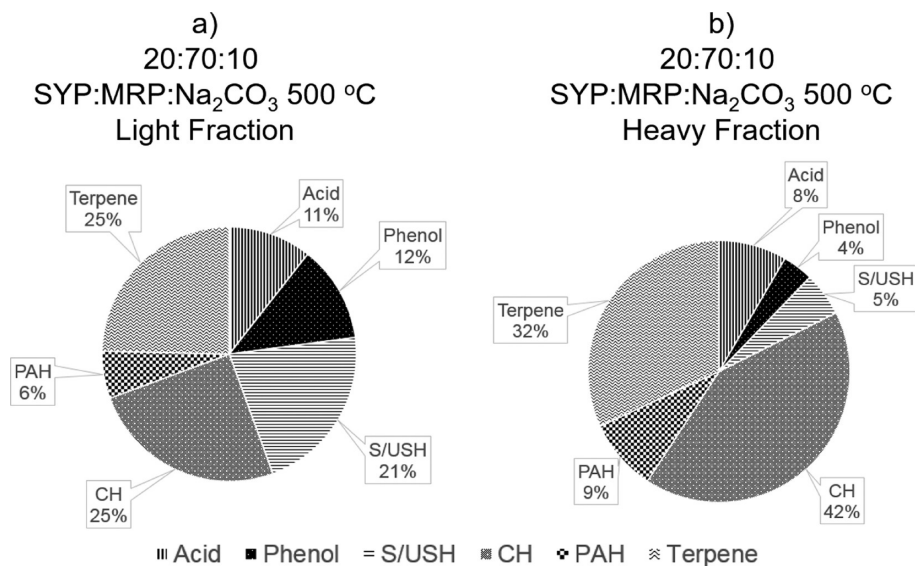


Figure 24. Catalytic chemical distribution of bio-oil using SYP:MRP: Na₂CO₃ at a ratio of 20:70:10. a) Light fraction at 500 °C; b) heavy fraction at 500 °C of SYP:MRP: Na₂CO₃. SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

DISCUSSION

The SYP/MRP/NiO feedstock mixture (Figures 14–19) decreased the GC–MS area percentage of acid concentrations at a creation temperature of 500 °C at ratios of 45/45/10 and 70/20/10 when compared to using only the co-fed pine and MRP feedstock (Figures 7–9). The SYP/MRP/catalyst at the 70/20/10 ratio resulted in large GC–MS areas of acids in the heavy fractions for both temperatures. The 20/70/10 ratio with a higher MRP mass decreased the amount of acids the most. Phenolic compound concentrations did not increase when compared to using only the co-fed pine and MRP feedstock for both temperatures (Figures 7–9). The concentration of the terpene (*D*-Limonene) remained in high concentrations for 500 °C in the heavy fraction, while higher temperatures diminished the terpene amounts over only the co-fed SYP and MRP. The 20/70/10 ratio with the higher MRP mass exhibited the highest

percentage of *D*-limonene. CH compounds created with the catalyst mixture decreased when compared to using only the co-fed pine and MRP feedstock. The acid content decreased with the addition of Na₂CO₃.

The SYP/MRP/Na₂CO₃ feedstock mixture results shown in Figures 20–25 show decreased acid concentrations in all ratios, but the acid compounds that did form were predominantly in the heavy fractions at 500 °C creation temperature. Phenol concentrations for the oil created with the Na₂CO₃ catalyst were similar to the NiO results. Terpene compounds formed at higher concentrations when the MRP mass was largest in the mixture. Higher GC–MS areas depicting terpene were found at 500 °C creation temperature when compared with 550 °C creation temperature. Only the 45/45/10 ratio exhibited an increase in the GC–MS area depicting terpenes at 550 °C creation temperature over the co-fed SYP and MRP

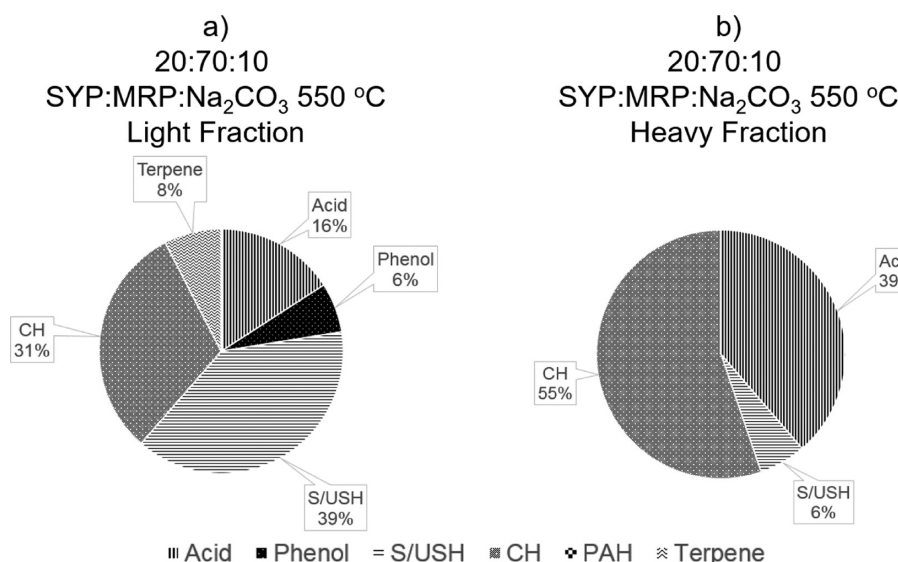


Figure 25. Catalytic chemical distribution of bio-oil using SYP:MRP: Na_2CO_3 at a ratio of 20:70:10. a) Light fraction at 550 °C; b) heavy fraction at 550 °C of SYP:MRP: Na_2CO_3 . SYP = southern yellow pine, MRP = micronized rubber powder. Highest 70% of the GC–MS area is listed in the pie chart. Classified as follows: acids, CH, phenols, PAH, S/USH, and terpenes.

Table 4. Catalytic Co-Fed SYP, MRP Pyrolysis Oil Water Content

	wp (%) 500 °C	wp (%) 550 °C
SYP:MRP:NiO: 45:45:10	47.2	15.3
SYP:MRP:NiO: 70:20:10	56.3	58.2
SYP:MRP:NiO: 20:70:10	54.0	28.3
SYP:MRP: Na_2CO_3 : 45:45:10	30.4	40.6
SYP:MRP: Na_2CO_3 : 70:20:10	45.2	49.8
SYP:MRP: Na_2CO_3 : 20:70:10	14.9	1.3

Wp = Percentage of water content prior to water extraction

raw materials. CH was formed in the light and heavy fractions with higher GC–MS areas when compared with only using the co-fed pine and MRP feedstock. The SYP/MRP/ Na_2CO_3 formed high concentrations of PAH in the pyrolysis oil when compared to using the NiO catalyst. The main PAH found in the pyrolysis oil was naphthalene at ratios of 45/45/10 and 20/70/10 in the heavy fraction for 500 °C, and the GC–MS areas for PAH were reduced at 550 °C.

CONCLUSIONS

Pyrolysis oil from SYP can have undesirable properties that need upgrading before the oil can be used in combustion engines. The co-pyrolysis of SYP and MRP produced varying results in char and oil yields. An increased ratio of MRP in the feedstock mixture increased char production. When MRP was mixed with other feedstock, it lowered the amount of acids when examining the top 70% components in the GC–MS area results. The terpene formed in the pyrolysis oil GC–MS area percentages increased as the MRP concentration increased in the feedstock. The pyrolysis of the pure SYP feedstock created oil with the highest water content, while the pure MRP created oil with the least amount of water. As the mass of MRP increased in the feedstock, the water content decreased.

The addition of NiO and Na_2CO_3 exhibited varying effects when co-pyrolyzed with SYP and MRP. Both catalysts produced high amounts of char at high feedstock concentration ratios of MRP. The addition of a co-fed catalyst (NiO or Na_2CO_3) did

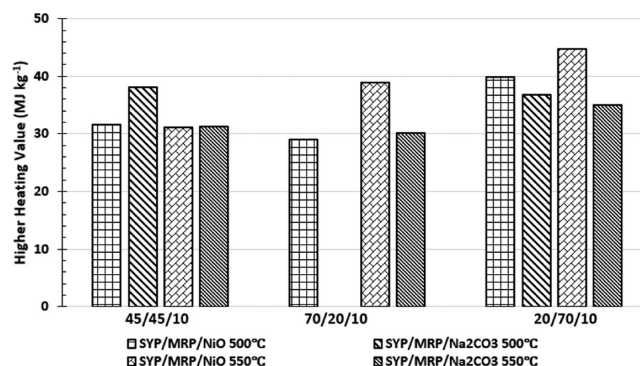


Figure 26. HHVs of Pyrolysis oil made with catalysts; Note: missing column indicates that oil would not ignite in the calorimeter.

not increase organic liquid yields when compared to using only the co-fed pine and MRP feedstock without a catalyst. Acids were greatly reduced in pyrolysis oil with Na_2CO_3 . Both NiO and Na_2CO_3 catalysts with SYP/MRP feedstock mixtures created high concentrations of the S/USH components in the oil. The catalysts used in this study did not substantially decrease the water generated in the pyrolysis oil overall. Only the Na_2CO_3 helped create oil with a reduced water content when compared to using only the co-fed SYP/MRP feedstock in the SYP/MRP/catalyst ratio 20/70/10. When the NiO catalyst was used, HHVs were higher when compared to those when using only the co-fed SYP/MRP. As the creation temperature increased, the HHVs increased. The feedstock containing MRP at a higher mass ratio with NiO produced oil with the highest HHV at the 20/70 SYP/MRP ratio, having values of 40 MJ kg^{-1} and 43 MJ kg^{-1} from creation temperatures of 500 °C and 550 °C, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01520>.

Pure SYP organic phase distribution (GC–MS area %).
Pure SYP at 500 °C and pure SYP at 550 °C; Pure MRP

organic phase distribution (GC–MS area %). a) Pure MRP at 500°C, b) pure MRP at 550°C; liquid characterization of the pyrolysis oil created from co-fed pine and MRP at different ratios; 50:50 SYP:MRP organic phase distribution (GC–MS area %). a) Ratio of 50:50 SYP: MRP at 500 °C, b) ratio of 50:50 SYP: MRP at 550°C; catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 45:45:10; catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 70:20:10; catalytic chemical distribution of bio-oil using SYP:MRP:NiO at a ratio of 20:70:10; catalytic chemical distribution of bio-oil using SYP:MRP:Na₂CO₃ at a ratio of 45:45:10; catalytic chemical distribution of bio-oil using SYP:MRP: Na₂CO₃ at a ratio of 70:20:10; and catalytic chemical distribution of bio-oil using SYP:MRP: Na₂CO₃ at a ratio of 20:70:10 (PDF)

AUTHOR INFORMATION

Corresponding Author

Jason Street – Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi 39762, United States; orcid.org/0000-0001-7317-216X; Email: jason.street@msstate.edu

Authors

Cody Wainscott – Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi 39762, United States

Austin C. Edwards – Department of Chemistry, Mississippi State University, Starkville, Mississippi 39762, United States

Brian Mitchell – Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi 39762, United States

Islam Elsayed – Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi 39762, United States; orcid.org/0000-0002-5148-3693

El Barbary Hassan – Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi 39762, United States; orcid.org/0000-0002-7980-9800

Todd E. Mlsna – Department of Chemistry, Mississippi State University, Starkville, Mississippi 39762, United States; orcid.org/0000-0002-4858-1372

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.iecr.1c01520>

Notes

The authors declare no competing financial interest.

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