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Enhancement of Bio Oil Yield and Aromatic Compounds Selectivity via Co-Pyrolysis of Paulownia Wood and Polypropylene Waste Blend on a Horizontal Reactor

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ABSTRACT

Thermochemical conversion of biomass and petrochemical wastes blend is an excellent method to produce valuable fuels and reduce environmental pollution. Bio-oil production via blending of paulownia wood and polypropylene plastic was investigated in a fixed bed horizontal reactor at different reaction temperatures and different Polymer/ Biomass weight ratios. Biomass showed the highest amount of bio-oil production (52.8 wt.%) at 500°C. The results show that with increase in temperature, the production of lighter products (with lower carbon number) has increased. Co-pyrolysis on a horizontal reactor showed positive synergy for the production of liquid and gaseous products. Bio-oil production increased to 61.03 wt.% and the relative oxygen content of the liquid products decreased. In co-pyrolysis with the ratio of 60:40 of PAW: PP, aromatic compounds with 35% by weight constitute the highest amount of liquid product and production of furans and aldehyde/ketones reduced. While this number is equal to 8% for blend of 5% PP and 95% PAW.

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INTRODUCTION

Today, the use of plastics in modern urban life has an increasing use in industry and homelike life. Plastics have advantages such as low weight, transparency, high quality and low cost, but their use has caused pollution of the terrestrial and terrestrial environment. An important challenge is the efficient management of urban waste. Due to the inefficient management of waste, the increasing accumulation of plastic materials has occurred and has caused alarming challenges at the community level. As a result, political laws have been enacted to minimize them(Idumah & Nwuzor, 2019). The degradation process of plastics involves several physical, chemical and biological categories. The production of plastics from crude oil and gas is non-renewable. Proper recycling, conversion and reprocessing can preserve these valuable resources and reduce oil pollution at the same time. The diagram of plastic waste management is shown in Fig 1. landfill of plastic waste has many risks for the environment, animals and groundwater. Burning plastics and generating heat are one of the methods of managing this waste, which will produce greenhouse gases. The produced heat energy can be used in various industries, but considering that plastic materials are valuable materials, burning causes a waste of their

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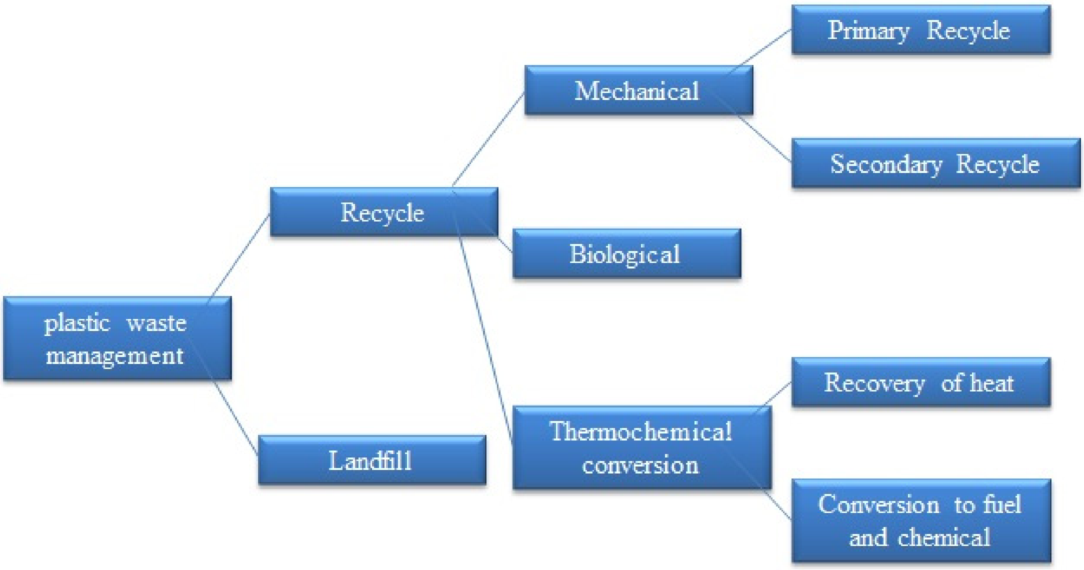

Fig. 1. plastic waste management Diagram(Idumah & Nwuzor, 2019).

resources and valuable materials (Van Emmerik et al., 2018; Vargas Santillán, Farias Sanchez, Pineda Pimentel, & Castro Montoya, 2016). Primary and secondary recovery of plastics requires separation, washing and drying, and plastics are reused (Alhazmi, Almansour, & Aldhafeeri, 2021).

Because of the chemical structure of polymers, which are a long chain of monomers, it is difficult to break the polymer chains at ambient temperature due to the strong chemical bonds between the monomers. Biological degradation of polymers requires a very long time(Singh, Ruj, Sadhukhan, Gupta, & Tigga, 2020; Thahir, Altway, & Juliastuti, 2019). The consumption of plastics has increased from 1.5 million tons in 1950 to 384 million tons and is expected to reach more than 1.1 billion tons in 2050. In 2019, the global production of plastics was 380 million tons per year(Rafey & Siddiqui, 2023){Rafey, 2023 #254}. According to the current production trend, 33 billion tons of plastic waste will accumulate in the earth. Almost 70% of European plastic wastes (18.5 MT/year) are not recycled due to technical and economic reasons and is instead landfill (17%) or burned (42%) (Gala, Catalán-Martínez, Guerrero, & Serra, 2021). Global population increase and the demand for energy, has increased overall consumption of fossil fuels over the past few decades resulting in environmental problems such as greenhouse gas emissions and air pollution. Besides, the universal economy is threatened by reduction of fossil fuel resources and price fluctuation of these fuels(Khodafarin, Tavasoli, & Rashidi, 2020; Kohansal, Tavasoli, & Bozorg, 2019; Nguyen et al., 2021; Ryu et al., 2020). Today, climate changes is one of the world's biggest problems. With increasing the temperature of air, millions of people are exposed to danger and the lives of millions of animals and plants at risk of extinction(Daioglou et al., 2017; Nejati, Adami, Bozorg, Tavasoli, & Mirzahosseini, 2020; Nikkhah, Tavasoli, & Jafarian, 2020; Shaw, 2013); (Gin, Hassan, Ahmad, Hameed, & Din, 2021; Guedes, Luna, & Torres, 2018; Holma et al., 2013; Staples, Malina, & Barrett, 2017). A method that has received attention in recent years is the method of converting biomass into biofuels using the pyrolysis process. Although, pyrolysis is in the early stages of development, it has received much attention in terms of its energy production potential. It can directly convert biomass into solid, liquid and gaseous fuels by thermal decomposition in the absence of oxygen (Ansari, Jafarian, Tavasoli, Karimi, & Rashidi, 2014; Bridgwater, 2013; Jafarian & Tavasoli, 2018). It is predicted that by 2050, 38% of the world's fuel and 17% of the world's electricity will be produced from biomass (Ansari et al., 2014).

Pyrolysis is chemical decomposition of organic materials that takes place using heat and in the absence of oxygen (inert atmosphere) and converts materials into smaller molecules. In the process of pyrolysis, the organic components of the material are broken down and converted into products that can be used as fuel or useful chemical resources or to generate heat and electricity (Balaghi Inaloo & Saidi, 2022; Q. He, Guo, Ding, Wei, & Yu, 2019; Mahari et al., 2018; Mahari et al., 2022; Pirbazari, Norouzi, Kohansal, & Tavasoli, 2019). The energy derived from biomass in the form of bio oil, biogas, and bio char has attracted great attention because of its obvious advantages such as being renewable, emitting relatively low carbon dioxide, and having negligible amount of sulfur (Taghavi et al., 2018). Bio oil can be used to produce heat, electricity and chemical compounds(Gin et al., 2021; Guedes et al., 2018; Holma et al., 2013; Staples et al., 2017), but it is not suitable for use as fuel in transportation. Bio oil has high acidity, which can cause corrosion of the motor vehicle, and requires quality improvement (Resende, 2016). The oxygen content of bio oil is about 35-50 wt.%, which causes a decrease in the amount of HHV (16-21 MJ/kg for bio-oil against 45-46 MJ/kg for diesel) and is not suitable to use in internal combustion engines (L. Chen, Wang, Meng, Wu, & Zhao, 2017; C. Liu, Wang, Karim, Sun, & Wang, 2014; Stummann et al., 2021). Due to their carbon nature, the biomass in future energy crises will be used as a source of fuel production. However, because of the low ratio H / C_{eff} ratio, the efficiency of their production will be low. Biomass with rich hydrogen content can efficiently increase the quality of the oil obtained from pyrolysis. That is, an increase in the H / C_{eff} ratio of feedstock can effectively increase the production of aromatic compounds(W. Chen et al., 2020; Gala, Guerrero, Guirao, Domine, & Serra, 2020; Hatefirad & Tavasoli, 2021; Su et al., 2019).

Pyrolysis of polypropylene was performed in 2018 by Anene et al. at a temperature of 370 °C, which resulted in the production of alkanes and short-chain alkenes (Anene, Fredriksen, Sætre, & Tokheim, 2018). Lushi sun et al performed the pyrolysis of PVC in a two-step route. The final product contained some aromatic compounds, coke and HCl gas (Yu, Sun, Ma, Qiao, & Yao, 2016). Feravelli pyrolysis of polystyrene at 300 temperature. The liquid product contained large amounts of styrene (Faravelli et al., 2001). Copyrolysis of HDPE and Jatropha residuum was performed by Rotliwala et al. Copyrolysis increases the liquid product in the gasoline range compared to HDPE (Rotliwala & Parikh, 2012). Copyrrolysis of cellulose and PE in a two-step process was carried out by Sophonrata et al. The results showed that the production of wax compounds and acidic compounds decreases and the liquid product is rich in hydrocarbons (Sophonrat, Sandström, Zaini, & Yang, 2018).

The low H/C ratio of biomass feedstock and high O/C ratio leads to the generation of syngas with a low H2/CO ratio and produce substantial quantities of tar and char. One of the effective ways to overcome the limitation is the simultaneous use of hydrogen-rich compounds as feed for hydrothermal gasification. Plastics are one of these hydrogen-rich compounds which are produced and accumulated in large quantities every year. The co-feeding of biomass and plastic waste in hydrothermal gasification not only solves the mentioned environmental problems but also improves the H/C ratio in the feed of the gasification process and increases the efficiency of hydrogen production and light hydrocarbons. Co-feeding of some biomasses and plastic wastes has been studied and discovered a synergistic effect in the co-gasification of plastic wastes and biomass with the greatest impact at a 50:50 mixing ratio. Pyrolysis of biomasses blended with plastics can also cause balance (equilibrium) of the contents of C, H, O, which is likely to affect the quality of the pyrolysis products(Lu, Huang, Bourtsalas, Chi, & Yan, 2018; Sharuddin, Abnisa, Daud, & Aroua, 2018).

In this research, plastic waste was used as co-feed to increase the H/C ratio in the feed and enhance the efficiency and overcome the environmental problems of plastic waste.

Providing the wood needs of industries, from paper factories to furniture and decoration, etc., has faced an important challenge. Forests and natural resources cannot be exploited industrially. The lack of forest resources to supply the needed wood has led countries to industrial wood cultivation. Paulownia, poplar and eucalyptus have been considered as fast-growing and early yielding trees. On the other hand, a solution should be thought for the waste of these industries(Jakubowski, 2022). Paulownia is one of the fastest growing trees in the world and a good plant can grow over 2.5 meters in one season(Rodríguez-Seoane, Díaz-Reinoso, Moure, & Domínguez, 2020). Chemical analysis shows that it has high cellulose and more than 30% hemicellulose. Lignin and ash are less than other types of wood. Therefore, Paulownia waste can be used as a suitable biomass for the production of bio-oils(Nagata, DuVal, Schmull, Tchernaja, & Crane, 2013; Rodríguez-Seoane et al., 2020). So far, few researches have been done on the co pyrolysis of Paulownia wood and olefinic polymers and the analysis of its liquid product.

The purpose of this research is to determine the appropriate point for the production of liquid product in co pyrolysis of Paulownia wood and polypropylene plastic in a horizontal reactor and and increasing the liquid product yield. In addition enhancement the yield of higher value products like Aromatics and decreasing the amounts of oxygenates compounds like furans is another objective of this research. The results of this research can be effective in increasing the efficiency of engineering processes for the production of valuable aromatic compounds from plastic and wood waste.

MATERIALS AND METHODS

Feed Preparation

Paulownia wood used in this study, collected from agricultural farms located in the north of Tehran. The collected samples were dried in ambient conditions for 24 hours and then crushed into particles smaller than 150 μm in diameter. To remove the metal elements, the biomass was washed by 2% HCl acid (Obtained from Merck's 37% HCl acid) for 12 hrs. After acid washing, the biomass washed with distilled water until the PH reached to neutral conditions.

Polypropylene (PP) was prepared from household waste with suitable quality, washed, dried and crushed into particles smaller than 150 μm in diameter.

Feed Characterization

A Perkin Elmer 2400 Series II CHNS System was used for ultimate feedstock analyses (C, H, N, and S). The yields of the products are calculated using equations 4–6(Balaghi Inaloo, Saidi, & Taheri Najafabadi, 2022; Daioglou et al., 2017).

Liquid Yield:

$$\mathrm{Oil}\left(\%\mathrm{wt.}\right)=\frac{\text{mass of oil}}{\text{mass of feed}}*100 \tag{1}$$

Char Yield:

$$\mathrm{char}\left(\%\mathrm{wt.}\right)=\frac{\text{mass of char}}{\text{mass of feed}}*100 \tag{2}$$

Gas Yield:

$$\mathrm{Gas}\ (\%\mathrm{wt.})=100\%-(\mathrm{Oil}+\mathrm{Char}) \tag{3}$$

Proximate and elemental analysis of paulownia wood and polypropylene plastic are presented in Table 2. The weight percentage of oxygen was calculated by the Eq. (4):

$$\mathrm{O\%}=100-\ \mathrm{C\%}-\ \mathrm{N\%}-\ \mathrm{H\%}-\mathrm{S\%}-\mathrm{Ash\%} \tag{4}$$

The higher heating value of samples (HHV) in MJ/kg is calculated using Eq. (5):

$$HHV\left(MJ/kg\right)=\left(0.3491\times C\right)+\left(1.1783\times H\right)+\left(0.1005\times S\right)-\left(0.1034\times O\right)-\left(0.0151\times N\right)-\left(0.0211\times A\right) \quad (5)$$

Where C, H, S, O, N, and A are the mass fractions of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash in the ultimate analysis, respectively.

Furthermore, a thermogravimetric analyzer (TGA/ SDTA851 and METTLER-TOLEDO compact) was used for the proximate analysis to determine the amounts of moisture, ash, and volatile matter in the feedstocks while operating in a nitrogen atmosphere at temperatures between 25 and 800 °C with a heating rate of 10 °C.min−1. Then, to measure the fixed carbon and ash, the atmosphere switched to oxygen gas at a temperature range of 800–900 °C. The ash content was calculated using the sample's remaining weight, and the fixed carbon content was calculated by the Eq. (6):

$$\text{Fixed carbon\%}=100-\text{ Ash\%}-\text{ volatile matter\%}-\text{ moisture\%} \quad (6)$$

Thermal stability examination of pure paulownia wood (PAW) and polypropylene waste (PP) and their blends PAW/PP 4:1, PAW/PP 1:1 and PAW/PP 1:4 were executed in a TGA (SDT Q600 V20.9 Build 20) system. 3.0 mg of the sample was taken in the sample holder and started heating from 25oC to 800oC with heating rate of 10 °C /min under continuous flow of nitrogen

Reaction testing

The thermal pyrolysis of Paulownia wood and co-pyrolysis of Paulownia wood and Polypropylene were carried out in a fixed bed horizontal reactor system. Figure 2 shows a simplified schematic diagram of the experimental setup. The system comprised a quartz glass pipe as the tubular reactor with 1000 mm long and 12 mm internal diameter located horizontally inside an electric furnace with 20 mm internal diameter and 800 mm length to carry out the experiments. The reactor temperature was controlled via a PID temperature controller and gas flow controlled via Brooks company gas flow mass controller. Argon (%99.99 purity) was used as inert carrier gas with exactly 20 ml/min flow rate to provide an oxygen-free atmosphere. Before the pyrolysis process, the biomass was placed in an oven at a temperature of 90 ºC. For each test, after placing a certain amount of feed (1g) in the reactor, the system was reached the desired temperature using the electric furnace. The bio-oil was collected using a trap embedded to the bottom of the reactor, and the biochar, after the process, remained as solid waste in the center of the reactor. The gaseous products were trapped over a sodium chloride saturated brine solution in a graduated column. At the end of reaction, the reactor cools down to the ambient temperature. The influence of the temperature (400-600 °C) on quality and quantity of bio-products derived from pyrolysis of mixed feed were investigated under similar conditions (reaction time of 30 min, feed content of 1g). Experiments have been conducted to determine the appropriate ratio of PAW and PP. Polypropylene is included in proportions of 5-40% by weight in pyrolysis to determine the appropriate percentage combination of the two feed components in co-pyrolysis. All experiments were performed three times for each feedstock, and the results presented below are the averages of those experiments.

Bio-products analysis

bio-oil samples were analyzed and characterized by gas chromatography/mass spectrometry (GC/MS, Agilent Technology (HP. Data processed by Agilent MSD Chemstation (Rev E.02.02.1413).

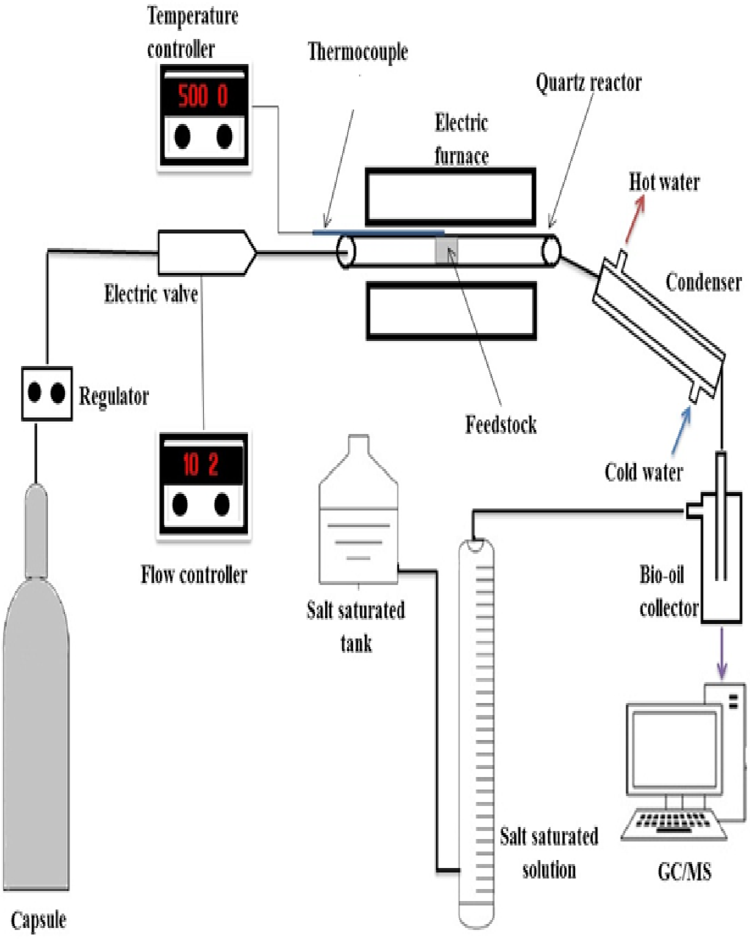

Fig. 2. Schematic representation of the experimental pyrolysis setup

RESULTS AND DISCUSSION

As shown, paulownia wood has low amounts of nitrogen, sulfur and low ash. Woody biomass mainly contains less ash than agricultural and herbaceous biomasses. Herbaceous biomasses have 5-9% and wood biomasses have 1-2% ash in their structures (Alam, Bhavanam, Jana, & Peela, 2020; Zhai, Burke, & Stewart, 2022). Polypropylene plastic analysis shows the presence of a high amount of hydrogen and free of oxygen, nitrogen and sulfur, which is suitable for use in the co-pyrolysis process. Table 1 also shows that, Polyolefin plastics have high content of hydrogen compared to biomass (14.64% for polypropylene and 6.6% for Paulownia). Biomasses have a lower HHV than polypropylene because they have nitrogen and oxygen in their structure(Seifali Abbas-Abadi & Nekoomanesh Haghighi, 2017).

The TGA curves for pure PAW, PP and their blends PAW/PP 4:1, PAW/PP 1:1 and PAW/PP 1:4 at heating rates of 10 °C/min are shown in Figure 3. In case of pure PAW and PP, the thermal degradation occurred in three stages and two stages, respectively. For PAW, the weight loss (less than10 %), corresponding to the first stage (50 – 110°C), is due to the removal of moisture and a marginal loss of light volatiles. For PP, the very small weight loss (less than 5%) in the first stage is due to moisture removal. The second step of weight loss occurred in the temperature range of 160-400°C and 300-460 °C for PAW and PP, respectively. For both samples this is the maximum degradation range and is termed as

Table 1. Proximate and element analysis of Paulownia wood and Polypropylene

	Polypropylene	Paulownia wood
Proximate analysis		
Moisture	-	7.1
Ash	-	0.9
HHV($\frac{MJ}{Kg}$)	50.16	31.26
Volatile matter	99.94	72.3
Elemental analysis		
C	85.36	47.55
H	14.64	6.6
O	0	43.64
N	0	1.31
S	0	0

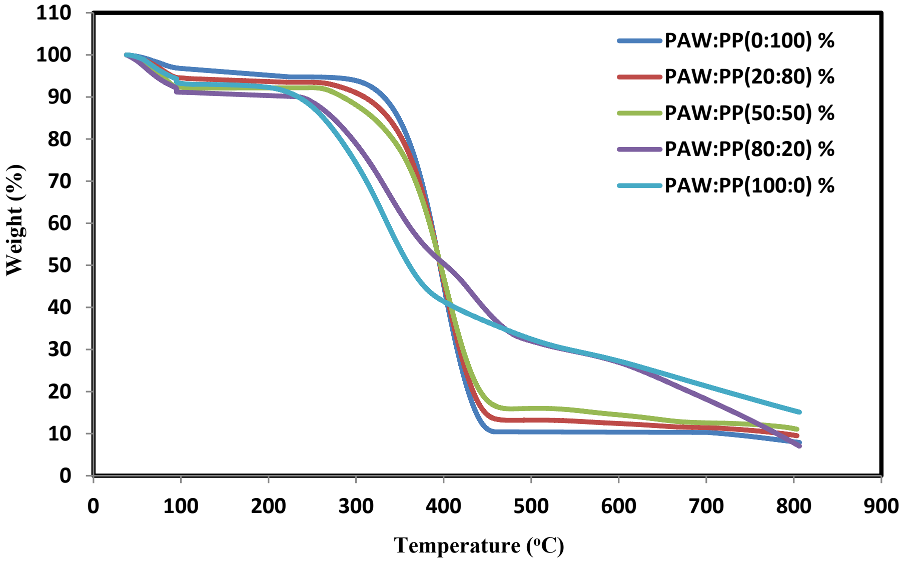

Fig. 3. Thermogravimetric analysis (TGA) diagrams for PAW, PP and their blends

active pyrolysis. The third stage of weight loss for PAW occurred in the temperature range of 450-800°C and could be attributed to the decomposition of lignin and carbonaceous material.

Figure 3 also shows the TGA curves for different blends of PAW and PP. This characteristic behavior of blend can be explained by the physical state of PP. First PP gets softened at about 300°C followed by a plastic state which inhibits the release of volatiles from PAW by formation of a coating layer on the surface of PA wood. The internal pressure of volatiles from PAW and plastic increases with increase in temperature. This could be the reason for the higher liquid production (or lower residual mass) during the thermal degradation of the blends. The thermal degradation of polyolefin occurs via a radical chain process. It consists of three steps i.e. initiation, propagation and termination. A large number of free radicals are evolved from lignocellulosic materials during co-pyrolysis. These free radicals accelerate the decomposition of feed by involving many reactions such as cracking, depolymerization and crosslinking reactions (Balaghi Inaloo et al., 2022; Q. He et al., 2019).

Pyrolysis

Paulownia wood was pyrolyzed at temperature ranges between 400-600°C to determine the optimal temperature. The maximum amount of liquid product was obtained at 500°C which is explained by the increase in the initial decomposition of biomass at this temperature(Anandaram et al., 2022; Kim et al., 2014). The results show (Figure 4) that at this temperature 52.8% liquid is produced. Increasing the temperature increased the amount of gaseous products from 23.7 to 29.9%. At the same time char decreased from 26.2 to 19.2%. The increase in gas production is due to the enhancement of secondary deoxygenation reactions of pyrolysis vapors such as decarboxylation and decarbonylation (Baykara, 2018; Chagas et al., 2016).

Figure 5 shows the product distributions in liquid products derived from pyrolysis of paulownia wood at various temperatures. As shown, furans and aldehyde/ketone compounds have the highest amount (40-48% by weight of total liquid products the results show that with increase in temperature, the production of lighter products (with lower carbon number) has increased. The highest amounts of compounds in the pyrolysis of Paulownia wood are oxygenated compounds, which include furans, aldehyde/ketones, phenols and organic acids.

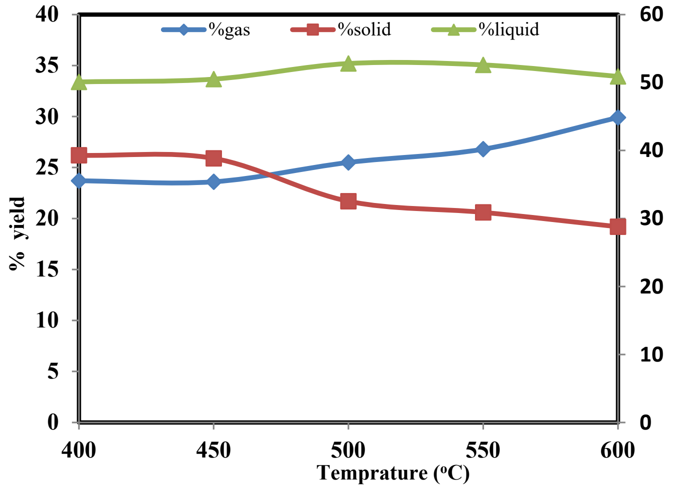

Fig. 4. Effect of temperature on pyrolysis of paulownia wood products distribution

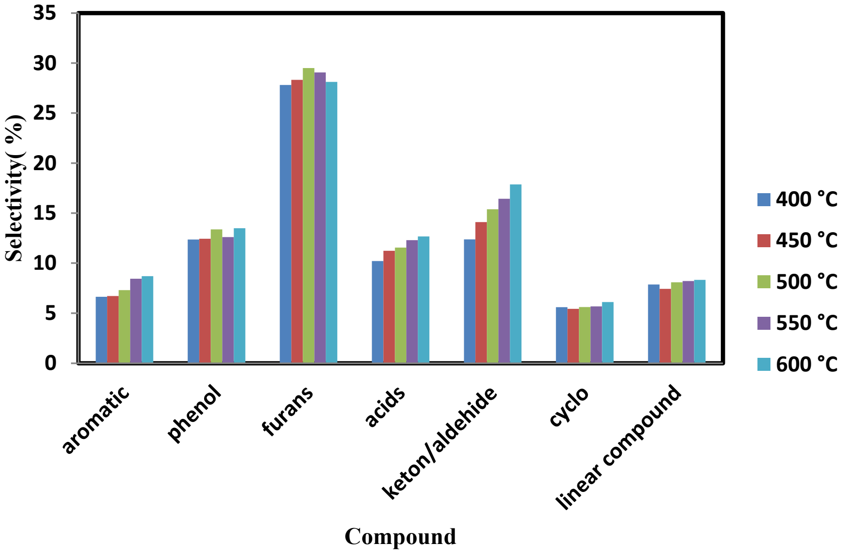

Fig. 5. Product distributions in pyrolytic liquid derived from PAW at various temperatures.

15-18% by weight of total products is aromatics and linear hydrocarbons.). Pyrolysis of oak wood also shows similar results that the liquid product contains furans and alcohol(Solarte-Toro, González-Aguirre, Giraldo, & Alzate, 2021). For all tests 5-13% by weight of total liquid products was the unidentifiable compounds by GC/MS analysis.

Thermal co-pyrolysis of PAW and PP blends (ratios of 5-40%) was investigated in the mentioned fixed bed horizontal reactor. According to the results presented on figure 2, softening PP at about 300°C and making a coating layer on the outer surface around the feed, inhibits the release of volatiles and increases the internal pressure of volatiles. This in turn leads to higher liquid production during the thermal degradation of the blends. Our studies showed that, this phenomena can takes place better and more efficiently on the horizontal reactors that the vertical gravity reactors. So, the horizontal reactor is used in this study. The results are shown on Figure 6.

As shown, by increasing the amount of PP content in the pyrolysis process, the production of liquid and gaseous products increased.

The theoretical values of the liquid product in co-pyrolysis are obtained by the weight average of the two compounds present in the mixture as follows (equation 7):

$$W_{\text{theorica}} = X_p W_p + X_b W_b \tag{7}$$

where x_p and x_b are the ratio of plastic and biomass and W_b and W_p are the liquid product in the pyrolysis of biomass and plastic. Experimental values of liquid efficiency are shown by $W_{\text{experiment}}$ The synergistic effect is the difference between two values of theoretical and experimental weight loss(L. Chen et al., 2017).

$$\Delta W = W_{theoretical} + W_{\text{experimental}} \tag{8}$$

The diagram of the theoretical and experimental liquid product is shown in Figure 7. The amount of liquid product is more than the theoretical amount, indicating the synergy effect.

The results show that there is a positive synergy in the co-pyrolysis of PP and Paulownia. This means that during co pyrolysis maximum synergy of liquid product is in the range of 20-40% by weight of plastic and the highest synergy is in 25% of polypropylene. During the copyrolysis process of biomass and plastic, there is synergy in yield and char reduction. Synergism is the result of the interaction of two primary materials during pyrolysis. The removal of hydrogen from the polymer by the biomass oxygens facilitates the decomposition of carbon-carbon bonds

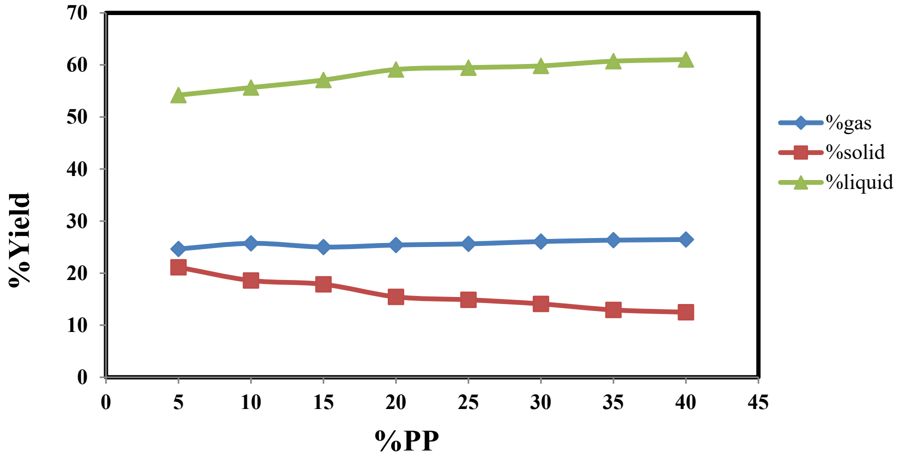

Fig. 6. Effect of PP content on Paulownia co- pyrolysis

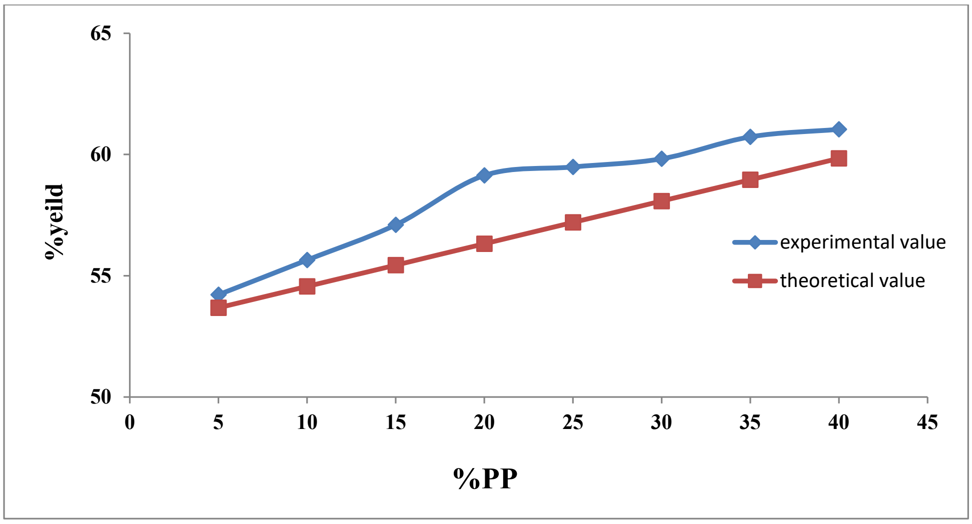

Fig. 7. Theoretical and experimental liquid product in co pyrolysis of PAW and PP.

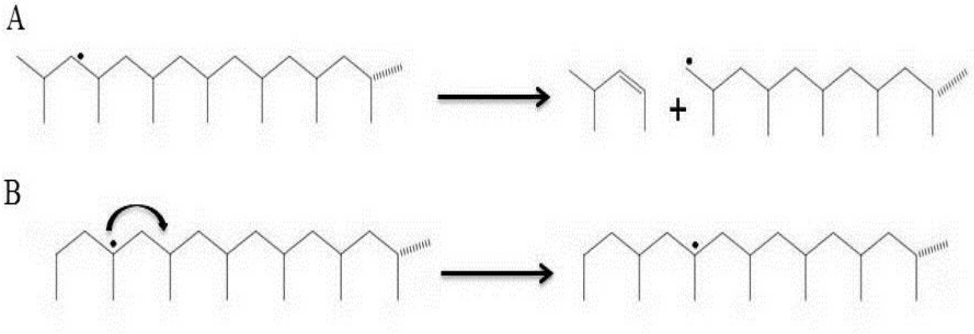

Fig. 8. Mechanisms of hydrocarbon production via pyrolysis of PP. A: Intramolecular hydrogen transfer reactions, B: mid-chain β-scission reactions(Park & Lee, 2021).

in the polymer, and the transfer of hydrogen from the polymer to the biomass oxygens reduces the production of char (Sajdak & Muzyka, 2014). In 2018, Yuan et al discovered the synergistic decomposition between polymer and cellulose through hydrogen transfer (Yuan et al., 2018). Hydrogen from olefinic polymer can cause cellulose decomposition and oxygen compounds from cellulose increase decomposition of polymer (Ryu et al., 2020).

In poly-olefin pyrolysis, the production of liquid hydrocarbons could have been produced via different mechanisms including disproportionation, chain fission, allyl chain fission, radical addition, radical recombination, mid-chain β-scission, end-chain β-scission, intermolecular hydrogen abstraction, and intermolecular hydrogen transfers. Among these possible mechanisms, mid-chain β-scission reactions, and intermolecular hydrogen transfers may be key for the production of C1-C35 hydrocarbons from PP pyrolysis. Intermolecular hydrogen transfer reactions are key reactions for the formation of hydrocarbons that have low molecular weights. The intermolecular hydrogen transfers are backbiting reactions originating from an end-chain radical. Backbiting reactions lead to the production of radicals at polymer chain. Mid-chain β-scission reactions also lead to the production of C1-C15 products(Park & Lee, 2021). Mechanisms of hydrocarbon production via pyrolysis of PP are shown in Figure 8.

During co-pyrolysis, plastics are broken down into small olefinic units and biomass is preferentially converted into light oxygenated units with less amount of charcoal. Short chain olefins participate in the Diels-Alder reaction with biomass derivatives (result from decarboxylation, decarbonylation, dehydration, etc.) and with positive synergy; they increase the production of aromatic hydrocarbons and reduce the production of charcoal. These results have been confirmed by other studies (Chaihad, Karnjanakom, Abudula, & Guan, 2022; Jung et al., 2023; Miandad, Barakat, Aburiazaiza, Rehan, & Nizami, 2016; Miandad et al., 2017; Muneer, Zeeshan, Qaisar, Razzaq, & Iftikhar, 2019; L. Wang, Lei, Liu, & Bu, 2018). The Diels–Alder reaction for the production of aromatic hydrocarbons shown in Figure 9 (Nkosi, Muzenda, Gorimbo, & Belaid, 2021).

Figure 10 shows the product distributions of liquid produced from co pyrolysis of paulownia

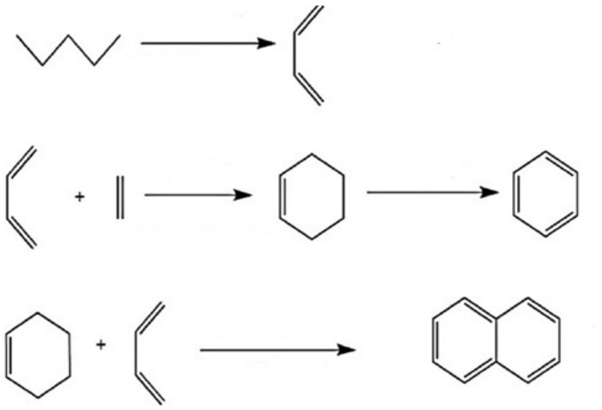

Fig. 9. The Diels–Alder reaction for production of mono and polycyclic aromatic hydrocarbons.

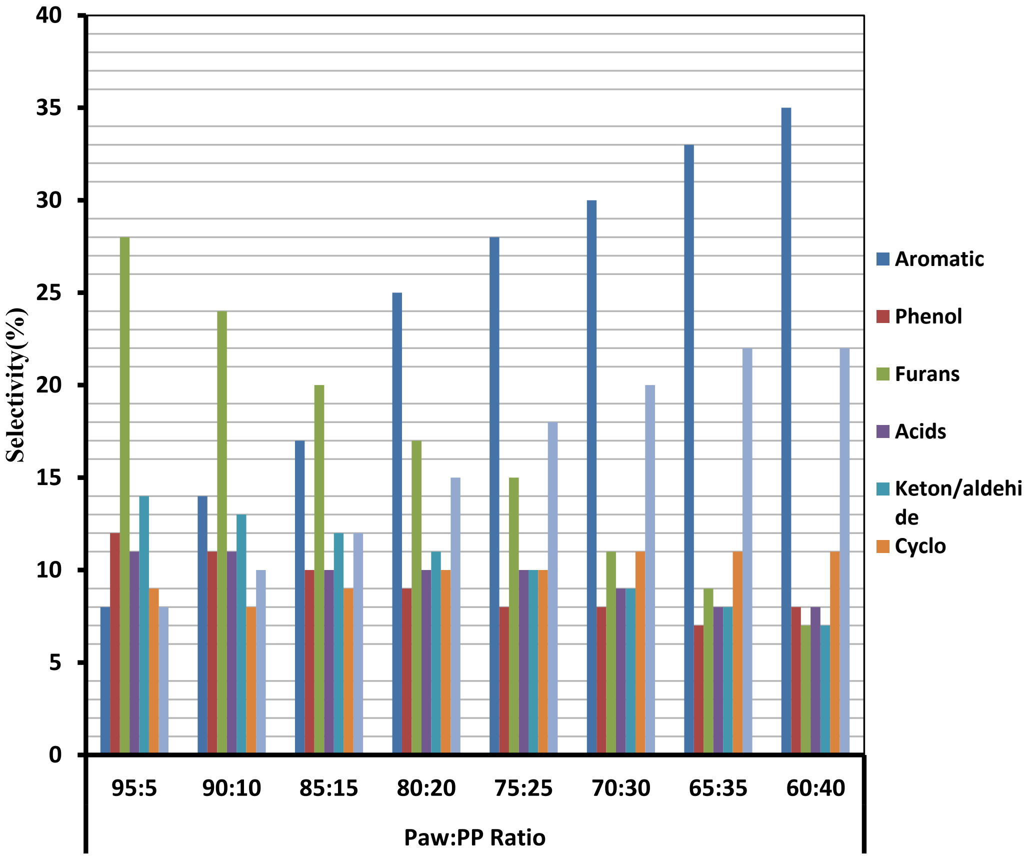

Fig. 10. Product distributions of liquid from co-pyrolysis of paulownia wood and PP blend.

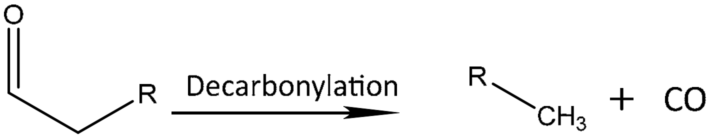

Fig. 11. Decarbonylation reaction pathway to produce hydrocarbons(S. Wang, Dai, Yang, & Luo, 2017).

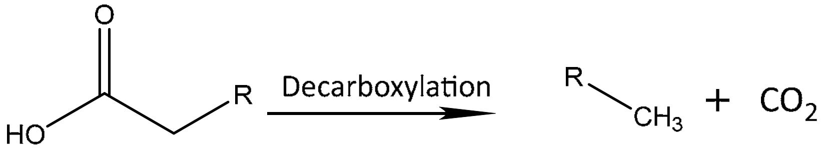

Fig. 12. Decarboxylation reaction pathway to produce hydrocarbons(S. Wang et al., 2017).

wood and PP. It is clear that with the increase of PP content, the production of oxygenated compounds (phenols, furans, aldehyde/ketones, acids, etc.) reduces, while the production of non-oxygenated compounds and aromatics increases. In co-pyrolysis with a ratio of 60:40 of PAW: PP, aromatic compounds with 35% by weight constitute the highest amount of liquid product. While this number is equal to 8% for blend of 5% PP and 95% PAW. At the same time, the production of furans and aldehyde/ketones reduced from 28% to 7%, and 14% to 8%, respectively. Linear and cyclic compounds increased and reached 22% and 11%, correspondingly. Acids are removed during decarboxylation and decarbonylation reactions of carboxylic groups(figure 11 and figure 12) ((Santillan-Jimenez & Crocker, 2012). Aliphatic hydrocarbons (alkanes and alkenes) are produced during the decarboxylation reaction along with the removal of oxygenated groups (Vichaphund, Sricharoenchaikul, & Atong, 2017). Abbas-Abadiet *al* in 2021 in co pyrolysis of oak wood and polypropylene with a ratio of 1: 1 in stirred reactors, reported that the efficiency of liquid product was 51% and the production of aromatic product was 38%(Abbas-Abadi, Van Geem, Fathi, Bazgir, & Ghadiri, 2021). In addition to Diaz-Alder reactions, Hydrogen radicals can cause the selectivity of aromatization and cyclization reactions. After cracking by some radicals (hydrogen radical or hydrocarbon), organic oligomers enter into aromatic and cyclization reactions and become stable and increase the selectivity of these reactions(X. Liu et al., 2020). Some studies have also had similar results. Co-pyrolysis of pine wood and polypropylene showed that the product is rich in ketone and phenolic compounds(S. He et al., 2021; Rutkowski, 2012). Co-pyrolysis of pine wood and polyethylene has increased the selectivity of aromatics and naphthalene(Zheng et al., 2018).

CONCLUSION

Production of bio-oil from paulownia wood and polypropylene plastic was investigated in a fixed bed horizontal reactor and the parameters of the reaction temperature and polymer weight ratio were investigated. The highest amount of bio-oil (61.03%) achieved at the temperature of 500°C in PAW: PP ratio of 60:40. The highest level of synergy was observed in 25% polypropylene. Also, the production of furans oxygenated compounds decreased significantly. The production of aromatic compounds reached 35% and the production of linear and cyclic aliphatic compounds reached 22 and 11%. Results showed that Paulownia wood and polypropylene have good potential to be used in the pyrolysis process to produce hydrocarbon materials due to their high volatile content.

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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