

Co-Pyrolysis of Neem Wood Bark and Low-Density Polyethylene: Influence of Plastic on Pyrolysis Product Distribution and Bio-Oil Characterization

Venkatachalam Selvaraj Kaushik (✉ kaushikvs84@gmail.com)

SNS College of Technology

Chandrasekaran Sowmya Dhanalakshmi

SNS College of Technology

Petchimuthu Madhu

Adithya Institute of Technology

Palanisamy Tamilselvam

SNS College of Technology

Research Article

Keywords: Co-pyrolysis, Neem wood bark, High-density polyethylene, Bio-oil, Characterization

Posted Date: September 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-829447/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In this study, the investigation on effect of plastic during co-pyrolysis with biomass has been carried out in a fixed reactor. Pyrolysis of neem wood bark (NB), low density polyethylene (LDPE) and their blends at different ratios is performed in order to evaluate the product distribution. The effects of reaction temperature, NB-to-LDPE blend ratio on product distribution and chemical compositions of bio-oil are examined. The co-pyrolysis of NB and LDPE increased the yield and quality of the bio-oil. The experiments are conducted under different LDPE addition percentage such as 20%, 40%, 50%, 60% and 80%. Under the optimum experimental condition of 60% addition of LDPE and temperature of 450°C, the maximum yield of bio-oil (64.8 wt%) and hydrocarbon (75.2%) are achieved with the lowest yield of oxygenated compounds. The calorific value of the co-pyrolytic oil is found to be higher than that of NB pyrolytic oil. The relation between NB and LDPE during co-pyrolysis has been validated by GC–MS analysis, which shows in decrease of oxygenated compounds.

1. Introduction

The total capacity of fossil fuel-based power plants is enlarging dramatically as a consequence of significant population growth and faster industrialization. The finite fossil fuel resources such as oil, gas and coal are in high demand in all type of power plants all over the world. Increased solid waste creation due to population and improved lifestyles provides carbon negative or neutral hydrocarbon energy resources. It deals both the generation of energy and waste disposal problems. The sluggish pace of technical advancement, waste management is one of the most critical global issues confronting humanity. Land filling is more unsustainable and cost effective one, since it produces smells and by-products that are harmful to the atmosphere and have a negative influence on living organisms (Hoorweg et al. 2013). To alleviate the energy problem and reduce pollutant emissions, several efforts have been made to find sustainable alternative energy sources. Renewable energy sources can help to reduce reliance on fossil fuels and negative environmental effects (Madhu et al. 2018).

Biomass is formed via photosynthetic process using solar power to confiscate CO₂ and H₂O in the form of carbonaceous solids (Mishra and Mohanty 2018). Biomass can produce a wide range of energy precursors (syngas, bioethanol, gaseous methane, bio-briquette and biodiesel) which are same as fossil-fuel incumbents (Wang et al. 2021). Biomass gives bioenergy and it is the only renewable energy source that can be easily transported and stored. The most common kind of biomass used for heat and power is solid biomass. Organic residues from forestry and agriculture, dedicated energy plants, industrial wastes or residues and household solid wastes also can be utilized to produce energy. Biomass pyrolysis is a leading research area due to its unique characteristics for the conversion of biomass into valuable biofuels (oil, char and gas) and chemicals. However, the presence of large quantities of moisture and oxygenated compounds in bio-oil, acids, alcohols, phenols, aldehyde, ketone, and furan restrict the usage for direct burning. These chemicals are undesirable for fuel because they reduce the heating value, making them unstable and corrosive (Ahmed et al 2018; Sowmya Dhanalakshmi et al. 2021).

The higher acidity and large quantities of oxygen content in the bio-oil produced from waste biomass is not appropriate for direct use in IC engines and furnaces. The presence of oxygen contents not only affect the heating value and also offer low thermal stability (Ryu et al. 2020). The co-pyrolysis of waste biomass with hydrogen rich material is a potential approach in the recent years to improve the yield and quality of bio-oil through synergistic interactions (Hassan et al. 2020). The synergetic effect is the combined effect produced by the co-processing of two or many components, which is greater than the sum of their individual effects (Onay and Koca, 2015). Pyrolysis of biomass with polyalkenes such as PE, PP, PS, PET and PVC are the hopeful way to increase the total H/C ratio of the feedstock, reduce the formation of coke and improve the catalytic activity (Hassan et al. 2020). The bio-oil obtained through co-pyrolysis of biomass blend with plastics has more homogenous composition compared to mixing of individual bio-oils which tends to separate with time (Gunasee et al. 2017). It is a more effective technique to produce high quality bio-oil without the need of catalysts or solvents (Abnisa and Daud, 2015). The synergistic effect during pyrolysis increases the oil stability, boost hydrocarbon synthesis and minimize reactive oxygenated molecules (Gin et al. 2021). By reducing waste separation requirements, it is an appealing method with great potential for mixed wastes. Generally the plastic wastes are having higher H/C and lower O/C ratio which supports biomasses during co-pyrolysis with intrinsically high O/C and low H/C.

The activation energies needed for co-pyrolysis of the biomass and plastic were lower than the energy needed for waste plastic. Many researchers have reviewed the research progress in co-pyrolysis. The benefits and quality enrichment of bio-oil obtained from biomass and waste plastic during pyrolysis were summarized by Abnisa and Daud (2014) and Hassan et al (2016). These experiments show that the yield and quality of bio-oil may be improved significantly by combining waste plastic with solid biomass. Wong et al. (2015) studied the technical characteristics of converting waste plastic into liquid fuel combining with waste biomass through microwave pyrolysis. Uzoejinwa et al. (2018) evaluated the benefits of co-pyrolysis in terms of yield, performance and operational conditions and found them to be a promising one compared to biomass pyrolysis. Chen et al. (2017) investigated the effect of co-pyrolysis of PET and paulownia wood to access the synergistic effects in both thermal behaviour and gas production. The results revealed that the co-pyrolysis of the blends resulted in a synergistic rise in char production. Furthermore, it increased the char yield when the blend ratio of PET was raised. The results revealed that the degradation of PET in the reactor acted as a controlling factor during co-pyrolysis for cross-linking reaction. The co-pyrolysis of municipal solid waste with PET was investigated by Ansah et al. (2016). The pyrolysis process were occurred between 360 and 480°C (> 220–380°C for biomass), according to their findings there was an interaction between municipal wastes and PET. Hassan et al. (2020) examined co-pyrolysis of sugarcane bagasse and HDPE at temperature of 400–700 ° to evaluate the synergistic effect and product distributions. There is an improvement in bio-oil yield and quantity (of about 61 wt%) comparing with the weighted aggregate value (of about 55 wt%). PVC is one of the important thermoplastic products, which also can be blended with biomass for maximum oil yield. During co-pyrolysis the bend of PVC with solid biomass, generally provide a positive synergy effect. The co-pyrolysis of pine wood and PVC produced more char and less oil than weighted aggregate values (Lu et

al. 2018). When compared to pure PVC and cellulose decomposition, the addition of PVC may promote cellulose breakdown at a lower temperature with a higher yield of char.

PP is the world's largest commodity of thermoplastics, accounting for around 23% of worldwide plastic material usage. Used PP is recycled into re-granulated PP by automotive manufacturers, but its usage is restricted due to stringent quality standards. There are some technological barriers with the production of good commodities from recycled material. The second most common commodity used thermoplastic is LDPE. It is the most affordable thermoplastic, accounting for roughly 17% of worldwide plastic use. It has more bending than HDPE and its intermolecular interactions are low. Generally LDPE has lower tensile strength and density than HDPE which is packed loosely with lower crystallinity (www.lilapolymers.com). It is more resilient and flexible. In comparison to individual pyrolysis, co-pyrolysis of LDPE and cellulose boosted the yield of liquid products synergistically, with a maximum of 83 % improvement in energy recovery (Wang et al. 2021). From the previous research it has been found that the heating value of oil produced by co-pyrolysis of LDPE and biomass, such as sugarcane bagasse, has significantly improved. During co-pyrolysis, the interaction between the biomass and LDPE lowered the yield of oxygenated compounds, resulting in higher heating of bio-oil up to 40 MJ/kg with reduced water content (Wang et al. 2021). LDPE can be used as a hydrogen donor material in the co-pyrolysis process to produce liquid. In comparison to individual biomass, liquid yield blends contained mostly aliphatic components and fewer aromatic compounds. Yang et al. (2016) studied the synergistic effects of co-pyrolysis of LDPE with three distinct biomass such as sunflower stalk, cedar wood and *Fallopia Japonica* stem and discovered the synergistic improvements in relative oil production. Dewangan et al (2016) conducted co-pyrolysis of SCB and LDPE, under different mixing ratios under different temperatures. The result showed a significant improvement in calorific value of the bio-oil compared to individual pyrolytic oil. GC-MS and FTIR analyses were used to confirm the interaction between SCB and LDPE during co-pyrolysis, which resulted in a reduction in oxygenated products, phenol, and acidic compounds, suggesting the co-pyrolysis process more suitable for the production of high heating value liquid fuel.

Inspired by the utilization of waste for energy concepts, the present study is focused the pyrolysis of neem wood bark and LDPE mixture. It investigates the biomass-plastic pair on the product distributions. Initially each of NB and LDPE is pyrolyzed separately and later it was co-pyrolyzed mutually by adding LDPE with the biomass at 20%, 40%, 50%, 60% and 80% by weight. The experiments have been carried out in a fixed bed reactor. The aim of this study is to increase the yield of bio-oil with enhanced quality. At the end of the study the physical and chemical properties of the bio-oil obtained under suitable conditions are characterized using various techniques.

2. Material And Methods

2.1. Materials

Azadirachta indica (Indian neem tree) is mahogany family tree and species of genus *Azadirachta*. It is a marvellous tree used for medicinal purposes. The wood of the tree has been removed from its bark and is

mostly used for carpentry work. Wood bark was gathered from a nearby agricultural field. It was crushed to obtain a particle size of 0.5 -1.0 mm and dried in both open air and a vacuum oven at 40°C. LDPE was obtained from Sri Kumaran Polypacks, Coimbatore, India. The collected materials were smashed and sifted using sieve shaker.

2.2. Feedstock characterization

NB and LDPE are categorised in terms of volatile matter, fixed carbon, moisture content and ash content using proximate analysis. The weight loss of the samples is used to calculate these properties. Vario EL-III, Germany Elementar analyzer is used to determine the components of the feedstock such as carbon, hydrogen, nitrogen, and sulphur. The oxygen content of the sample is found by the weight difference from the total compositions. The lignocellulosic content of the NB is determined using the traditional wet chemistry method.

2.3. Experimental setup

All the experiments are performed under atmospheric pressure in a fixed-bed reactor with diameter 100 mm and height 150 mm. In most cases, the co-pyrolysis experiments are carried out in fixed-bed reactors rather than variety of other reactors (Fei et al. 2012). The electric furnace with a heating element encircled the reactor is used to heat the reactor. The temperature within the reactor was measured using two K-type thermocouples placed at various locations. Figure 1 show the reactor used for this work, which is same as that employed in a previous paper by the literature Sowmya Dhanalakshmi and Madhu (2019). The cooling system is provided with ice water that is maintained at a temperature of 5°C. The PID control system fixes and control the temperature of the reactor bed. Mineral wool and Chromel – Alumel were used to insulate the reactor. The extracted bio-oil obtained through pyrolysis was collected in a conical flask. The quenching process was carried out until the reactor had cooled down. The char were collected from the bottom of the reactor. The residual material balance was used to compute the amount of noncondensable gas. The yield of the bio-oil, char and gas were calculated using Eqs. (1), (2) and (3).

$$Y_o = \frac{W_o}{W} \times 100 \quad (1)$$

$$Y_c = \frac{W_c}{W} \times 100 \quad (2)$$

$$Y_g = 1 - (Y_o + Y_c) \quad (3)$$

The synergetic effects on the yields were compared to the predicted yield. The individual pyrolysis yields of NB and LDPE, were used to determine the predicted yields using Eq. (4) (Zhao et al. 2020).

$$\text{Predicted Yield} = (X1 * W1 + X2 * W2) \quad (4)$$

All the experiments were conducted thrice and the mean has been taken for the calculation.

2.4. Experimental procedure

Prior to the pyrolysis experiments, thermogravimetric analyses of the individual samples are done to evaluate the thermal stability. Afterwards the pyrolysis experiments have been conducted. The first series of pyrolysis experiments are designed based on the TGA curve which is used to find the effect of temperature on pyrolysis yield of NB and LDPE. The experiments were conducted at different temperatures of 350, 400, 450, 500, and 550°C with an average heating rate of 30°C/min. The second series of the experiments were conducted to determine the product yields during co-pyrolysis. For this purpose the experiments have been conducted with the addition of LDPE with biomass at five different proportions such as 20%, 40%, 50%, 60% and 80% by weight under the constant temperature of 450 °C with an average heating rate of 30°C/min. At the end of the study the bio-oil obtained at optimum condition was analyzed for its physical and chemical compositions.

2.5. Bio-oil characterization

The pH of the bio-oil is measured using a digital pH metre (TES-1380). The viscosity of the oil sample is measured using a BROOKFIELD LV-DV-II Pro viscometer (Brookfield Engineering Laboratories, Middleboro, MA, USA). The density of the bio-oil is determined by weighing the sample's known volume. The flash point of the bio-oil is found by Pensky Martens closed-cup apparatus. A CHNS/O elementary analyzer is used to find the elements of the bio-oil sample (Elementar Vario EL-III). The calorific value of the obtained bio-oil is determined using calorimetric thermometer (Parr-6772). Gas chromatography mass spectroscopy (GC-MS) (Thermo MS DSQ II) is used to find the chemical compound present in the bio-oil. The analyzer is attached with a capillary tube of inner diameter 0.25 mm, length 30 mm and film thickness 0.25 µm. The injector is maintained at 300°C and carrier gas (Helium) flow rate for the column is set to 10 ml/min. 1 mL sample is instilled with the split ratio of 20:1. The GC oven initially is maintained at the 70°C for 2 min, after that it was heated to 250°C at a rate of 10°C/min. The mass spectrometer was operated in the mass/charge ratio range of 50–650 *m/z*. Mass spectrum libraries (NIST14.L) were used to identify the chemical compounds.

3. Results And Discussion

3.1. Characterization of feedstocks

The proximate and ultimate analysis of NB and LDPE are shown in Table 2. It is evident that NB and LDPE are high in volatile matter and so can be used to produce bio-oil. According to elemental analysis, NB has higher oxygen content, which is the major contributor in the production of volatile oxygenates, resulting in bio-oil acidity. LDPE, on the other side has higher hydrogen content with less oxygen, will act as a hydrogen donor for biomass intermediates, facilitating the formation of hydrocarbon molecules. It is the key factor for synergistic effect during co-pyrolysis of lignocellulosic biomass with LDPE (Dewangan et al. 2016). The moisture content diminishes conversion efficiency, lowers biomass calorific value, and increases aqueous phase pyrolysis formation. The higher volatile matter in both the feedstocks offers high volatility and reactivity for the production of large quantities of bio-oil (Dhanalakshmi et al. 2021). Proximate study revealed that both NB and LDPE have higher volatile content with 69.8 % and 100 %

respectively shows the suitability for the experiment. During co-pyrolysis hydrogen abstraction by biomass-derived oxygenates and reactive free radicals is most likely to facilitate the scission of polymer chains and derivatives (Matsuzawa et al. 2001). Analysis of lignocellulosic content is also important for the yield of biofuel. When compared to cellulose and hemicellulose, lignin is the primary source of reactive free radicals in biomass pyrolysis (Brebou and Spiridon, 2012). When biomass and LDPE are co-pyrolyzed, lignin may have a significant impact on the degradation of LDPE. During the co-pyrolysis process, the generation of char, CO, and CO₂ was also found to be inhibited (Xue et al. 2016). Table 3 shows the total lignocellulosic content of NB.

Table 2
Proximate and component analysis of
the raw material

| Parameters | NB | LDPE |
|-------------------------------------------------------|-------|-------|
| Proximate analysis in wt% | | |
| Volatile matter | 69.8 | 100 |
| Fixed Carbon ^a | 15.7 | 0 |
| Moisture Content | 10.3 | 0 |
| Ash | 4.2 | 0 |
| Ultimate analysis ^b in wt% | | |
| Carbon | 41.51 | 79.9 |
| Hydrogen | 7.30 | 13.9 |
| Nitrogen | 5.41 | 1.82 |
| Oxygen ^a | 45.36 | 3.17 |
| Sulfur | 0.42 | 1.21 |
| H/C molar ratio | 2.032 | 2.114 |
| O/C molar ratio | 0.821 | 0.030 |
| ^a by difference ^b dry ash basis | | |

Table 3
Lignocellulosic content of the
neem bark

| Content | Value (wt%) |
|----------------|-------------|
| Cellulose | 17.58 |
| Hemi-cellulose | 42.56 |
| Lignin | 39.86 |

3.2. Thermal degradation characteristics

The TG and DTG curves of individual feedstocks are shown in Figs. 2 and 3. This study assisted in determining the temperature at which the sample begins to degrade. From figure it has been noted that the thermal stability of NB is low and starts to breakdown at 150°C, whereas LDPE begins to decompose at 300°C. According to Alvarez and Vázquez (2004) the biomass pyrolysis is characterised by three decomposition stages, but the plastic decomposed in a single stage (Alvarez and Vázquez, 2004). The structural of the biomass material is the main reason for the early decomposition. Biomass is mainly made up of cellulose, hemicellulose, and lignin with adequate moisture. But the LDPE is a long chain polymer (Wang et al. 2008). The decomposition of NB starts at 50°C and continued until 125°C with a weight loss of 10.3 %, followed by a weight loss of 78.5 % from 250°C to 380°C. The final portion was decomposed between the temperature ranges from 380°C and 480°C. The first stage is mainly related to the release of water contents along with hydrolysis of some extractives. At 125°C, NB loses their moisture and light components upto 10.3 wt%. The degradation of cellulose and hemicellulose occurred at the intermediate stage. After that the final decomposition occurs due to the presence of lignin. The next stage of NB degradation occurred between 250°C and 480°C with a maximal rate of degradation occurring at 450°C whereas the maximum mass loss for NB is 52 %. The thermal overlapped degradation of cellulose and hemicelluloses are the main reason for the greatest mass loss (Shafaghat et al. 2019). Several researchers have observed that a depolymerisation reaction occurs in the temperature range of 300°C to 550°C, which is dominated by bond integration, resulting in the formation of liquid products with variety of organic elements (d'Almeida et al. 2008). The TGA curve for LDPE is also observed similar to the previous results (Sowmya Dhanalakshmi and Madhu, 2019; Al-Maari et al. 2021; Brebu et al. 2004). In comparison to NB, the decomposition of plastic happened in a single stage at elevated temperature over a very short period of time. This is due to the homogeneous composition of plastic material. In the temperature range of 300 to 475°C, LDPE lose 98% of their mass. The temperature exceeding this limit, there is no decomposition is recorded. From the figure it has been noticed that both the curves were overlapped at the temperature range of 440 to 470°C based on the maximum volatiles loss. In the case of LDPE, there was no residues were left after reaching 550°C. But there is some residue in the case of NB, due to the presence of ash content (Dewangan et al. 2013). Based on the aforementioned thermal decomposition characteristics data, the appropriate pyrolysis temperatures for NB, LDPE and mixtures are selected as 450°C.

3.3. Pyrolysis products yield

3.3.1. Effect of temperature on pyrolysis of NB

A series of tests were conducted at temperatures ranging from 350°C to 550°C with an average heating rate of 30°C/min to explore the effect of temperature on the yield of NB pyrolysis products. The variations of product yields with temperatures are given in Fig. 4. Temperature has been shown to have a significant impact on the yield of pyrolysis products. During pyrolysis, biomass undergoes end-to-end primary and secondary processes including heat and mass transfer mechanisms. In this process, major products are formed by the decomposition of cellulose, hemicelluloses, and lignin. In pyrolysis heat is the primary role for the decomposition of biomass linkages. The bio-oil yield is increased from 32.4 wt% to 36.8 wt% when the temperature is increased from 350 to 550°C. The results reveal that when the reactor temperature increases upto 450°C, the bio-oil yield increases to 40.3 wt%. The yield of bio-oil is decreased beyond 450°C. When the temperature of the reactor is increased from 350 to 550°C, the char yield is lowered from 38.2 wt% to 23.1 wt%, with increased gas yield from 29.4 to 36.8 wt%. The bio-oil yield was only 32.4 wt% at a lower temperature of 350°C, but the yield of char was 38.2 wt%. More char yield is obtained by the decomposition of particle at a lower temperature, which happens at heteroatoms inside the structure (Sowmya Dhanalakshmi and Madhu, 2021). Massive molecular dislocation occurs when biomass is broken up at elevated temperatures, resulting in the production of variety of chemical compounds. When the temperature is held below 350°C, the conversion efficiency of biomass into bio-oil is quite low. A substantial quantity of biomass is transformed to bio-oil and its fragments at temperatures between 400 and 500°C. After 500°C the yield will be reduced due to secondary cracking reactions of the pyrolysis vapour (Sohaib et al. 2017). Many researchers investigated the effect of temperature on product yields in order to maximise the bio-oil yield. The results confirmed that 450°C is the optimum temperature for pyrolysis of NB since it maximised the bio-oil yield.

3.3.2. Effect of temperature on pyrolysis of LDPE

The variations of product yields on LDPE pyrolysis with respect to temperature is given in Fig. 5. From the experiment it was identified that there is no volatile has been released till the temperature of the reactor reaches 350°C. The bio-oil yield is changed with respect to reactor temperature. The bio-oil yield increased from 63.1 wt% to 73.2 wt% when the temperature is increased from 350 to 500°C. The char yield, on the other hand reduced from 18.6% to 2.5 wt%. The yield of gas is gradually increased from 18.3 wt% to 26.2 wt% with the increase of pyrolysis temperature. During this experiment the maximum yield of bio-oil of 73.2 wt% was obtained at the temperature of 500°C. The yields of bio-oil and gas products are increased due to the variation in the thermal stability of polymer chains. The thermal stability of both linear and branched hydrocarbons decreases as the temperature increases. It break the C = C bonds more frequently at 500°C, resulting in higher volatile product yields (Sharypov et al. 2002).

3.3.3. Co-pyrolysis characteristics

Figure 6 shows the yield of pyrolysis products obtained from co-pyrolysis of NB and LDPE at various ratios. The experiments have been conducted at optimum temperature of 450°C. The pyrolysis behaviour of NS was similar to other types of biomass samples, with higher bio-oil yield of 40.3 wt% (from Fig. 4). For this series of experiments the biomass and plastic blend ratios were changed from 20–100%. Bio-oil yield obtained from co-pyrolysis was significantly higher than biomass pyrolysis. As the percentage of addition increased from 20–60%, the bio-oil yield is increased from 44.12 wt% to 64.8 wt%. The yield of char and gas is steadily decreased from 21.78 wt% to 12.54 wt% and 33.13 wt% to 24.15 wt% respectively. The properties of LDPE were the primary reason of these phenomena. Table 1 show that LDPE has a high volatile content of 100 wt%, with no ash content. This may be the reason for maximum bio-oil product with less solid phase. Generally, polyolefin polymers are the excellent hydrogen donors during co-pyrolysis reaction which enhances the bio-oil conversion (Zhou et al. 2006; Guo et al. 2001). According to Onal et al. (2014) the co-pyrolysis experiments create the radical interaction favours the generation of bio-oil with no phase separation

Table 1
GC-MS conditions

| Items | Parameter |
|---------------------------------|-------------------|
| GC conditions | |
| Type | Thermo MS DSQ II |
| Column oven initial temperature | 70 °C |
| Injection type | Split |
| Temperature range | 200 to 250 °C |
| Spit ratio | 10 |
| Flow | Linear velocity |
| Column flow rate | 10 ml/min |
| Carrier gas | Helium |
| Column oven temperature range | 70–250 °C |
| Holding time | 5–7 min |
| Heating rate | 10 °C/min |
| Column | DB-35 |
| Length | 30 m |
| Diameter | 0.25 mm |
| Film thickness | 0.25 µm |
| MS Conditions | |
| Ionization energy (eV) | 70 |
| Ion source temperature | 200 °C |
| Interface temperature | 250 °C |
| Scan range | 50–650 <i>m/z</i> |

For further investigations, the experimental yields were compared to predicted yields in to assess the synergistic effect shown in Fig. 6. It should be noted that the experimental value for the bio-oil yield for the blend up to 40% LDPE is just lower than the theoretical value. On the other hand the char and gas values are higher than the theoretical value. The yield of bio-oil is more than theoretical value when more than 40% of LDPE is blended with NB. There is no major difference is recorded for char yield above 40% blend of LDPE. The increment in plastic blend decreases the yield of gas. The results show that various synergistic effects on bio-oil, char, and gas production are observed between different biomass-plastic

blends. When compared to theoretical values, there was 8.1 % positive synergy effect on bio-oil yield at 40 % LDPE blend. The synergetic effect in these experiments was endorsed to the radical secondary reactions, which is the cause for condensation of non-condensable elements (Özsin and Pütün, 2018). Furthermore, LDPE acts as a hydrogenation medium for biomass, potentially limiting the polymerization and cross-linking processes resulting in greater biomass weight loss (Aboulkas et al. 2012; Yuan et al. 2018).

3.4. Characterization of bio-oil

Some of the physical properties of the bio-oils derived from NB and NB:LDPE (60% LDPE blend) are shown in Table 4. The lower water content is found to be beneficial synergistic effects for co-pyrolytic oil. The water content of the raw pyrolytic oil was 28.0 wt% and it was almost decreased with the blend of LDPE and then it decreased to 0 for LDPE pyrolysis oil. The pH value of the bio-oil also decreased with the increase of blend ratio. The decrease in pH value in co-pyrolytic oil is due to creation of NH_3 by protein pyrolysis which dissolved in the bio-oil (Tang et al. 2019). All the parameters were measured under ASTM standards. The hydrocarbon and oxygen content of bio-oil plays an important role in its calorific value. The increased calorific value of the co-pyrolytic oil obtained under 60% addition of LDPE may be explained by the significant drop in oxygen from 40.59% to 17.91 %. The co-pyrolysis, process is the effective strategy contributed bio-oil with high calorific value.

Table 4
Physical properties of the bio-oil

| Properties | NB | NB:LDPE (40:60) | Unit |
|----------------------------|----------------------------------------------------------|-----------------------------------------------------------|-------------------|
| Density | 1015 | 1075 | kg/m ³ |
| Viscosity | 8.1 | 8.3 | cSt |
| Flash point | 155 | 95 | °C |
| pH | 4.1 | 3.6 | - |
| Carbon | 49.12 | 72.16 | wt% |
| Hydrogen | 9.2 | 9.5 | wt% |
| Nitrogen | 0.88 | 0.34 | wt% |
| Sulfur | 0.21 | 0.09 | wt% |
| Oxygen ^a | 40.59 | 17.91 | wt% |
| H/C molar ratio | 2.231 | 1.568 | - |
| O/C molar ratio | 0.620 | 0.186 | - |
| Empirical formula | CH _{2.231} N _{0.015} O _{0.62} | CH _{1.568} N _{0.004} O _{0.186} | - |
| Heating value | 21.6 | 33.5 | MJ/kg |
| ^a By difference | | | |

The GC–MS analysis was used to detect the various chemical compounds present in the bio-oils. This method is offering structural information at the molecular level. Alcohols, ester, phenols, organic acids aromatic compounds, nitrogen and hydrocarbon elements were considerably identified in NB bio-oil. Figure 7 depicts the effect of addition of LDPE on the variation in chemical composition of bio-oil. The NB-LDPE ratio produced substantial impact on the composition of bio-oil. With the addition of LDPE, the fraction of hydrocarbon is enhanced to the maximum yield of 75.32% at 60% LDPE addition. But the fraction of hydrocarbon at 20% addition of LDPE is 30.25%. The increased amount of hydrocarbon might be understood by improved hydrocarbon pool mechanisms, in which the alkene produced by LDPE degradation may be served as a hydrogen donor (Chi et al. 2018). The proportion of hydrocarbon is decreased with further increase in LDPE with NB. It can be explained by hydrogen supply in the hydrocarbon pool, as well as the high H/C ratio, that could not sufficiently retort with the oxygenated compounds (Ding et al. 2018). There is a slight increase in alcohol yield with the addition of NB-LDPE ratio. The alcohol content is just increased from 13.9–16.9% as the LDPE addition is increased from 20–80%. The hydrogen appendage from the plastic-derived alkane assisted the cracking of lignocellulosic contents of NB to generate more alcohol. The proportion of aromatic compounds in the bio-oil is decreased and diminished with the increase of LDPE. The aromatic compounds are increased from 20.1–

5.3% as the LDPE is mixed from 20–80%. It is due to the presence of excess alkenes derived from LDPE relative to oxygenate obtained from NB. In order to generate more aromatic compounds, the excess alkenes must undergo a series of reactions including hydrogen transfer, oligomerization, cyclization, and aromatization (Li et al. 2014).

4. Conclusion

In this study, pyrolysis of NB combined with LDPE was carried out for the production of high-grade bio-oil. The study produced maximum bio-oil of 64.8 wt% at the ideal temperature 450°C with 60% addition of LDPE. The bio-oil obtained at this condition has lower oxygenated compounds with higher calorific value of 33.5 MJ/kg. The synergistic effects during co-pyrolysis were also analyzed in terms product distribution. The results showed that the synergistic effects occurred at 60% addition of LDPE, resulting in 8.1% increase in bio-oil yield in comparison to theoretical value. The synergetic effect gives positive effects on lower water content and higher calorific value as compared to that of bio-oil derived from NB. This is due to the hydrogen released from LDPE, which stabilises the free radicals generated during co-pyrolysis. The increased amount of hydrocarbon is also implicit by improved hydrocarbon pool mechanisms, in which the degradation of LDPE may be served as a hydrogen donor. The lower phenolic and acid content of the co-pyrolysis oil may increase its stability to use as a potential fuel. Further research is also recommended to understand the reaction kinetics of the plastic blend, application and feasibility of co-pyrolysis process to offer number of benefits in waste treatment and utilization.

Abbreviations

| | | |
|-----------------|---|----------------------------|
| PE | - | Polyethylene |
| PP | - | Polypropylene |
| PS | - | Polystyrene |
| PET | - | Polyethylene terephthalate |
| PVC | - | Polyvinyl chloride |
| HDPE | - | High density polyethylene |
| LDPE | - | Low density polyethylene |
| NB | - | Neem wood bark |
| SCB | - | Sugarcane bagasse |
| CO | - | Carbon monoxide |
| CO ₂ | - | Carbon dioxide |
| W | - | Initial weight of the feed |
| W_o | - | Weight of bio-oil |
| W_c | - | Weight of char |
| Y_o | - | Yield of bio-oil |
| Y_c | - | Yield of char |
| Y_g | - | Yield of gas |
| W_1 | - | Pyrolysis yield of NB |
| W_2 | - | Pyrolysis yield of LDPE |
| X_1 | - | Mass ratios of NB |
| X_2 | - | Mass ratios of LDPE |

Declarations

Author contributions

Venkatachalam Selvaraj Kaushik - Conceptualization, Methodology, Writing

Chandrasekaran Sowmya Dhanalakshmi - Supervision, Investigations, Writing

Petchimuthu Madhu - Writing, Investigations

Competing interests:

The authors declare that they have no competing interests.

Ethical Approval - Not applicable

Consent to Participate - Not applicable

Consent to Publish - Not applicable

Availability of data and materials- Not applicable

Funding:

There is no financial support for this work

References

1. Abnisa, F., & Daud, W. M. A. W. (2014). A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management*, 87, 71-85.
2. Abnisa, F., & Daud, W. M. A. W. (2015). Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire. *Energy Conversion and Management*, 99, 334-345.
3. Aboulkas, A., Makayssi, T., Bilali, L., Nadifiyine, M., & Benchanaa, M. (2012). Co-pyrolysis of oil shale and plastics: Influence of pyrolysis parameters on the product yields. *Fuel processing technology*, 96, 209-213.
4. Ahmed, N., Zeeshan, M., Iqbal, N., Farooq, M. Z., & Shah, S. A. (2018). Investigation on bio-oil yield and quality with scrap tire addition in sugarcane bagasse pyrolysis. *Journal of Cleaner Production*, 196, 927-934.
5. Al-Maari, M. A., Ahmad, M. A., Din, A. T. M., Hassan, H., & Alsobaai, A. M. (2021). Co-pyrolysis of oil palm empty fruit bunch and oil palm frond with low-density polyethylene and polypropylene for bio-oil production. *Arabian Journal of Chemistry*, 103282.
6. Alvarez, V. A., & Vázquez, A. (2004). Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites. *Polymer degradation and stability*, 84(1), 13-21.
7. Ansah, E., Wang, L., & Shahbazi, A. (2016). Thermogravimetric and calorimetric characteristics during co-pyrolysis of municipal solid waste components. *Waste management*, 56, 196-206.
8. Brebu, M., & Spiridon, I. (2012). Co-pyrolysis of LignoBoost® lignin with synthetic polymers. *Polymer degradation and stability*, 97(11), 2104-2109.
9. Brebu, M., Bhaskar, T., Murai, K., Muto, A., Sakata, Y., & Uddin, M. A. (2004). Thermal degradation of PE and PS mixed with ABS-Br and debromination of pyrolysis oil by Fe-and Ca-based

- catalysts. *Polymer Degradation and Stability*, 84(3), 459-467.
10. Chen, L., Wang, S., Meng, H., Wu, Z., & Zhao, J. (2017). Study on gas products distributions during fast co-pyrolysis of Paulownia wood and PET at high temperature. *Energy Procedia*, 105, 391-397.
 11. Chi, Y., Xue, J., Zhuo, J., Zhang, D., Liu, M., & Yao, Q. (2018). Catalytic co-pyrolysis of cellulose and polypropylene over all-silica mesoporous catalyst MCM-41 and Al-MCM-41. *Science of the Total Environment*, 633, 1105-1113.
 12. d'Almeida, A. L. F. S., Barreto, D. W., Calado, V., & d'Almeida, J. R. M. (2008). Thermal analysis of less common lignocellulose fibers. *Journal of Thermal Analysis and Calorimetry*, 91(2), 405-408.
 13. Dewangan, A., Pradhan, D., & Singh, R. K. (2016). Co-pyrolysis of sugarcane bagasse and low-density polyethylene: Influence of plastic on pyrolysis product yield. *Fuel*, 185, 508-516.
 14. Dhanalakshmi, C. S., Mathew, M., & Madhu, P. (2021). Biomass Material Selection for Sustainable Environment by the Application of Multi-Objective Optimization on the Basis of Ratio Analysis (MOORA). In *Materials, Design, and Manufacturing for Sustainable Environment* (pp. 345-354). Springer, Singapore.
 15. Ding, K., Zhong, Z., Wang, J., Zhang, B., Fan, L., Liu, S., ... & Ruan, R. (2018). Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemicellulose and plastic in the dual-catalyst bed of CaO and HZSM-5. *Bioresource technology*, 261, 86-92.
 16. Fei, J., Zhang, J., Wang, F., & Wang, J. (2012). Synergistic effects on co-pyrolysis of lignite and high-sulfur swelling coal. *Journal of Analytical and Applied Pyrolysis*, 95, 61-67.
 17. Gin, A., Hassan, H., Ahmad, M., Hameed, B., & Din, A. M. (2021). Recent progress on catalytic co-pyrolysis of plastic waste and lignocellulosic biomass to liquid fuel: The influence of technical and reaction kinetic parameters. *J. Chem*, 14, 103035.
 18. Gunasee, S. D., Danon, B., Görgens, J. F., & Mohee, R. (2017). Co-pyrolysis of LDPE and cellulose: Synergies during devolatilization and condensation. *Journal of Analytical and Applied Pyrolysis*, 126, 307-314.
 19. Guo, J., & Lua, A. C. (2001). Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model. *Biomass and Bioenergy*, 20(3), 223-233.
 20. Hassan, H., Hameed, B. H., & Lim, J. K. (2020). Co-pyrolysis of sugarcane bagasse and waste high-density polyethylene: Synergistic effect and product distributions. *Energy*, 191, 116545.
 21. Hassan, H., Hameed, B. H., & Lim, J. K. (2020). Co-pyrolysis of sugarcane bagasse and waste high-density polyethylene: Synergistic effect and product distributions. *Energy*, 191, 116545.
 22. Hassan, H., Lim, J. K., & Hameed, B. H. (2016). Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. *Bioresource Technology*, 221, 645-655.
 23. Hoornweg, D., Bhada-Tata, P., & Kennedy, C. (2013). Environment: Waste production must peak this century. *Nature News*, 502(7473), 615.
 24. <http://lilapolymers.com/polyethylene.php> accessed on 17th July 2021

25. Li, X., Li, J., Zhou, G., Feng, Y., Wang, Y., Yu, G., ... & Wang, B. (2014). Enhancing the production of renewable petrochemicals by co-feeding of biomass with plastics in catalytic fast pyrolysis with ZSM-5 zeolites. *Applied Catalysis A: General*, 481, 173-182.
26. Lu, P., Huang, Q., Bourtsalass, A. T., Chi, Y., & Yan, J. (2018). Synergistic effects on char and oil produced by the co-pyrolysis of pine wood, polyethylene and polyvinyl chloride. *Fuel*, 230, 359-367.
27. Madhu, P., Kanagasabapathy, H., & Manickam, I. N. (2018). Conversion of cotton residues to bio-oil and chemicals through flash pyrolysis in a fluidised bed reactor. *International Journal of Energy Technology and Policy*, 14(1), 20-33
28. Matsuzawa, Y., Ayabe, M., & Nishino, J. (2001). Acceleration of cellulose co-pyrolysis with polymer. *Polymer degradation and stability*, 71(3), 435-444.
29. Mishra, R. K., & Mohanty, K. (2018). Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis. *Bioresource technology*, 251, 63-74.
30. Önal, E., Uzun, B. B., & Pütün, A. E. (2014). Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. *Energy conversion and management*, 78, 704-710.
31. Onay, O., & Koca, H. (2015). Determination of synergetic effect in co-pyrolysis of lignite and waste tyre. *Fuel*, 150, 169-174.
32. Özsin, G., & Pütün, A. E. (2018). A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: Synergistic effects and product characteristics. *Journal of Cleaner Production*, 205, 1127-1138.
33. Ryu, H. W., Kim, D. H., Jae, J., Lam, S. S., Park, E. D., & Park, Y. K. (2020). Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. *Bioresource technology*, 310, 123473.
34. Shafaghat, H., Lee, H. W., Tsang, Y. F., Oh, D., Jae, J., Jung, S. C., ... & Park, Y. K. (2019). In-situ and ex-situ catalytic pyrolysis/co-pyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts. *Chemical Engineering Journal*, 366, 330-338.
35. Sharypov, V. I., Marin, N., Beregovtsova, N. G., Baryshnikov, S. V., Kuznetsov, B. N., Cebolla, V. L., & Weber, J. V. (2002). Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases. *Journal of analytical and applied pyrolysis*, 64(1), 15-28.
36. Sohaib, Q., Muhammad, A., & Younas, M. (2017). Fast pyrolysis of sugarcane bagasse: Effect of pyrolysis conditions on final product distribution and properties. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 39(2), 184-190.
37. Sowmya Dhanalakshmi, C., & Madhu, P. (2019). Utilization possibilities of *Albizia amara* as a source of biomass energy for bio-oil in pyrolysis process. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 41(15), 1908-1919.
38. Sowmya Dhanalakshmi, C., & Madhu, P. (2021). Biofuel production of neem wood bark (*Azadirachta indica*) through flash pyrolysis in a fluidized bed reactor and its chromatographic

- characterization. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 43(4), 428-443.
39. Sowmya Dhanalakshmi, C., Madhu, P., Karthick, A., & Vigneshkumar, R. (2021). Combination of woody and grass type biomass: waste management, influence of process parameters, yield of bio-oil by pyrolysis and its chromatographic characterization. *Journal of Scientific and Industrial Research (JSIR)*, 80(02), 172-180.
 40. Tang, Z., Chen, W., Chen, Y., Yang, H., & Chen, H. (2019). Co-pyrolysis of microalgae and plastic: Characteristics and interaction effects. *Bioresource technology*, 274, 145-152.
 41. Uzoejinwa, B. B., He, X., Wang, S., Abomohra, A. E. F., Hu, Y., & Wang, Q. (2018). Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide. *Energy conversion and management*, 163, 468-492.
 42. Wang, G., Li, W., Li, B., & Chen, H. (2008). TG study on pyrolysis of biomass and its three components under syngas. *Fuel*, 87(4-5), 552-558.
 43. Wang, Z., Burra, K. G., Lei, T., & Gupta, A. K. (2021). Co-pyrolysis of waste plastic and solid biomass for synergistic production of biofuels and chemicals-A review. *Progress in Energy and Combustion Science*, 84, 100899
 44. Wong, S. L., Ngadi, N., Abdullah, T. A. T., & Inuwa, I. M. (2015). Current state and future prospects of plastic waste as source of fuel: A review. *Renewable and sustainable energy reviews*, 50, 1167-1180.
 45. Xue, Y., Kelkar, A., & Bai, X. (2016). Catalytic co-pyrolysis of biomass and polyethylene in a tandem micropyrolyzer. *Fuel*, 166, 227-236.
 46. Yang, J., Rizkiana, J., Widayatno, W. B., Karnjanakom, S., Kaewpanha, M., Hao, X., ... & Guan, G. (2016). Fast co-pyrolysis of low density polyethylene and biomass residue for oil production. *Energy conversion and management*, 120, 422-429.
 47. Yuan, H., Fan, H., Shan, R., He, M., Gu, J., & Chen, Y. (2018). Study of synergistic effects during co-pyrolysis of cellulose and high-density polyethylene at various ratios. *Energy conversion and management*, 157, 517-526.
 48. Zhao, Y., Yang, X., Fu, Z., Li, R., & Wu, Y. (2020). Synergistic effect of catalytic co-pyrolysis of cellulose and polyethylene over HZSM-5. *Journal of Thermal Analysis and Calorimetry*, 140(1), 363-371.
 49. Zhou, L., Wang, Y., Huang, Q., & Cai, J. (2006). Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. *Fuel processing technology*, 87(11), 963-969.

Figures

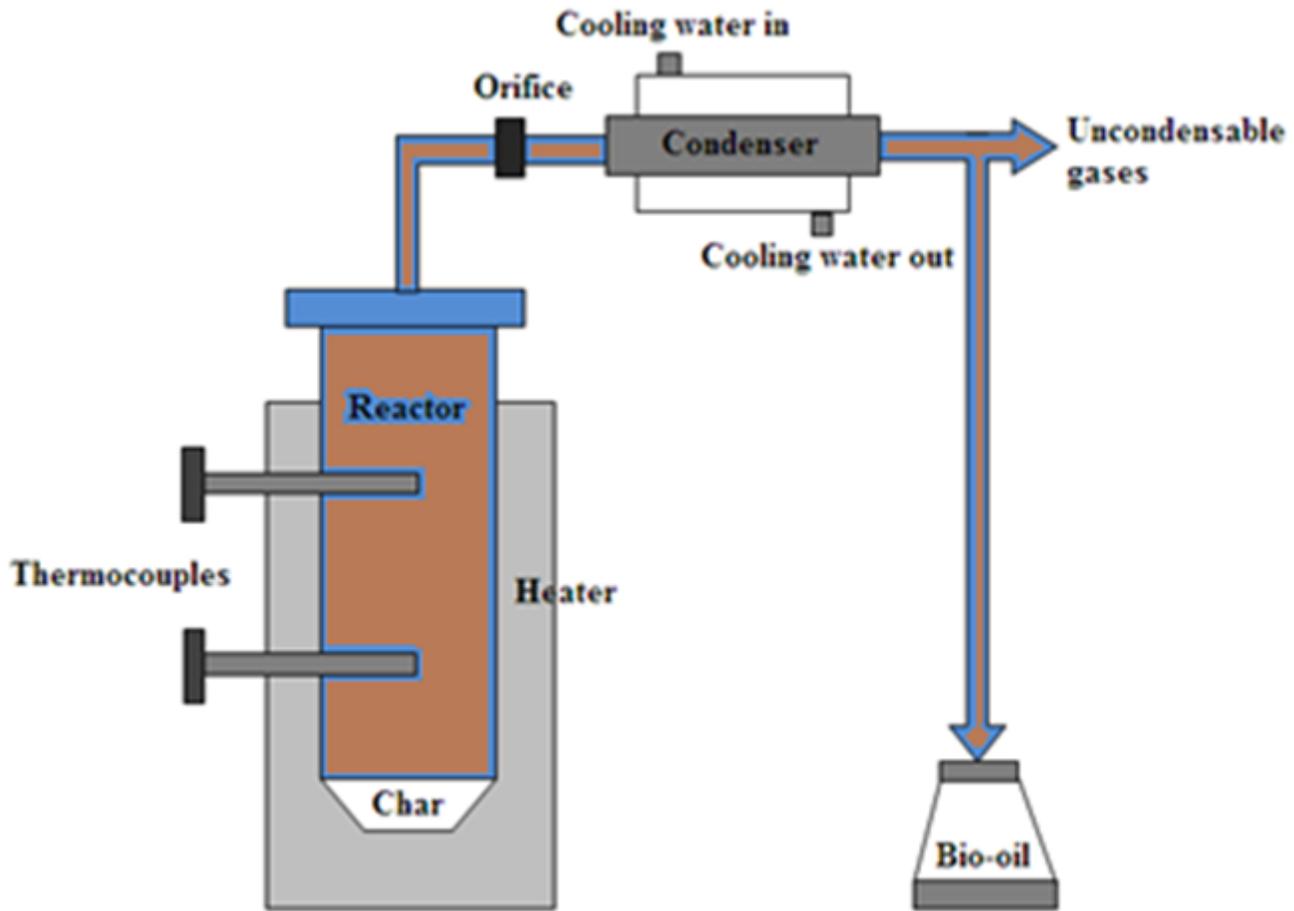


Figure 1

Reactor set up

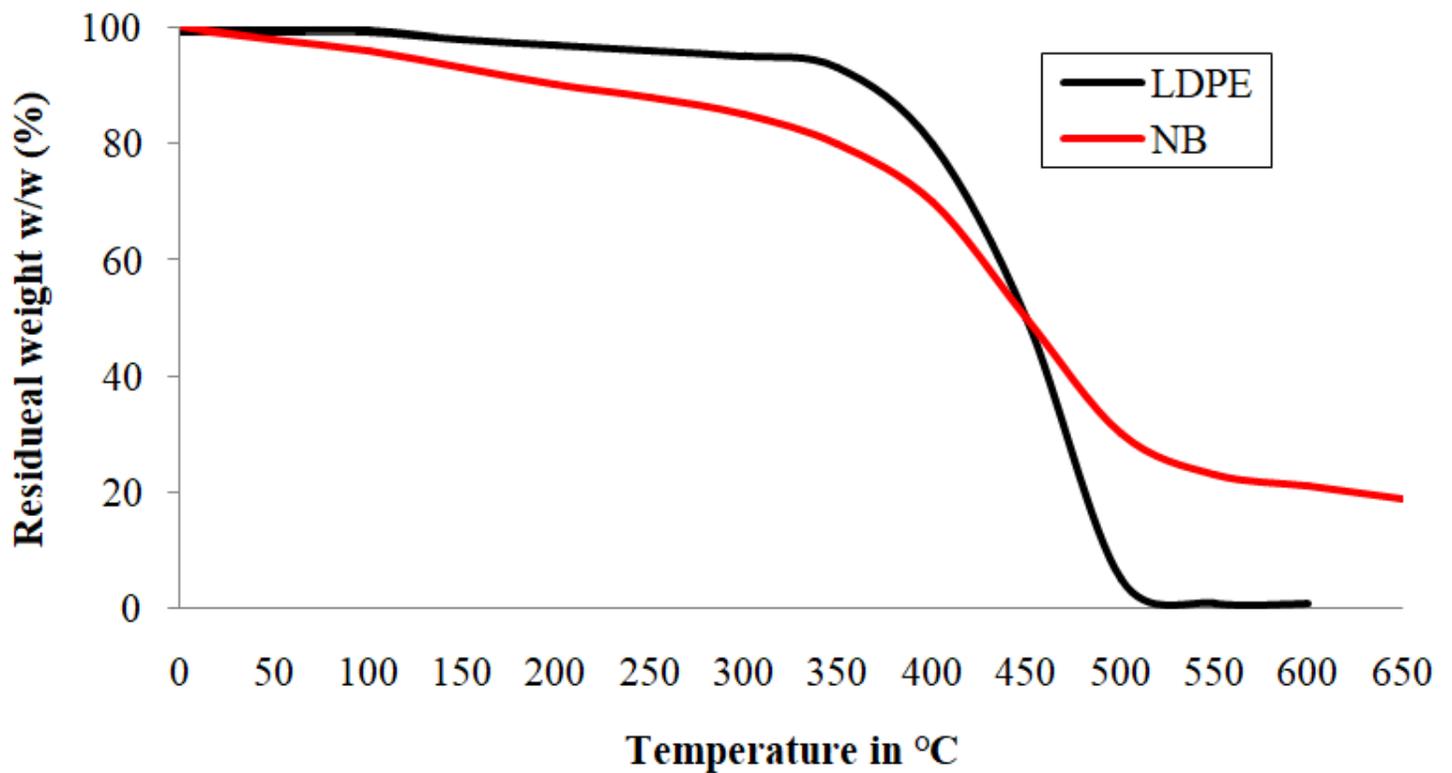


Figure 2

Thermogravimetric (TG) graphs for NB and LDPE

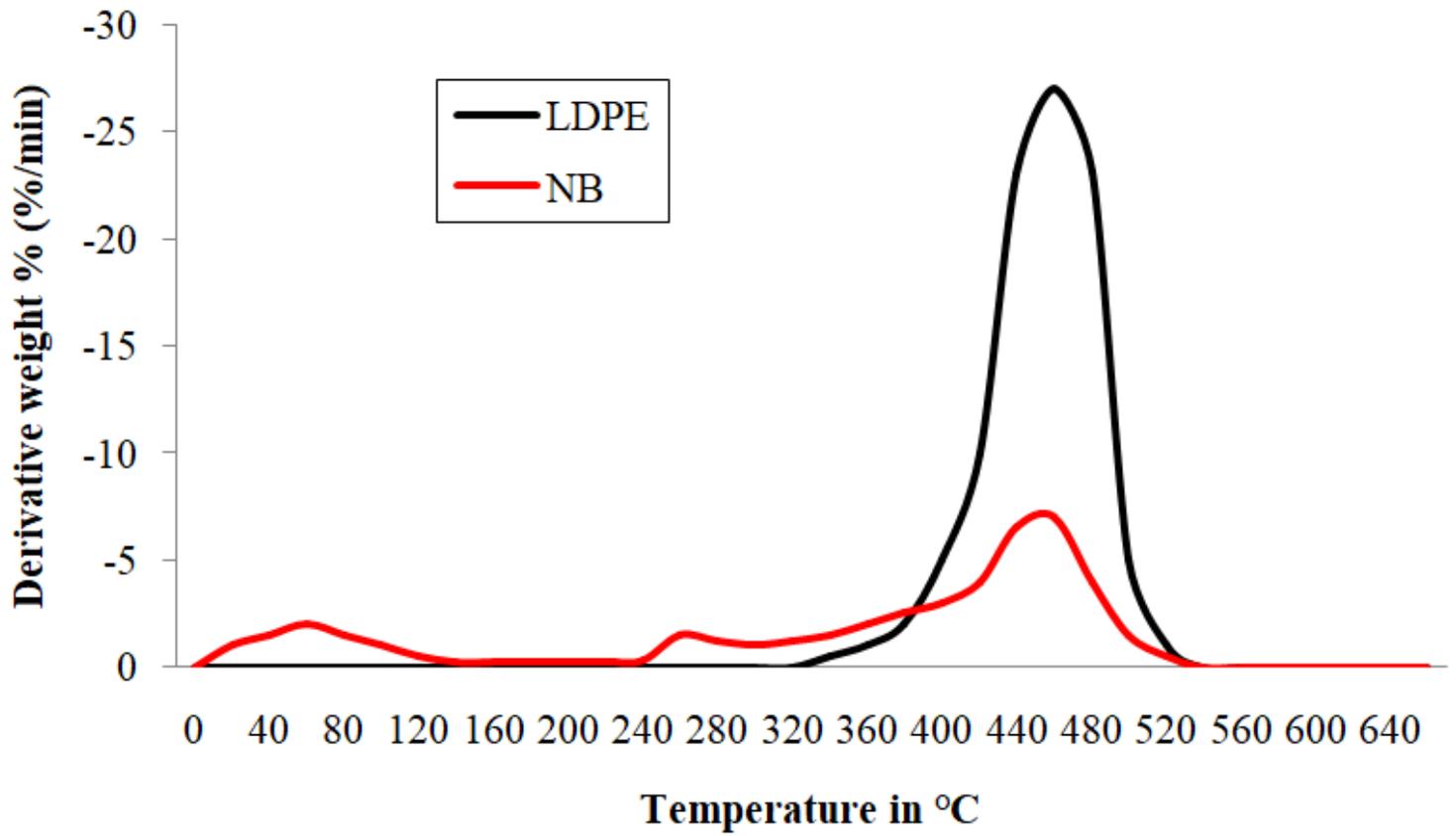


Figure 3

Differential thermogravimetry (DTG) graphs for NB and LDPE

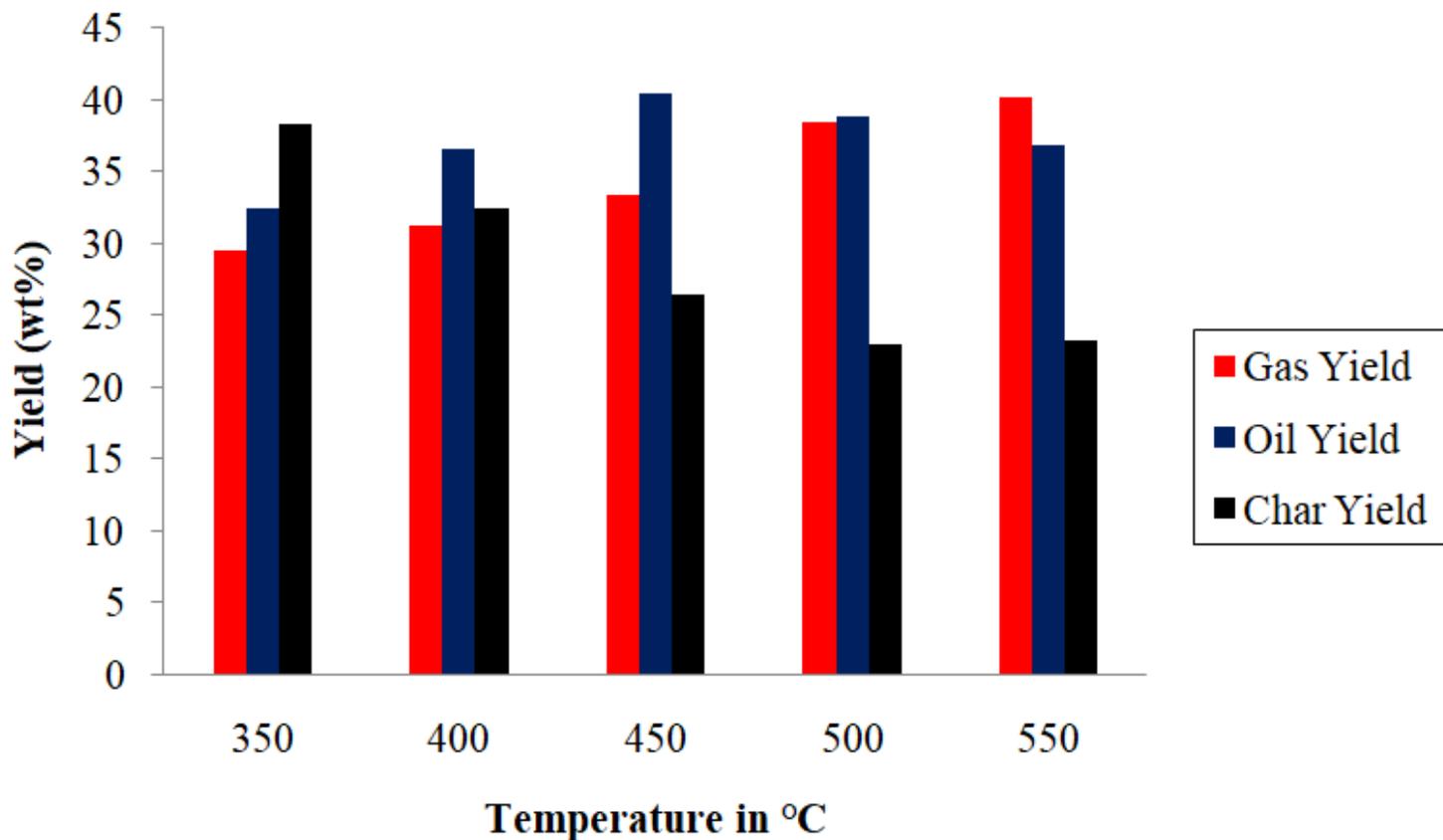


Figure 4

Effect of temperature and pyrolysis product yield of NB

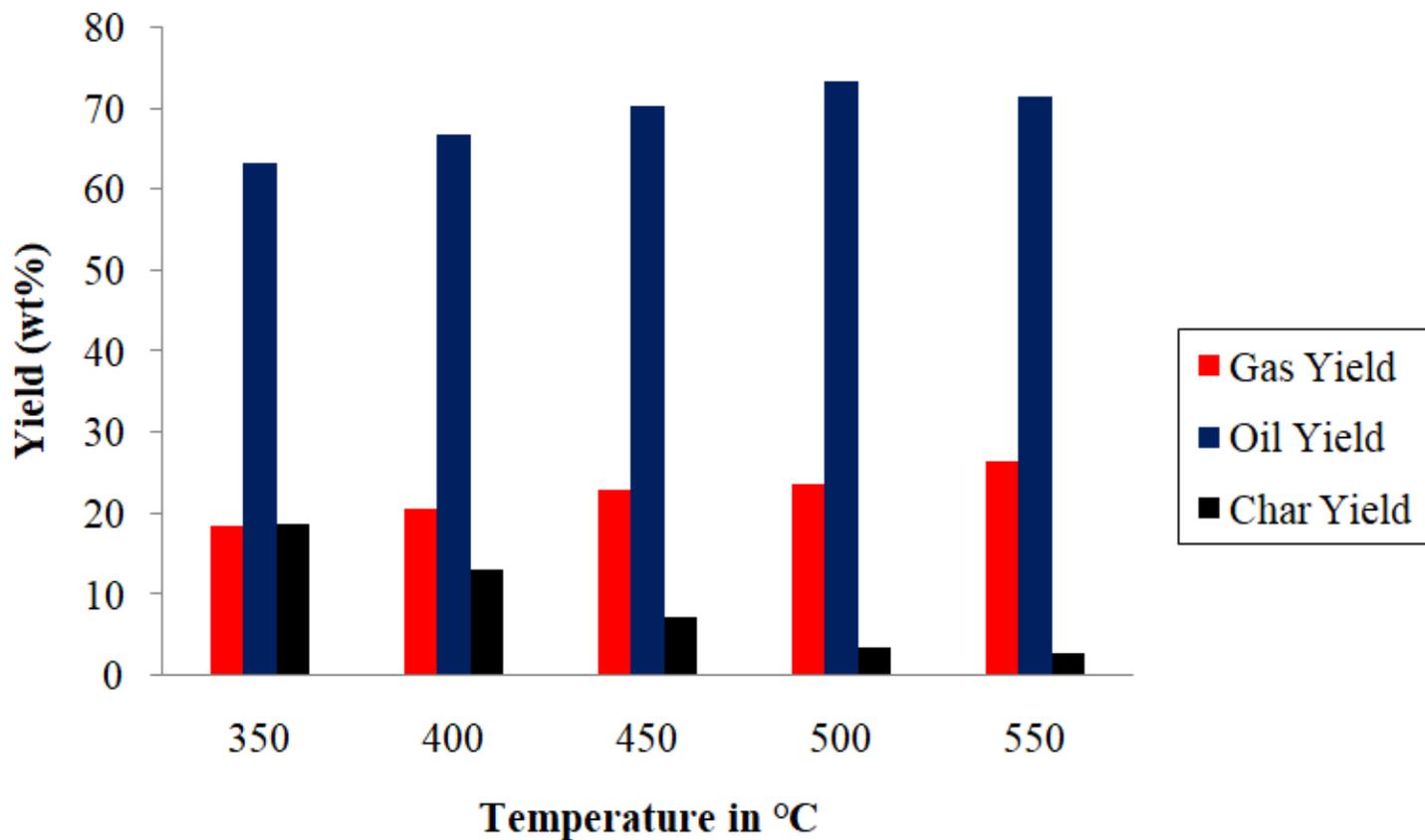


Figure 5

Effect of temperature and pyrolysis product yield of LDPE

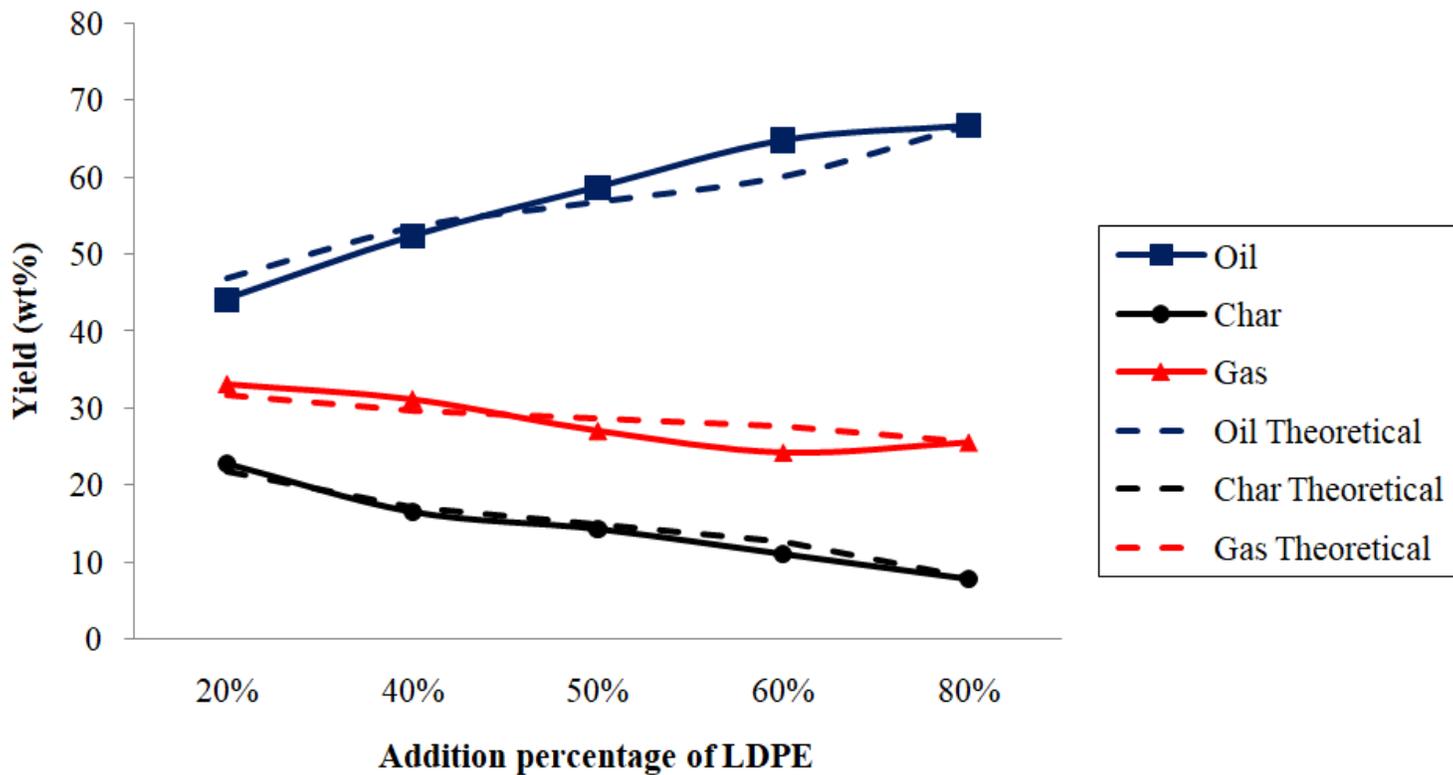


Figure 6

Evaluation of synergistic effect for NB/LDPE pair on product yield.

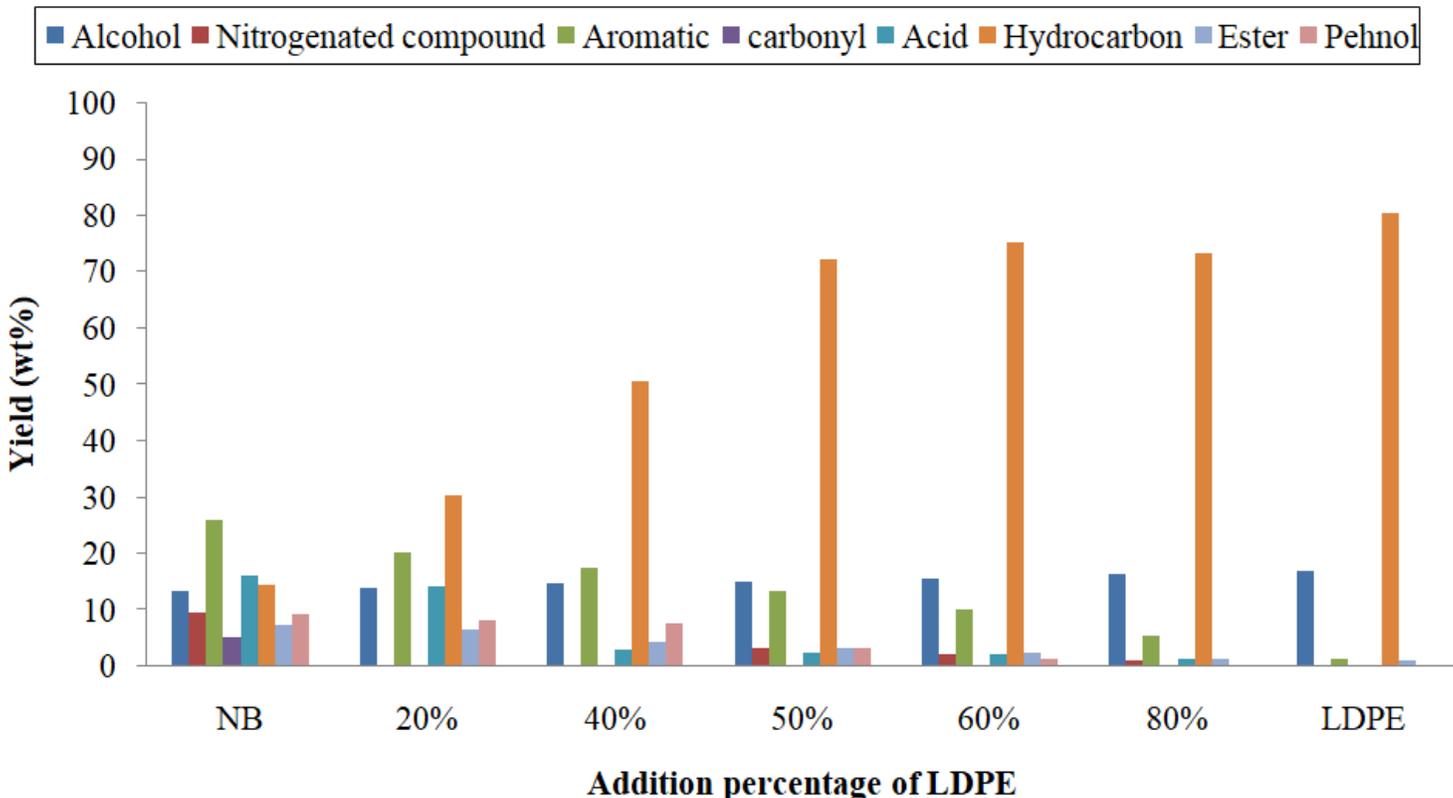


Figure 7

Chemical composition of bio-oil from the co-pyrolysis of NB and LDPE