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Non-Catalytic and Catalytic Conversion of Fruit Waste to Synthetic Liquid Fuel via Pyrolysis

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Abstract: In terms of obtaining fuels as well as chemicals with or without catalysts at different conditions, the plum seed stands out as an alternative biomass source. Under varying heating rates (10, 50, and 100ºC min^{-1}) and pyrolysis temperatures (400, 450, 500, 550 and 600 °C), the plum seed was pyrolysed at constant sweep gas flow at a constant rate (100 cm^{3}min^{-1}) in a tubular fixed bed reactor. According to the results, an oil yield reaching to a maximum of %45 was procured at the heating rate of 100 ºCmin^{-1} and the pyrolysis temperature of 550ºC in non-catalytic procedure. The catalytic pyrolysis was carried out in optimum conditions with two selected commercial catalysts, namely ZSM-5 and PURMOL-CTX and clinoptilolite (natural zeolite, NZ) with catalyst ratio of 10 % of raw material. Along with the catalyst addition, the quantity and the quality of bio-oil increased including the calorific value, removal of oxygenated groups, and hydrocarbon distribution. An increase related to the desirable products like phenols, alkene, and alkane and a decrease in undesirable products like acids were observed in the presence of catalysts. When all the results are considered and evaluated, using zeolite materials in the pyrolysis as catalysts is a recommendable option to achieve enhanced chemicals and fuels.

Keywords: catalytic pyrolysis; plum seed; TGA; bio-oil; zeolite

1. Introduction

Fossil fuel ranks first among the energy sources across the world. Although it is widely used, it is acknowledged to have high emission values such as SOx, COx and NOx causing global warming and adversely affecting the health of humanity. Higher levels of greenhouse gas emissions also constitute a great risk in terms of ecosystem. The fact that global warming is intricately connected to hazardous human activities like the use of fossil fuels and deforestation is broadly recognized. Due to the accelerating consumption of fuel, oil reserves are being spent and greenhouse gas emissions are increasing. Therefore, being one of the most considerable sources for renewable energy in terms of chemical synthesis and liquid fuel, non-food lignocellulosic biomass is becoming more and more prominent recently. Carbon neutral lignocellulosic biomass, which is available in abundance to meet the world's fuel demand, has the ability to achieve a global reduction in carbon dioxide emissions [1]. The commissioning of biomass in the energy application for power, transportation, and heating instructs a multi-step transformation. Hence, lignocellulosic biomass procured from forests, agricultural and agro industries is employed in the production of liquid fuel using thermochemical decomposition methods like liquefaction and pyrolysis. Converting lignocellulosic biomass to especially bio-oil and other chemicals, biomass pyrolysis produces bio-oil, a liquid fuel bearing a high density, which can work as an alternative to fuel-oil [2]. Proven to achieve a high degree of combustion efficiency by being tested in gas turbines and boilers, biofuel is seen as a prospective nominee in terms of ensuring energy security with beneficial effects on the environment and economy as well as the society. It is now known with certainty that oil reserves will be depleted eventually, whereas bio-based fuels are renewable and sustainable. Almost 84% of total greenhouse gases are CO_2 from the combustion of fossil fuels By comparison, the biofuel combustion is deemed carbon neutral due to the photosynthesis during which plants recycle CO_2 [3]. However, bio-oil shows some disadvantages. Although the calorific capacity of bio-oils is less than the known 40 to 45 MJ/kg for conventional fossil fuels, with a value of 16 to 19 MJ/kg, it approximates the value of oxygenated fuel such as ethanol. The low calorific capacity of bio-oils is influenced by highly oxygenated compounds. In addition, since bio-oils contain water, it poses a problem for the direct use of oil in transportation. The oxygenated compounds and water together cause some disadvantages during storing such as high acidity, non-volatility, corrosiveness and aging. During storing, the bio-oil demonstrates intense instability and inclination to re-polymerize during storage as a reaction for aging, accountable for the disadvantages in its fuel characteristics [1]. Removing water can enhance the values of viscosity and stability as well as reducing its acidity, but it is a costly and advanced procedure. When it comes to producing renewable, low-cost and non-polluting bio-based aromatics and transportation fuels such as phenol and BTX (Benzene, Toluene, and Xylene) [3,4] which have an accelerating demand in transportation and petrochemicals, the catalytic pyrolysis has received considerable attention since the catalysts enhance the characteristics of pyrolysis oil by means of cracking, oligomerisation, deoxygenation, cyclization, alkylation, aromatisation, polymerisation and isomerization [1]. The catalytic enhancement primarily boosts the energy density (calorific value) of the bio-oil. Zeolites which have acidity (Lewis and Brønsted acid sites) and unique pore structure are the predominant catalysts employed in bio-oil upgrading via catalytic pyrolysis. Zeolite-type catalysts transform different hydrocarbons and oxyhydrocarbon feeds into aromatic products akin to gasoline components. By producing bio-oil with high heating capacity and low oxygen content, the zeolite ZSM-5 predominantly used in pyrolysis showed perfect efficacy in deoxygenation reactions of aromatic compounds [5]. Among numerous various catalysts, matchless shape selective and solid acid characterization of ZSM-5 zeolites lead to unique selectivity to gasoline type hydrocarbons [6,7]. Many studies have reported influence of zeolites on the biomass pyrolysis products to advance to high grade fuels and petrochemicals. Galadima and Muraza reviewed that zeolites had textural, topological and acidic properties to upgrade the yield of bioaromatics/gasoline as an industrial and sustainable option in fast pyrolysis of biomass [8]. Likewise, Rezaei et al. studied the catalyst actions of multiple acidic zeolite catalysts in terms of the selective production of olefins and aromatics in connection with the conditions of pyrolysis [9]. Kantarli et al. reported 54.2 wt% bio crude yield at 500 ºC fluidized bed semi-pilot scale pyrolysis with 100 g poultry meal added ZSM-5 [10]. Bio-oil yield increased while coke and light gases decreased in fluidized pyrolysis of hybrid poplar wood bed using ZSM-5. As the ZSM−5, H_2, CH_4 levels increased, the level of CO_2 decreased and the levels of C_4–C_5 hydrocarbons elevated. ZSM−5 catalysts improved the bio-oil properties [11]. Wang et al. used ZSM-5 as a catalyst at catalytic pyrolysis of douglas fir pellets in microwave quartz flask reactor at 400–600 ºC. The catalyst and the pyrolysis conditions transformed the bio-oil so that it contains 50–82% compounds of aromatic hydrocarbons, guaiacols, and phenols [12]. Naqvi et al. investigated catalytic pyrolysis of paddy husk biomass in a drop-type fixed-bed pyrolyser at 450 °C and varying catalyst loading ratio from 0.5 to 2. Having SiO_2/Al_2O_3ratio and surface area 23 and 425 m^2/g, respectively, the commercial type of MFI zeolite ZSM-5 was used as the catalyst. The degree of oxygen removal was utilized to assess the oxygen content conveyed from the biomass to the bio-oil. The maximum de-oxygenation rate (84.6%) and catalytic pyrolysis oil gain (%) were obtained with the ratio 0.5. The bio-oil achieved with this ratio included less carbonyl and acidic contents, but high phenol and phenolic compounds [13]. There is an increasing interest in synthetic zeolites which are generally utilized for developing the catalysts, namely ZSM-5 [2]. However, the use of cheap and being the most abundant natural zeolite (clinoptilolite) as tar cracking catalysts is an attractive option. Pütün et al. [14] checked the catalytic pyrolysis of olive oil production residues employing clinoptilolite and ZSM-5. They came to the conclusion that for deoxygenating the bio-oil, the synthetic zeolite was more efficient than the clinoptilolite, but, utilizing the clinoptilolite as catalyst lead to less coke. Messina et al. investigated use of natural clinoptilolite and two modified clinoptilolites obtained from natural clinoptilolite in-situ catalytic pyrolysis of peanut shells. Improved and deoxygenated bio-oil with higher heating value had properties that could be used instead of conventional fuels.

The feedstocks of lignocellulose biomass are are remarkably assorted, low-cost and abounding non-food biomass. Every year, 150-170×10^9t of non-food lignocellulosic biomass is produced on a global scale, including municipal waste, agroindustrial wastes and leftovers as well as a large proportion agricultural and forestry wastes. Enormous amount of the empty fruit bunches (EFB) are thrown away due to ineffective usage of the accessible biomass[1]. Numerous kinds of by products including stones, seeds, solid residue of peel, pulp and stem are a large unused potential in the juice processing wastes. There are lots of fruits containing considerable amounts of stones to obtain value-added compounds like biofuels. One of these fruits is plum (Prunus cerasus L.). Food and Agriculture Organization reports that in the year 2022, a total of 12255073 tones of plum were manufactured globally on 2637316 hectares. In Turkey, plum is cultivated in an area of approximately 21521ha. It grows 332533 tons annually [15]. Plum wastes generated after juice production correspond to approximately 15% of the total production. Pyrolysis of several fruit wastes such as cherry stones [16], banana empty fruit bunch and delonix regia fruit pod. [17], date seed and mandarin peel [18], fruit pulps [19–21] has been studied so far to produce bio-oil or carbonaceous solids. However, no detailed data has been collected in the topic of plum seed pyrolysis and catalytic pyrolysis.

In the light of above explanations, the present investigation aims to report laboratory-scale results of fruit juice industry solid waste (plum seed) on both catalytic and non-catalytic pyrolysis. The novelty of the study lies behind the difference in the selected raw material and as well as the product distribution and characteristics of the pyrolytic oil. In the non-catalytic section, seeds pyrolysis was conducted without catalyst and the effects of essential pyrolysis parameters including pyrolysis temperature, calorific rate on product distributions were inquired. In the catalytic section, the effects of natural zeolite (NZ), ZSM-5, Purmol CTX catalysts on product distributions as well as bio-oil compositions were detected and then, a comparison was made between non-catalytic and catalytic pyrolysis.

2. Experiment

2.1. Catalyst

The commercial catalysts ZSM-5 and PURMOL CTX to be employed in the experiments were procured from Damla Chemistry. The clinoptilolite samples abundant in the west Turkey were gathered from the Balikesir-Bigadiç area. Türkiye has rich resources of low-cost natural zeolite (45 billion tons). Clinoptilolite mineral has adsorption and ion exchange properties as well as catalytic properties [22]. The elemental composition of the zeolite was detected by an X-ray fluorescence (XRF), utilizing a Panalytical kit, model epsilon 3. XRD patterns of catalysts were recorded using a Panalytical axios X-raydiffractometer.

2.2. Material

Plum seed (PS) currently known as agro-industrial waste were obtained from a Turkish juice factory. Being dried in open air in a dark room naturally up to three months; the seed samples were milled and sifted to have the particle size between Dp<0,224 mm and Dp>1.8 mm. Pyrolysis of biomass was carried out at mean particle size measured as 1.22 mm. Component and proximate analyses were performed on plum seed samples. The mean bulk density of this raw material was identified as 590 kgm^{-3} (ASTM-E 873-82).

2.3. Pyrolysis Experiments

The pyrolysis experiments were conducted under nitrogen atmospheres employing laboratory scale reactor. The detailed explanation for both the pyrolysis experiments and the reactor can be accessed [23]. The experiments aimed to identify the catalyst impact on the pyrolysis yields. For all the experiments, the catalyst/biomass ratio of 10% were applied at the optimum conditions. For each run, the physically homogenized raw material with catalyst in ratio of 10 % by weight was put into the reactor. Then, the reactor was heated at a rate of 100ºC min^{-1} to the final temperature of 550ºC under 100 cm^3 min^{-1} N_2 flow as sweeping gas.

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2.4. Analysis Methods

The calorific values are critical thermal characteristics for the designing and evaluating the systems of thermal conversion systems. The gross calorific values of bio-oils and biomass sample were calculated by the Dulong formula (Equation (1)):

$$QGCV\ (MJ\ kg^{-1}) = 33.83C + 144.3(H - O/8) \tag{1}$$

where C, H, O represents the mass fractions of carbon, hydrogen and oxygen, respectively [24]. The final analysis was conducted utilizing an elemental analyzer (Carlo Erba, EA 1108). Thermal behavior of the plum seed was examined by Setaram Labsys Evo thermogravimetric analyzer (TGA) in environments of nitrogen and air. The sample which was close to 20 mg, was heated to 1000 °C with a heating rate of 10 °C min^{-1} under nitrogen and air atmospheres (100 cm^3 min^{-1}). Fourier Transform Infrared Spectroscopy (FT-IR) analysis of plum seed was conducted with a Perkin Elmer Spectrum 100 to detect structural groups in the range of 4000-400 cm^{-1}wavelength by the ATR technique. ^{1}H-NMR spectra were obtained with a Bruker Ultrashields 500 Plus NMR. An Agilent HP 6890/5973 GC/Mswas used for gas chromatography-mass spectrometry (GC/MS) analyses. The technique of liquid column chromatographic was used to determine the chemical class compositions of the bio-oils. Further expanations for these techniques can be found elsewhere [25].

3. Results and Discussion

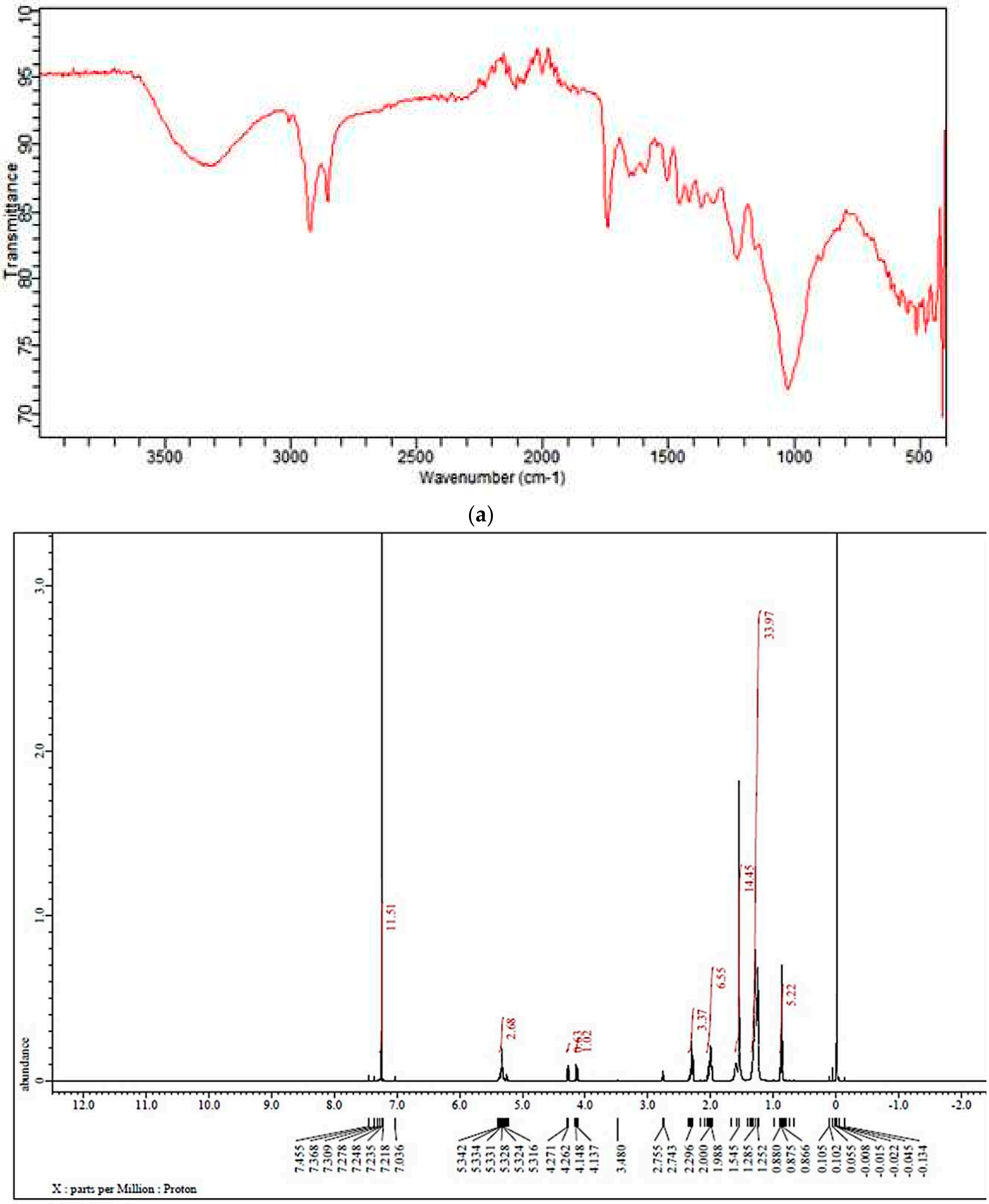
3.1. Characterization of the Biomass Sample and Catalysts

Table 1 shows the proximal and final analysis outcomes, which are atomic H/C and O/C ratios, calorific value and content of the biomass sample. PS contains volatile matter (VM) of 83.84% and little amount of ash (inorganic content) of 0.91, thus making this more advantegous for thermal processes since a high yield of bio-oils and biogas are obtained [26]. Raw material has low moisture contents (5–9%), average carbon (48.53%) and no sulfur content with a H/C ratio of 1.45. Biomass chemical composition has significant effects on pyrolytic properties. In this way, in this study, the chemical structure of the plum seed is revealed by FT-IR, 1H-NMR, as well as the final and proximal analysis. Figure 1a shows the plum seed spectrum. The overlapping bands between 3600 and 3100 cm^{-1} attributed to OH stretching vibrations in hydroxyl groups (mainly due to the moisture contents in the raw material), acidic or phenolic groups can be seen in the spectrum. Asymmetric and symmetric C–H bands which submit the presence of alkyl groups for aliphatic and olefinic structure are seen with two strong bands at 2924 and 2857cm^{-1} respectively. The stretching vibration band between 1770 and 1650 cm^{-1} is related to carbonyl groups. The C=C vibrations in aromatic structure are detected between 1650 and 1600cm^{-1} that demonstrates the lignin presence. The bands between 1060 and 1100 cm^{-1} are because of the C–O vibrations in olefinic and aromatic structures such as saturated ethers which denote the presence of hemicellulose, cellulose, and lignin [27]. The ^{1}H-NMR spectra of plum seed is submitted in Figure 1b. It is clear in Figure 1 that biomass sample contains 80% aliphatic and 20% aromatic compounds.

Table 1. Properties of plum seed.

	wt. %		**wt. %**
Moisture^c	8.87	C^a	43.50
Ash^b	0.91	H^a	5.24
Volatile matter^b	83.84	N^a	0.73
Fixed carbon^b	6.38	O^a	50.53
Hemicellulose^c	44.58	H/C	1.45
Lignin^b	31.97	O/C	0.87
Oil^c	7.17		
Excractives^b	18.30	HHV(MJ/kg)	13.16

^{a} Dry-ash-free basis. ^{b} Dry basis^c As received. HHV:Higher Heating Value.

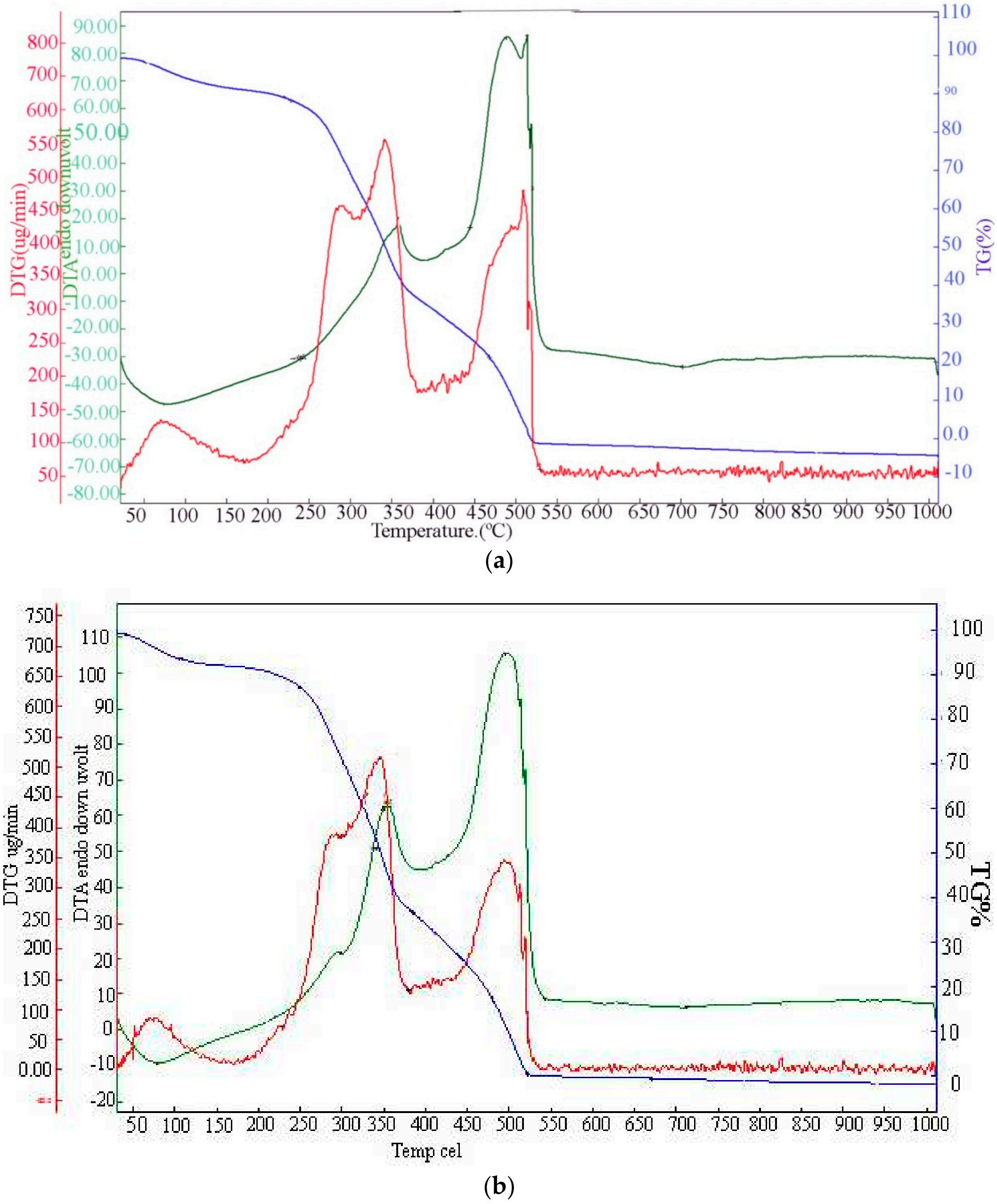


(**a**)

(**b**)

Figure 1. Plum seed of FT-IR spectrum(a) and ^{1}H-NMRspectrum (b).

DTG, TGA, and DTA analyses of plum seed are submitted in Figure 2a,b and Table 2. Lignocellulosic biomass predominantly consists of natural biopolymers like cellulose, hemicelluloses, as well as lignin. There is general agreement that the major pyrolytic degradation of the lignocellulosic structure is related to the decomposition of hemicellulose (220-315 ºC); cellulose (315-400ºC) and lignin degradation (150-450ºC) [28]. Pyrolysis reactions can be defined by DTG peaks at the lower temperature up to 200 ºC after the release of moisture at approximately 90– 105 ºC with a weight loss of 7.89% in the sample. The maximum loss of weight was detected at 228–400ºC temperature ranges. Hemicellulose begins to degrade at 228ºC and ends at 353 ºC, whereas the cellulose decomposition range is between the temperatures of 355–393ºC. Therefore, the losses of weight mentioned here may be associated with the decomposition of these two. Degradation of lignin takes between the temperatures of 230-540ºC, but, lignin continues to degrade up to higher temperatures [29]. Since hemicellulose is a heterogeneous polysaccharide composed of different hexoses and pentoses with a lower polymerization degree, its decomposition temperature is lower than that of cellulose; thus, the intermolecular bond strength is lower than that in cellulose. Being a homogeneous polysaccharide consisting of only D-glucopyranose, has a uniform crystal structure. Hemicellulose and cellulose increase the formation of or volatile compounds, and lignin increases the formation of char [30,31]. Devolatilization begins at about 200 ºC and removing the volatiles is completed at approximately 530 ºC. The maximum heat losses and the pyrolytic reactions took place below 550 °C, the most active temperature range. After 540 ºC, no weight loss was seen. Therefore the optimum pyrolysis temperature convenient to maximize bio-oil was 550 ºC. CS lost 95.199 and 97.994% of its beginning value up to the final temperature of 900 °C in nitrogen and air environments respectively.



(a)

(b)

Figure 2. TG, DTG and DTA thermograms of plum seed under nitrogen (a) and air atmosphere (b).

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Table 2. Results of the thermal analysis at at nitrogen and air atmospheres.

Plum seed	Max degradation temperature T_1 (˚C)	Max degradation rate (%/min)	Max degradation temperature T_2 (˚C)	Max degradation rate (%/min)	Total mass loss (%)
N_2	340	-7.04	508	-4.71	95.199
Air	345	-10.29	495	-7.15	97.994

Analysis of XRD is an efficacious technology in detecting the crystalline structures of the zeolites. The structure of the catalysts examined with XRD patterns is given in Figure 3. The featural peaks regarding the orthorhombic, hexagonal, monocilinic, cubic aluminosilicates structure of the zeolites were observed in the XRD patterns, in line with the literature. A significant diffraction peak was near 2θ=10-20º and 21–35°, akin to the zeolite crystalline [32]. Table 3 shows the results from the XRF analysis of the catalysts are given in Table 3. The Si/Al (w/w) ratio was of 5.30, 116.57 and 1.06 in the clinoptilolite, ZSM-5 and Purmol -CTX (as revealed by XRF) respectively. The application of zeolites in biomass advancement is related to the acidic properties of the zeolite as well as its structure and textural properties. The lower silica to alumina ratio was beneficial for cracking, in addition to converting bio-oil oxygenates into aromatics with the help of successive actions such as dehydration, cracking, decarbonylation, decarboxylation, oligomerization, alkylation, cyclization and aromatization as well as surface acidity and enhanced thermal stability. Lowering the Si/Al ratio increases the acidity of catalyst which at the same time alters the surface area and the particle size of zeolites [26]. Clinoptilolite and PURMOL CTX were attributed to a higher proportion of K and Na, respectively.

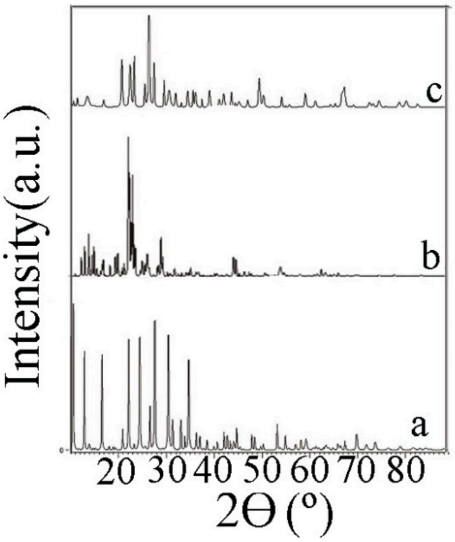


Figure 3. X-ray diffractions of NZ (a), ZSM-5 (b), Purmol CTX (c).

Table 3. Results of XRF analysis of catalysts.

Component	NZ(%)	ZSM-5(%)	Purmol CTX-1(%)
Si	35.82	88.59	20.86
Al	6.76	0.76	19.68
K	3.76	-	0.06
Ca	2.76	0.04	0.29
Fe	0.95	1.01	0.03
Na	0.09	1.27	13.07

3.2. Pyrolysis Yields

Pyrolysis temperature is the most important parameter impacting the chemical compositions of the char, liquid, and gas products as well as the yields. Bhoi et al. [3] summarized that majority biomasses had an active pyrolytic temperature between 400–600 ºC obtained by thermogravimetric analysis due to their alike compositions in terms of lignin, cellulose, and hemicellulose. In this study, firstly, pyrolysis experiments were conducted at temperature values of 400, 450, 500, 550 and the rate of a sweeping gas flow was 100 cm^3 min^{-1} under a steady heating rate of 100 °C min^{-1}. The sweeping gas deports the volatiles from the pyrolysis environment in course of the reaction. Due to the pyrolysis reactions the nitrogen flow affects the residence duration of the produced gas; thus, minimazing the secondary reactions including char formation, recondensation, and repolymerization [33]. The temperature-dependent relationships of plum seed yields are given in Figure 4. As shown in the figure, while the pyrolysis temperature increases, the gas yields also increase, however, the solid yields (char) decrease. For the most part, a temperature increase assisted the gasification of the formed tar; so, less liquid was acquired at elevated temperatures (550 °C). It can be assumed that at elevated temperatures, secondary reactions of the liquid fraction of volatiles and more decomposition of the char particles achieved in the reactor [29]. Accordingly, the highest yield of char processed at 400 °C was 29%, and the lowest yield of gas processed at the equal temperature was 16.3%. The bio-oil water content declined from 29% to 19%, as the temperature was shifted from 400 to 600 °C. At a pyrolysis temperature of 550 °C, the yield of liquid attained the highest which was 29.43%. Prior studies stated that the optimum temperature of pyrolysis to maximize the oil yield was between 500 and 600 °C [7,19,34–38]. Further temperature increases reaching to 600°C only boosted the products of gas. The highest yield of gas yield procured at 600◦C pyrolysis temperature was 29.06%. As the temperature increases, the rate of reaction also increases and the long-chained compounds are divided into smaller pieces resulting in an increase in the yield of gas. Similarly, Naqvi et al. found that at values higher than 450 - 600 °C, the yield of gas was enhanced due to the secondary oil cracking and the biochar decomposition.

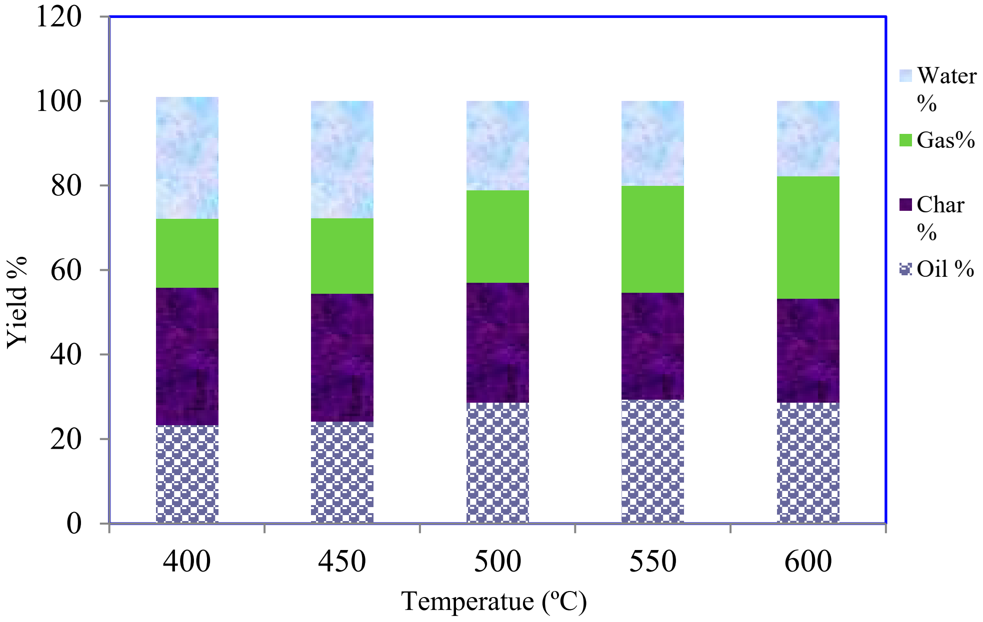


Figure 4. Yields of pyrolysis products at different pyrolysis temperatures.

During the second part, experiments of pyrolysis were performed at heating rates of 10, 50 and 100 °C min^{-1}; the rate of the sweeping gas flow was steady at 100 cm^3 min^{-1} and the temperature of pyrolysis was 550 °C. Gained results are submitted in Figure 5. As the heating rate increased, the yields of liquid also increased whereas the yields of char declined. According to the results, the yield of char was 28.70% at 10 °C min^{-1} but at 100 °C min^{-1} it declined to 25.24%. The pyrolysis reactions and their related order as well as the composition of products and overall yield are affected by the rate of the heating. Due to the low energy input per unit of time, slow heating rates result in no cracking of biomass contributing to higher coke and biochar formation [39]. When compared, a higher rate of heating lowers the exposure duration of biomass; thus, limiting the primary and secondary cracking reactions to interfere with one another. Higher heating enables diminshing secondary reactions and promotes decomposing of the products formed earlier. Therefore, the yield of bio-oil enhances with higher rates of heating compared to less rates of heating. In studies made by Ateş et al. [25,40] pyrolysis of wheat straw carried ot at 500°C in a fixed-bed reactor. They determined that the yield of bio-oil was as 19.1% in 7°C/min heating rate, it reached up to 31.9% in 300°C/min heating rate.

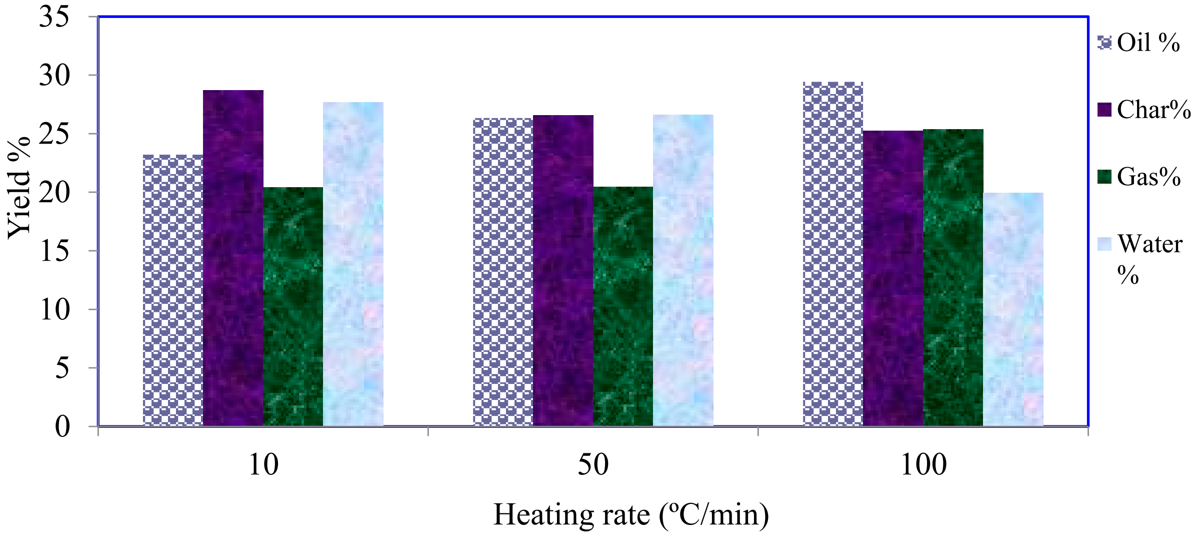


Figure 5. Yields of pyrolysis products at different heating rates.

In order to procure the peak yields of oil, catalytic pyrolysis experiments were conducted in the optimum conditions in which the rate of heating was 100 °C min^{-1}, the temperature of pyrolysis was 550 °C and the rate of sweeping gas flow was 100 cm^3 min^{-1} in the presence of synthetic zeolites ZSM-5, Purmol CTX and NZ. As can be seen from the results given in Figure 6, the highest gas yield procured was 20.21% with NZ, whereas the highest liquid obtained was 33.20% with ZSM-5 which is an acidic catalyst, and acknowledged for generating nearly 40% of the bio-oil yield [41]. Akhtar and Saidina Amin [42] studied the impact of severity on zeolite catalysed biomass pyrolysis on the highest yield of the targeted bio-oil. Lappas et al. [43] assessed the zeolite acid catalyst application in biomass pyrolysis for transportation fuel production. Putun et al. [7] carried out the catalytic pyrolysis of cotton seed cake with natural zeolite (clinoptilolite) selected as the catalyst at pyrolysis temperature of 550ºC with the sweeping gas flow rate of 100 mLmin^{-1}. The highest yiled of liquid was 30.84% with catalyst the amount of 20wt.% of raw material. The liquid products obtained as a result of pyrolysis processes posses a high amount of oxygen which leads to an acidic, corrosive and unstable result with a comparatively low energy density when highly present in the bio-oil. Despite the fact that they are utilized in numerous applications for generating heat and power, they induce an efficiency decrease if employed in motors and turbines. These oils may be enhanced by catalytic cracking for lowering the content of oxygen with the aim of using them directly as conventional transport fuel. Soongprasit et al.[44] studied fast pyrolysis of millettia (Pongamia) pinnata waste at 400–600 ºC under sweeping gas(He) flow rate of 5 mL/ min with 30% zeolite (USY) catalyst loading in a micro-batch pyrolyzer PY- 2020iD. Non catalytic bio-oil included 34.1–66.5% of oxygenated compounds. The catalytic pyrolysis enhanced the yield of hydrocarbon to 99%, at which the conversion of the oxygenated compounds into aromatic and aliphatic hydrocarbon using decarboxylation and dehydration took place. Table 4 shows the elemental compositions of the non-catalytic and catalytic bio-oils. There were higher carbon content, less oxygen content and higher energy density in the catalytic bio-oil compared to non-catalytic bio-oil. The pyrolysis oil oxygen content was 25.03% and declined to 21.33%, 16.54%, and 17.30%, with NZ, ZSM-5, and Purmol CTX, respectively by catalytic treatment. As indicated, the zeolites action for removing the oxygen from the pyrolysis oil is obvious. Removing more oxygen causes the calorific value of the fuel to increase.

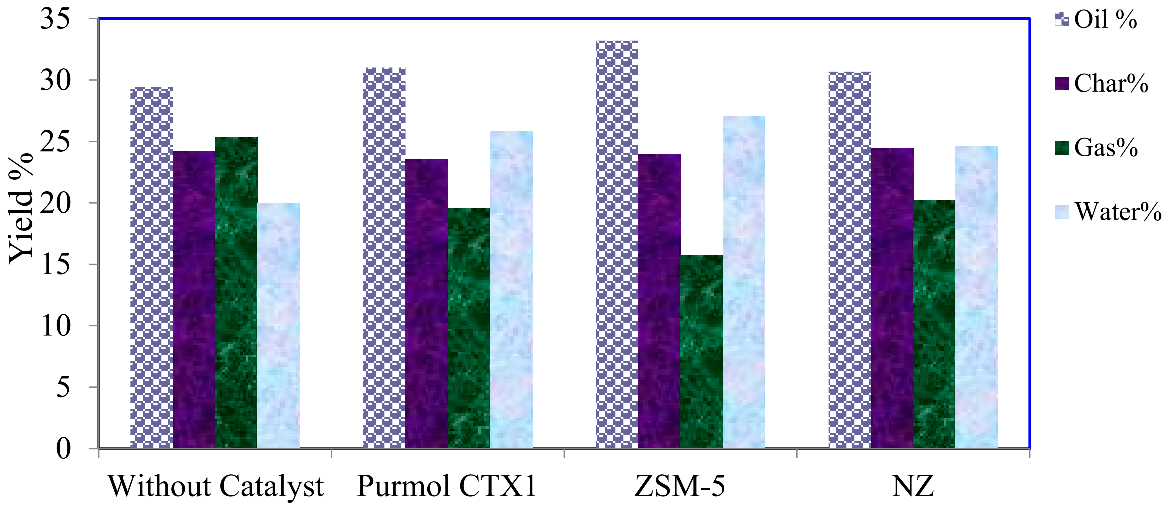


Figure 6. The variation of the product yields with different catalysts.

In terms of environment, a higher H/C ratio which is 1.58 for heavy fuel oil, 1.8 for diesel fuel, and 2 for gasoline enables lower greenhouse gas emissions along with enhanced fuel qualifications. Obviously, catalytic enhancement raises the H/C ratio of bio-oil. The H/C ratio of pyrolysis oil found to be 1.52 was raised using catalytic enhancement and the subsequent the ratios were 1.69, 1.75, and 1.77 with NZ, ZSM-5, and Purmol CTX, respectively. Comparison of H/C ratios with conventional fuels showed that the H/C ratios of the oils procured within the scope of this study are between light and heavy petroleum products. The catalysts advanced the bio-oils calorific value to 24.97-41.75 MJ/kg corresponding to other conventional fuels like LPG (45.75 MJ/kg), petroleum (43 MJ/kg), and kerosene (41 MJ/kg) [24]. When Zhang et al. [169] employed ZSM-5 for ex-situ mode catalytic pyrolysis of corncobs with a fluidized bed reactor, the obtained bio-oil demonstrated a decrease for oxygenated compounds by 25% with a high calorific value of 34.6 MJ/kg, and that was akin to the values of heavy fuel oil and diesel [45].

Table 4. Elemental composition and calorific values of bio-oils.

Component	**Without catalyst (%)**	**ZSM-5 (%)**	**natural Zeolite (%)**	**Purmol CTX-1 (%)**
C (wt.%)	59.32	74.75	79.76	74.78
H (wt.%)	7.52	10.89	11.29	11.02
N (wt.%)	0.18	0.32	0.21	0.84
O (wt.%)	32.98	14.04	8.45	13.36
H/C	1.52	1.75	1.69	1.77
O/C	0.42	0.14	0.079	0.13
Empirical formula	$CH_{1.3}N_{0.0026}O_{0.42}$	$CH_{1.65}N_{0..0037}O_{0.14}$	$CH_{1.42}N_{0.0023}O_{0.079}$	$CH_{1.32}N_{0..096}O_{0.13}$
Higher heating value (MJ/kg)	24.97	38.47	41.75	38.79

Table 5 shows the results obtained from adsorption chromatography. Pyrolysis oil of plum seeds contained 54% asphaltenes and 46% n-pentane solubles. The oil fraction was 19% for aliphatic, 36% for aromatic and 45% for polar. The fraction of maltenes (n-pentane solubles) was raised to nearly 71% applying catalytic pyrolysis. The reason for this increase can be explained by the cracking degree in the course of catalytic pyrolysis. The percentage of the maximum aromatics procured with ZSM-5 was 45.45%, and the percentage of the maximum aliphatics procured with NZ was 24.28% both of which may be due to the properties of zeolites. The increase in aromatics (e.g., toluene and benzene) and aliphatics (e.g. alkanes and iso-paraffins) are considered favorable for using products as value-added chemicals and fuels. Also, using catalyst leads to a decrease in polar fractions (generally oxygenated groups). The polar fraction includes primarily carboxylic acids, phenols, aldehydes, furans, and ketones. Thus, the polar fraction of non-catalytic pyrolysis oil declined from 57.34% to 363.34% subsequent to the catalytic application with ZSM-5.

Table 5. The results of the column chromatograph bio-oils**.**

Bio-oil	Pentane Non-solubles (%)	Pentane Solubles (%)	Aliphatics (%)	Aromatics(%)	Polars(%)
Without catalyst	76.45	23.55	15.19	27.77	57.04
Natural zeolite	56.12	43.88	24.28	34.42	41.30
Purmol CTX-1	59.27	40.73	18.00	33.06	48.94
ZSM-5	55.69	44.31	21.21	45.45	33.34

^{1}H NMR is reported to be a requisite and precise technique in order to identify hydrogen distributions in bio-oil. [46,47]. If the hydrogen atoms (major isotope ^{1}H) are abundant in an organic compound, this feature makes it better suited for a ^{1}H NMR spectroscopy analysis to detect bio-oil constituents. Thus, this technique offers a faster analysis with more precise results [48]. Table 6 shows a summary of the hydrogen percentages of bio-oils procured from both catalytic and non-catalytic pyrolysis of plum seed. The ^{1}H NMR spectra were splitted in three interest regions related to the chemical shifts of specific proton types. The 0.5-3.0 ppm chemical shift region is where the aliphatic resonances appear, 4.5-6.0ppm region is where the olefinics resonances appear and 6.0-9.0 ppm region is where the aromatic resonances appear. High hydrogen content in aliphatic CH_3–CH_2– and CH– group is typical for all studied oils. The non-catalytic pyrolysis oil aliphatic content (68%) rose to 72.60% with ZSM-5. These results are coherent with the column chromatography findings. The aromatic hydrogen intensity occurring mostly between the 6.4–7.5 ppm suggests that the aromatic species are mostly phenolic. Together with phenols, IR spectroscopy pointed out that ketones/aldehydes and carboxylic acids are also significant organics containing oxygen found in the polar fractions. ^{1}H-NMR spectra of the bio-oils demonstrate that the aroma of the natural zeolite bio-oil of catalytic pyrolysis is greater than the non catalytic and other catalytic pyrolysis oils. Bio-oil procured with NZ catalytic pyrolysis gave the highest aromatic hydrocarbons percentage of 35.23 %. Bio-oils procured with natural zeolite catalytic pyrolysis contain more paraffin and aromatics in comparison to that of uncatalyzed and other catalysts products. Several authors have investigated bio-oil structure with NMR spectroscopy [46–49].Tessarolo et al. utilized ^{1}H NMR for examining bio-oils made from sugarcane bagasse and pine wood. At various temperatures, the bio-oils were produced through non-catalyzed and ZSM-5-catalyzed pyrolysis. All bio-oil samples' ^{1}H NMR chemical shift integration ranges are shown. In comparison to non-catalytic sugarcane bagasse bio-oil, the bio-oil from sugarcane bagasse pyrolyzed with ZSM-5 had a higher hydrogen content from aromatic and conjugated alkenes and a lower hydrogen content from oxygen-containing groups. The identical ZSM-5 catalyst effect was seen on pine wood bio-oils [49].

Table 6. ^{1}H-NMR Results of the bio-oils.

Hydrogen type		**Hydrogen in Bio-oil (Percentage of Total)**			
	Chemical shift (ppm)	**Without catalyst**	ZSM-5	Purmol CTX-1	NZ
CH_3 γ or furter from aromatic ring and paraffinic CH_3	1.0-0.5	20.10	16.40	11.90	15.97
CH_3; CH_2 and CH β to araomatic ring	1.5-1.0	18.55	20.10	19.76	19.63
CH_2 and CH attached to naphthenes	2.0-1.5	10.15	11.80	10.20	5.33
CH_3; CH_2 and CH α to araomatic or aceytlenic	3.0-2.0	19.20	24.30	25.83	12.99
Total aliphatics	3.0-0.5	68	72.60	67.69	53.67
Hydrokyl. ring-joining methylene. methine or methoxy	4.0-3.0	7.80	6.60	5.53	6.34
Phenols. non-conjugated olefins	6.0-4.0	10.90	6.30	9.92	4.76
Aromatics. conjugated olefins	9.0-6.0	13.20	14.50	16.86	35.23

Abnisa et al. utilized FTIR for deciding the chemical structure of purge natural product brunches, mesocarp fiber buildups, and palm shells [50]. The FTIR spectra appear the comparable useful bunches in both the EFB and mesocarp strands as evident within the shapes and the power of their spectra. The infrared spectrum of palm oil shell demonstrates weaker IR absorbance in comparison with those of mesocarp fiber and EFB, which reflects the nearness of lower volatile substance compared to the mesocarp strands. Figure 7 shows the FT-IR spectra of the oil. The presence of alcohols and phenols is indicated by the O–H stretching vibrations between 3200-3400 cm^{-1}; the presence of alkenes is indicated by the C–H stretching vibrations between 2800-3000 cm^{-1} and C–H deformation vibrations between 1350-1475 cm^{-1}. The presence of aldehydes or ketones is indicated by the C=O stretching vibrations between 1650 and 1750 cm^{-1}. The presence of aldehydes or ketones are indicated by the C=O stretching vibrations between 1650 and 1750 cm^{-1}. As an indicative of aromatics and alkenes, the C=C stretching vibrations are represented by the absorbance peaks between 1575-1675 cm^{-1}. It is seen from the spectra that the functional groups of the oils in compliance with those of the oils and chromatographic functions procured from cotton-seed cake.

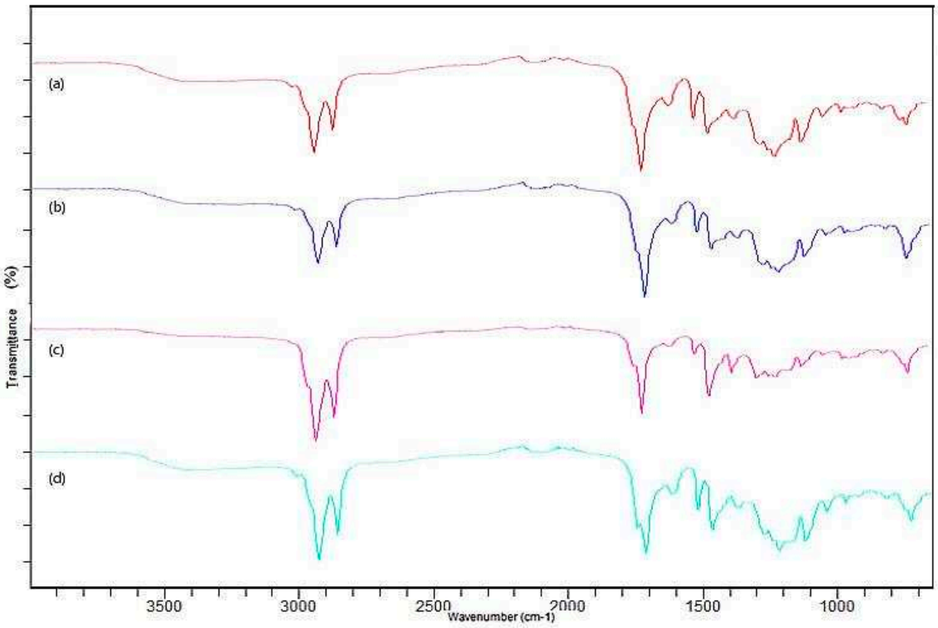
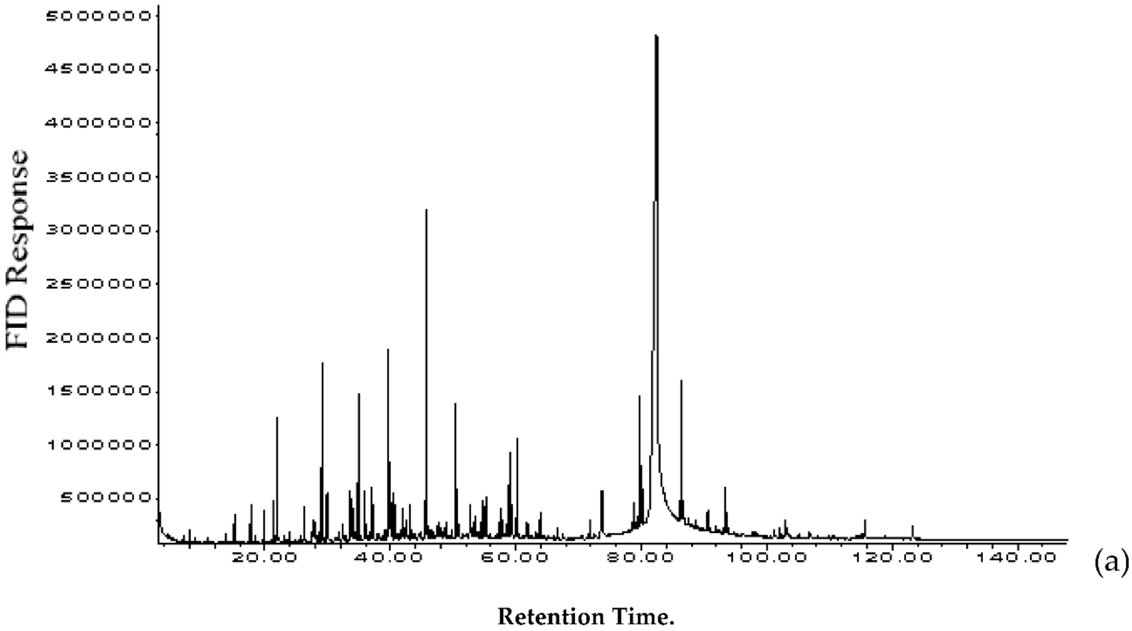


Figure 7. FTIR spectra of bio-oils with ZSM-5 (a) NZ (b) Purmol CTX-1 (c) without catalyst (d).

Gas chromatography/mass spectrometry (GC/MS) is considered a fast, advantageous and an effective tool to define bio-oil samples which are heterogeneous and complex [51]. The bio-oil chemical composition was examined with GC/MS tool for the purpose of throughly understanding the way catalysts affected the biomass pyrolysis chemistry. Figure 8 shows the bio-oil gas chromatograms achieved with and without catalyst. In addition to being utilized as fuel in boilers and diesel engines, pyrolysis bio-oils are also evaluated as a beneficial source for organic chemicals. The rates of different compounds such as hydrocarbons (aliphatic + aromatic), carbonyls, acid, phenolics and alcohols found in the non-catalytic and catalytic plum seed bio-oils can be seen in Figure 9. According to the above-mentioned findings, Figure 9 should be studied more carefully in terms of aliphatics percentage which is evident to be greater with catalysts. It can be concluded that utilizing the catalyst leads to a advantegous result since aliphatics are critical compounds regarding the alikeness with fuels [52]. Being invaluable industrial products (such as resins, solvents, medicine raw materials, and pesticides) due to the high commercial value they have [40], phenols are the second most crucial compound found in plum seed bio-oil as can be seen in Figure 9. Phenols, alkyl phenols, and methoxy phenols are the primary phenolic compounds detected in bio-oils as oligomers and monomeric units extracted from lignin. The total percentage of phenolics compounds was 27.17% at non-catalitic bio-oils and increased to 29.28%, 30% and 35% with ZSM-5, Purmol, NZ catalysts respectively. Pattiya et al. examined cassava rhizome pyrolysis with 4 catalysts and concluded that the most efficient catalyst was ZSM-5 since it caused a noteworthy rise in phenols and aromatics [53]. Using commercial catalysts in-bed and ex-bed mode, Samolada et al. found out that phenols hightened in both modes in comparison with non-catalytic application [54]. It is acknowledged that biomass liquids exhibit an acidic structure. However, the presence of acids in pyrolysis oils is undesirable because of their corrosive effects. In this study, carboxylic acids were reduced in bio-oils utilizing catalysts. The total percentages of the carboxylic acids observed in the oils were 4.6%, 3.1%, 1.22% and 0.95% in non-catalytic experiments and using ZSM-5, PURMOL, NZ catalysts, respectively. Low percentage acidic compounds observed in bio-oils of catalytic pyrolysis of plum seed can be evaluated as a superiority regarding the final quality of the fuel. Since the carbonyls undergo condensation reaction resulting in the formation of higher molecular weight components and enhanced viscosity, their presence leads to the issue of instability. Yet, the amount of carbonyls in the bio-oil is decreased by the catalyst. Subsequent to the deoxygenation and cracking of the oil which occurs in the catalyst pores, the processes of cyclization, isomerization, and aromatization takes place. Based on the results of GC/MS, comparing the products procured from the pyrolysis regarding the oxygenated compounds, it is found that the compunds are reduced using a catalyst. In their study which focused on advancing fast pyrolysis bio-oils with various catalysts in a fixed-bed micro-reactor, Adjaye and Bakshi [55,56] observed that H–Y, silicaalumina, and silicate provided more aliphatic hydrocarbons than aromatic hydrocarbons whereas HZSM-5 and H-mordenite provided more aromatic hydrocarbons than aliphatic hydrocarbons.

Table 7 shows a detailed component analysis of the aliphatic sub-fractions of pentane soluble bio-oil employing GC/MS, which includes the compound name, the peak area, and the retention time without catalyst and with a catalyst conditions. Primarily, three groups were formed to divide the bio-oil carbon number which were respectively C_5-$C_1$1 (gasoline fraction), C_{12}-C_{18} (kerosene-diesel fraction), and C20-C38 (heavy oil fraction). For non-catalyst pyrolysis processes, these fractions were distributed as follows: 3.64wt% (C_5-C_{11}), 57.94 wt% (C_{12}-C_{18}) and 38.41 wt% (C_{20}-C_{38}). For catalytic pyrolysis, the carbon number distribution was of C_5-C_{11}, C_{12}-C_{18}, and C_{20}-C_{38}; in ZSM-5 pyrolysis bio-oil was 13.08, 66.32 and 20.59 wt% ; in NZ pyrolysis bio-oil was 12.57, 69.09 and 18.33 wt%, and in PURMOL CTX pyrolysis bio-oil was 18.58, 68.80 and 12.60 wt%, respectively. These results show that after the catalytic application, the long chains of alkanes and alkenes of the pyrolysis oil were transformed into hydrocarbons which were lower in weight. Branched hydrocarbons of 3.29% obtained without catalyst raised 8.11%, 10.60%, and 11.97% using ZSM-5 Purmol CTX and NZ catalysts, relatively.


FID Response
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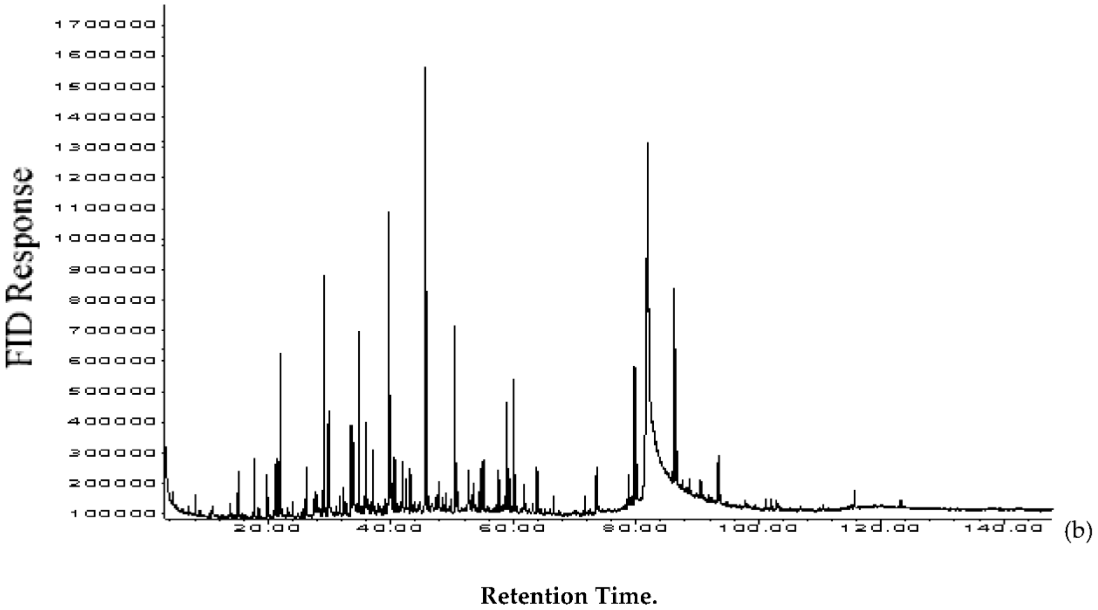
100.00
120.00
140.00
(a)
Retention Time.


FID Response
1700000
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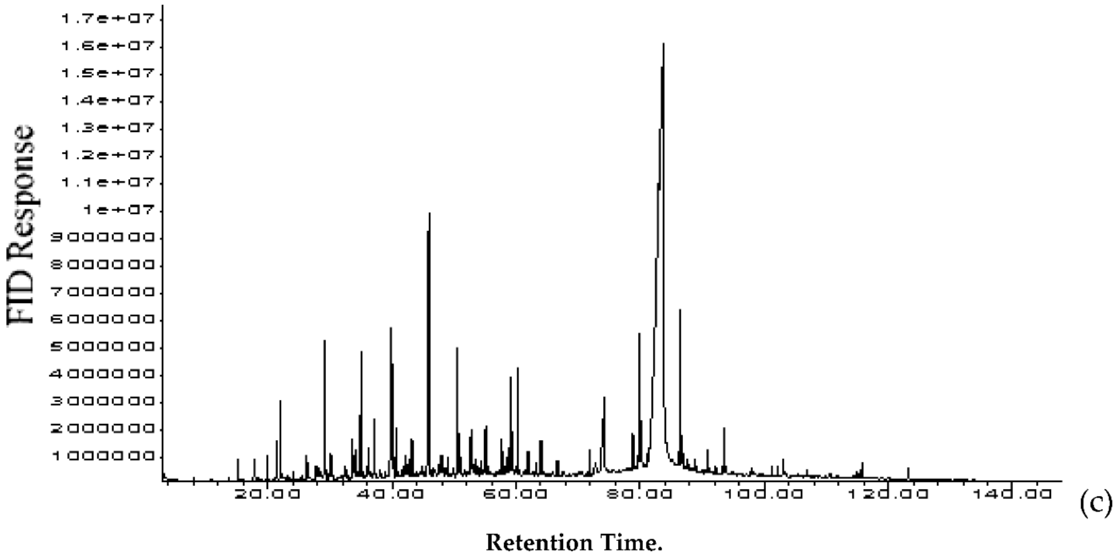
40.00
60.00
80.00
100.00
120.00
140.00
(b)
Retention Time.


FID Response
1.7e+07
1.6e+07
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
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8000000
7000000
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5000000
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20.00
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(c)
Retention Time.

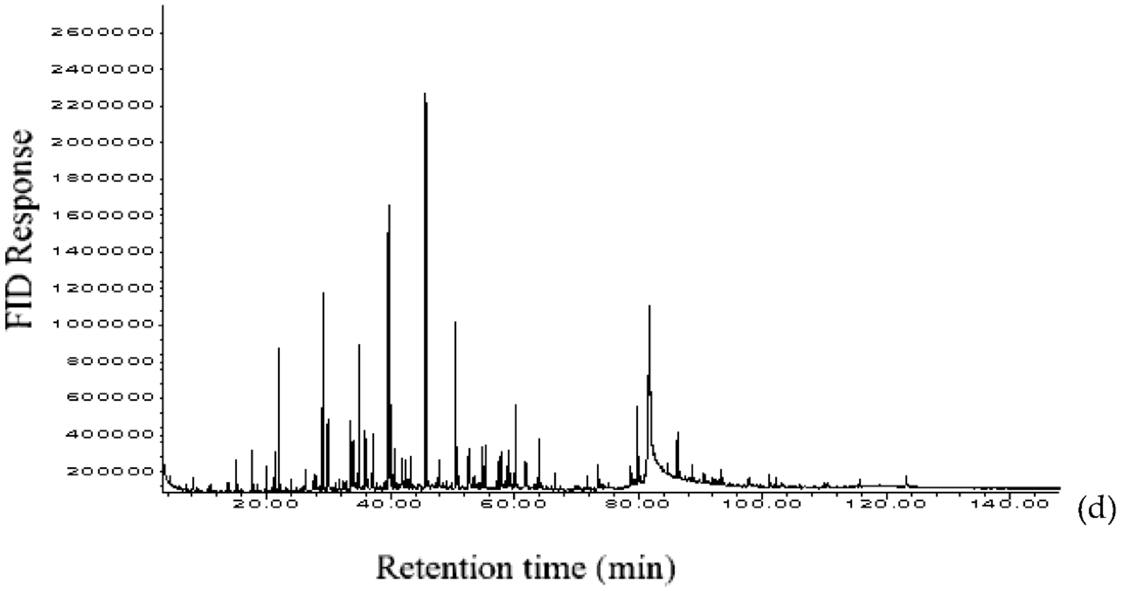

Figure 8. Gas chromatogram of the of plum seed bio-oils (a) without catalyst, (b) with NZ catalyst, with ZSM-5 catalyst, with Purmol CTX-1 catalyst.

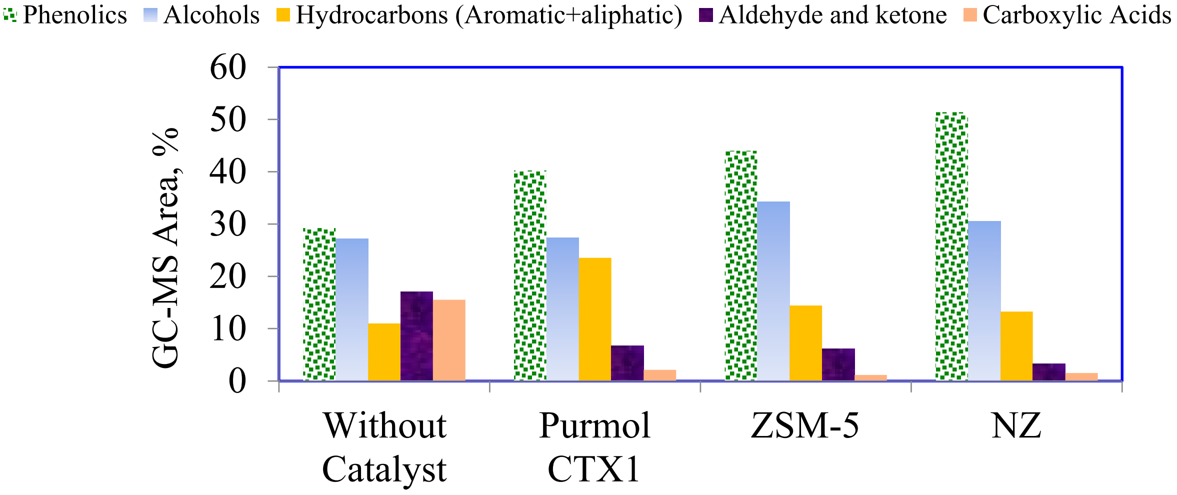

Figure 9. The main compounds in bio-oils detected by GC/MS, relative area %.

Table 7. Relative proportions (area%) of the main pyrolysis compounds in n-pentane sub-fractions.

Compound	Area %			
	Without catalyst	NZ	Purmol CTX-1	ZSM-5
1-Tetradecene		0.97	-	0.24
Tetradecane	-	0.10	-	0.08
1,13-Tetradecadiene	1.20	-		0.16
trans-7-pentadecene	-	-	-	0.30
1-Pentadecene	-	0.71	1.10	0.36
Dodecane	-	1.49	2.41	1.04
n-Nonylcyclohexane		0.79	1.08	0.64
Bicycloheptane, 7-pentyl	-	-	-	0.40
Cyclododecene	-	5.34	5.19	1.52
3-Hexadecene	-	1.11	1.40	0.69

8-Hexadecene	-	-	-	1.04
Hexadecane	-	1.41	1.43	1.45
methylcyclododecane	-	1.02	-	0.72
Cycloundecene, 1-methy	-	-	-	0.30
Cyclohexane, 2-propenyl-	-	-	0.74	0.38
Cyclohexane,	-	0.30	-	1.03
6,8-Heptadecadiene	-			1.25
8-Heptadecene	0.96	6.89	10.69	3.01
Heptadecane	1.91	2.25	2.21	0.99
1-Heptadecene	-	-	-	0.39
6,9-Heptadecadiene	-	-	1.03	2.46
1,6-Tridecadiene	-	-	-	0.71
1-8-10-Tridecatriene	-	-	-	0.21
1,9-Tetradecadiene	0.60	0.84	1.10	0.69
3-Octadecene	-	-	1.10	0.48
9-Octadecene	-	-		0.66
1-Octadecene	-	0.56	0.51	0.39
Octadecane	0.76	-	0.41	0.24
1-Hexadecyne		-		0.39
Cyclotetradecane		-	0.58	0.70
1-Nonadecene	3.03	0.96	1.33	0.92
Nonadecane	0.85	1.3	0.48	0.29
1-Hexadecene	-	0.25	2.04	0.34
Eicosane	2.23	0.89	0.71	0.32
1-Docosene		0.41	0.45	0.67
Docosane	0.42	0.64	0.76	1.28
11-Tricosene	-			0.76
Tricosane		0.17	0.05	0.65
17-Pentatriacontene			0.08	0.27
Tetracosane	2.28	1.04	1.56	0.48
Pentacosane	1.26	1.04	0.59	0.59
13-Methyl -14-nonacosene	-	-	-	0.20
Spiro[4.5]decane	-	-	-	0.93
Heneicosane	0.60	0.63	0.95	0.48
Octacosane			0.30	0.31
Nonacosane	2.04	1.42		0.57
Heptacosane	1.06		0.60	0.16
Heptane, 2,4-dimethyl-		0.05		-
Propylidencyclohexane		0.52	0.59	-
cis,cis-1,6-Dimethylspiro[4.5]decane		0.31	-	-
Heptadec-8-ene	5.50	4.55	-	-
Cyclopropane, 1-methyl-2-pentyl	0.92	1.27	-	-
9-Octadecyne	-	1.46	-	-
3-Methyl- 4,6-hexadecadiene	-	0.35	-	-
2,6,6,10-Tetramethyl-undecane	-	0.86	-	-
9-Tricosene	-	0.48	0.24	-
Hexacosane	-	0.86	-	-
n-Pentacos-3-ene	-	0.65	-	-
3,11-dımethyl-nonacosane	-	0.15	-	-
Octane	-	-	0.05	-

Cyclohexene, 1-methyl	-	-	0.03	-
Hexane, 3-ethyl-4-methyl-	-	-	0.06	-
2-Tetradecene	-	-	0.60	-
Cyclopentane, nonyl-	-	-	0.52	-
7-Methyl-1,6-octadiene	-	-	0.25	-
5-Undecyne	-	-	0.18	-
Bicyclo[4.1.0]heptane, 7-butyl	-	-	0.14	-
1-hexene	-	-	0.70	-
3-Heptadecene,	-	-	1.04	-
1-Heptene, 2-isohexyl-6-methyl	-	-	1.16	-
bıcyclo[3.1.1]heptane, 2,6,6-trımethyl	-	-	1.16	-
Cyclohexadecane	-	-	0.58	-
1-Hexacosene	-	-	0.06	-
Tricosane	-	-	0.05	-
Heneicosane, 3-methyl-	-	-	0.07	-
Cyclopentane, 1,2-dibutyl	0.29	-	-	-
1-Pentadecyne	0.45	-	-	-
9-Tricosene, (Z)	0.73	-	-	-
10-Heneicosene	0.44	-	-	-
Cyclotetracosane	0.80	-	-	-
11-Hexacosyne	0.22	-	-	-
13-Hexacosyne	2.17	-	-	-

4. Conclusions

The experiments were done for catalytic with zeolite and non-catalytic pyrolysis on a fixed tubular reactor which involved plum seeds due to their cost being low and their availability being high as a biomass waste. The catalysts utilized in this study has led to liquid production upgrading both in quality and quantity so that the production of fine chemicals, including aromatics or light hydrocarbons (gasoline or diesel C range) can be realised. In comparison to non-catalytic experiments, higher amounts of aliphatics were achieved in catalytic experiments. In addition, according to non-catalytic experiments, an increase in valuable compounds such as phenol, alkanes+alkenes, aromatic and cyclic compounds and a decrease in oxygenated compounds were observed. Zeolite materials have provided a favourable effect on reducing the percentage of oxygen which is undesirable in the fuel due to lowering its thermal value. The catalytic upgrading produced a high level of de-oxygenation (74.38 %) when compared to non-catalytic pyrolysis and this considerably de-oxygenated oil produced had a increased calorific value with a beneficial combustibleness. Utilizing the catalysts, the acidic and carbonyl components causing the bio-oil to be more acidic and unstable were decreased. The low percentage carboxylic acids detected in plum seed liquid products may be seen as a noteworthy gain while evaluating. It is the exponential growth of gasoline and diesel usage in the field of transport raises concerns about ecological emissions. However, it is the development of sustainable, low-cost and eco-friendly biobased fuels which will overcome these concerns since it is widely acknowledged that building large-scale plants processing tons or even thousands of tons of feedstock per day is a workable solution. With the decrease in fossil fuel reserves, their costs will inevitably rise. Therefore, the gainfulness of catalytic pyrolysis for the liquid fuel substitute production will be quite significant in the future as well as reaching to higher product specificity in industrial uses to enhance petroleum-like products produced from renewable sources such as biomass, waste, and plastic.The results of this study emphasize the usefulnes of catalytic pyrolysis in terms of upgrading the bio-oil production from plum seeds. Also, further studies exploring the usage for new catalysts and zeolite enhancements optimizing the process of catalytic pyrolysis in order to amplify the energy output of the products are suggested considering these results.

Taking the efficiency and properties of bio-oils into consideration, it is clear that plum seed is an encouraging feedstock in the production of bio-oils and characterizes a hopeful potential for biofuel utilizations that will be used more widely in the near future.

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