

Catalytic fast pyrolysis of Pearl Millet and *Sida cordifolia* L. to investigate products distribution and bio-oil quality

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Abstract

Fast pyrolysis is an attractive way of converting abundant biomass resources into valuable products such as bio-oil. Nevertheless, high oxygenated compounds and water content of bio-oil limit its direct use as fuel or chemicals. Catalytic fast pyrolysis (CFP) is able to improve bio-oil properties so that downstream upgrading processes can be economically feasible. In this study five different catalysts such as zeolite socony mobil-5 (ZSM-5), cerium dioxide (CeO_2), zirconium dioxide (ZrO_2), zinc oxide (ZnO), and sodium carbonate (Na_2CO_3) were employed due to their potential in enhancing bio-oil properties. CFP of pearl millet (PM) and *Sida cordifolia* (Sida) was performed to investigate the effects of catalysts on the products distribution and chemical contents of bio-oil. The results showed that bio-oil yield decreased during CFP regardless of catalyst and biomass types. Among all catalysts, CeO_2 was found to be the most suitable to produce acids and alkanes from CFP of PM; and acids, ketones, and aromatics from CFP of Sida. The high production of ketones from PM and alkanes from Sida was observed with Na_2CO_3 catalyst. The ZrO_2 catalyst indicated the high aromatics production from PM, whereas alcohols, amines, and others were abundant in bio-oil from CFP of PM using ZSM-5. Overall, PM and Sida can be used to produce fuel or value-added chemicals through CFP.

1. Introduction

The increase in the worldwide population combined with the strong industrialization result in an increase in the world energy demand which is largely supplied by fossil fuels. The depletion of fossil fuels and their adverse environmental impacts require the exploration of new energy resources [1]. Recently, there has been a great focus on biomass because of its importance as a renewable source that can be converted to fuel and value-added chemicals. Biomass has gradually served as a supplement or an alternative for fossil fuels [2]. Lignocellulosic biomass is one of the alternatives and most abundant renewable energy sources, which is estimated to contribute 10–14% to the world's total energy supply [3–5]. It is a promising feedstock for the production of renewable liquid fuels and valuable chemicals due to its abundance and special chemical composition [6–7]. Pyrolysis is an attractive way of converting biomass into valuable products. The pyrolysis process has been widely used to produce fuels and chemicals such as charcoal, activated carbon, methanol and high hydrocarbon fuels and gasoline, diesel and jet fuels [8]. Fast pyrolysis is a thermochemical technology for direct conversion of lignocellulosic biomass into mainly bio-oil for fuels and chemicals [9].

Pyrolysis oil or bio-oil is a black or dark brown-coloured viscous liquid including more than 300 oxygenated compounds, which are responsible for low heating value of bio-oil ($16.79\text{--}19 \text{ MJ kg}^{-1}$) as compared to fossil fuels ($40\text{--}45 \text{ MJ kg}^{-1}$) [10–11]. Bio-oil contains chemical compounds such as acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers [12]. The foremost technical challenge of fast pyrolysis comes from the lack of commercial application of bio-oil with high viscosity, moisture, oxygen content, acidity (pH 2–3), and hence corrosivity [9, 12]. Moreover, due to the presence of reactive compounds in bio-oil, it has low stability as compared to fossil fuels. Therefore, it is necessary to

improve the quality of bio-oil so that it can compete with the existing hydrocarbon fuels and can be used as a transportation fuel [13–14].

The application of a catalyst in fast pyrolysis, also called catalytic fast pyrolysis (CFP), can produce upgraded bio-oil with a lower oxygen content and acidity/corrosivity, and higher heating values, etc. [9]. CFP using a wide range of catalysts has been studied to produce high-quality bio-oil. The operating conditions of pyrolysis process especially reaction temperature and catalyst type and amount have a major impact on the products distribution and quality. The use of metal-supported or metal-oxide catalysts reduces water and oxygen contents and corrosiveness of bio-oil by limiting the yield of carboxylic acids and oxygenated compounds and increasing hydrocarbon yields. The use of zeolites catalyst with varying pore size and Si/Al ratio favour the selectivity of aromatic hydrocarbons [15]. Zeolites with different pore sizes and active sites, mostly acidic, enhance the deoxygenation reactions of oxygenates and increase the aromatic yield. ZSM-5 is the most efficient catalyst among all zeolites [16].

Several fast pyrolysis studies have been conducted by using different biomasses and catalysts to investigate the effects of different operating conditions on the products distribution and bio-oil quality [7, 17–24]. The feasibility, byproducts, and comprehensive characterization of pearl millet (PM) and napier grass hybrid [25] and the physicochemical, nutritive, and spectral properties of biochar prepared from India's four important agricultural residues including PM [26] have been studied. Biodiesel was produced from seeds of *Sida cordifolia* (Sida) by transesterification method [27] and thermal characterization of fibers from the stems of Sida by using TGA under nitrogen atmosphere was made [28]. In addition, pyrolysis and combustion kinetics of Sida by using thermogravimetric analysis (TGA) were studied [29]. The CFP of eucalyptus woodchips with ZSM-5 [21], water hyacinth with Ce-doped γ -Al₂O₃/ZrO₂ [23], cotton stalk with ZnO and ZrO₂ [30], and bamboo sawdust and waste plastics with CeO₂/ γ -Al₂O₃ and HZSM-5 [7] were studied. Even though the same catalysts have been used in different fast pyrolysis studies with different operating conditions by using different biomasses, to the best of our knowledge, there is no study conducted to investigate the effects of these catalysts on the distribution of products and quality of bio-oil obtained from PM and Sida in especially optimized process conditions.

Therefore, the objective of this study was to investigate the effects of five different catalysts such as zeolite socony mobil-5 (ZSM-5), cerium dioxide (CeO₂), zirconium dioxide (ZrO₂), zinc oxide (ZnO), and Sodium carbonate (Na₂CO₃) on the products distribution and bio-oil quality during the CFP of PM and Sida under the optimized process conditions. Bio-oil samples were characterized by ultimate analysis and gas chromatography-mass spectrometry (GC-MS). GC-MS of bio-oil samples from catalytic and non-catalytic fast pyrolysis (NCFP) was performed in order to determine their chemicals contents. Chemicals such as acids, ketones, alkanes, aromatics, and others (alcohols, amines/amides, and aldehydes) contained in bio-oil samples were quantitatively examined.

2. Materials And Methods

2.1. Materials

2.1.1. Biomass

PM and Sida used as biomasses in this study were collected from field and pasture area respectively, in Niger. PM is known as one of the most growth cereal in the world and produces high amount of waste usually left in the field after harvest and still underutilized [31]. *Sida cordifolia* (Malvacea) is one of the 200 species of genus Sida, distributed throughout the world as weeds in marginal lands [29]. The freshly cut biomasses were left for air drying before being packaged and sent to the laboratory. To obtain particles used during the analyses and experiments, biomasses were milled by using the biomass mill located in the laboratory at Environmental Engineering Department of Akdeniz University, and sieved by using several sieves to get the desired biomass particle size. Biomass particles of 180–212 μm were used in proximate and components analyses, while particles of 1500–1700 μm considered as 1.5 mm were used during fast pyrolysis experiments. Biomass particles < 100 μm were used in ultimate analysis.

2.1.2. Catalyst

The catalysts used in this study was supplied by Nanography Company and some of their characteristics are given in Table 1. These catalysts were applied to determine their effects on the products distribution and bio-oil quality of fast pyrolysis of PM and Sida. Catalysts ZnO, CeO₂, ZrO₂, and Na₂CO₃ received in the powder form were pressed in hydraulic press at the Mechanical Engineering Laboratory of Akdeniz University to get about 20 g of pellets and then these pellets and granular form ZSM-5 were crushed by a hand-tool to obtain the desired particles size (1–2 mm).

Table 1
Catalyst properties.

Catalyst	Purity (%)	Particle size (nm)
Cerium oxide (CeO ₂)	99.98	8–28
Sodium carbonate (Na ₂ CO ₃)	99.50	-
Zinc oxide (ZnO)	99.99	18
Zirconium oxide (ZrO ₂)	99.95	30
Zeolite (ZSM-5)*	-	-

*Specific area: 250 m² g⁻¹, SiO₂/Al₂O₃ molar ratio: 38–525 g.

2.2. Methods

2.2.1. Biomass Characterization

Proximate analysis which aimed to determine the moisture, ash, volatile matter, and fixed carbon contents of biomass was performed by using the ASTM standards at the Environmental Engineering

Laboratory of Akdeniz University. Carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) contents were determined by using the Elemental Analyzer (CHNS-932 LECO) at the Scientific and Technological Research Laboratory of İnönü University, while oxygen (O) content was calculated by difference. Components analysis was also performed to determine cellulose, hemicellulose, lignin, and extractives contents of biomass. The results of these analyses are given in Table 2.

Table 2
Biomass characterization.

Biomass characterization	Pearl millet	<i>Sida cordifolia</i>
<i>Proximate analysis (%mass)</i>		
Moisture	3.61 ± 0.06	6.22 ± 0.04
Ash	34.51 ± 5.12	10.31 ± 1.15
Volatile matters	61.29 ± 2.46	65.15 ± 0.59
Fixed carbon	0.59 ± 5.16	18.32 ± 1.62
<i>Ultimate analysis/mass %</i>		
Carbon	43.66	41.38
Hydrogen	6.30	6.44
Oxygen ^a	49.54	50.89
Nitrogen	0.45	1.15
Sulphur	0.06	0.14
Heating value (MJ/kg)	17.53	16.38
<i>Components analysis</i>		
Extractives	4.26 ± 0.80	6.25 ± 0.12
Cellulose	48.93 ± 1.35	49.17 ± 1.92
Hemicellulose ^a	3.16 ± 0.80	21.91 ± 2.05
Lignin	15.75 ± 0.40	12.04 ± 0.40
^a calculated by difference.		

2.2.2. Pyrolysis Experiments

Drop-tube-reactor pyrolysis system was used in this study to performed fast pyrolysis experiments (Fig. 1). The system consists of a quartz glass reactor with a length of 110 cm and a diameter of 2.5 cm, and two furnaces fitted with a control system. Temperature of 400 °C, particle size of 1.5 mm, and nitrogen gas flowrate of 200 mL min⁻¹ determined previously as optimum pyrolysis process parameters

to produce the maximum bio-oil yield from fast pyrolysis of PM and Sida [32] were used in this study. During non-catalytic pyrolysis experiments about 10 to 15 cm glass wool was placed into the reactor in order to retain biomass. The reactor was weighed (reactor before reaction (RBR)) before being hooked to the system. Then 15 g of biomass sample was poured into the feeding system equipped with a valve and the carrier gas opened to take out oxygen contained in biomass. Then, nitrogen gas heated to 150 °C was introduced to the system in order to facilitate the evacuation of vapour to the condenser containing a mixture of liquid nitrogen and acetone (~ -25 °C). Thus, condensable gases were recovered in the condenser which had been previously weighed (condenser before reaction (CBR)); and non-condensable gases were removed from the system through a pipe attached to the condenser. The feeding valve was opened in the last position and then closed again as soon as the biomass sample passes into the system to prevent steam rising due to heat. After 5 minutes duration of each reaction the condenser containing bio-oil was weighed (condenser after reaction (CAR)) and then placed in hot water to facilitate its melting. Bio-oil recovered in a sealed tube was placed in refrigerator to avoid reactions. At the end of reaction, the reactor was weighed (reactor after reaction (RAR)) to determine biochar yield. As in non-catalytic pyrolysis, during catalytic pyrolysis glass wool was placed in the reactor before and after catalyst to retain catalyst and biomass, respectively. In each experimental run 5 g of catalyst was used with catalyst:biomass ratio of 1:3. The yields of products such as biochar, bio-oil, and gases were calculated as follows:

$$\text{Biochar (\%)} = \frac{\text{RBR}-\text{RAR}}{15} \times 100 \quad (1)$$

$$\text{Bio - oil (\%)} = \frac{\text{CAR}-\text{CBR}}{15} \times 100 \quad (2)$$

$$\text{Gases (\%)} = 100 - (\text{biochar} + \text{bio - oil}) \quad (3)$$

2.2.3. Bio-oil Characterization

Bio-oil samples obtained from non-catalytic and CFP experiments were analysed in order to highlight the effects of catalysts on bio-oil properties. Thus, ultimate analysis of bio-oil samples was performed by using the Elemental Analyzer (CHNS-932 LECO) at the Scientific and Technological Research Laboratory of İnönü University to determine their C, H, N, S, and O contents. Higher heating value (HHV) was calculated from the results of ultimate analysis. GC-MS analysis was performed by using Perkin Elmer Clarus 600/680 analyzer at the Scientific and Technological Research Laboratory of İnönü University to determine chemical compounds in bio-oil samples. GC-MS instrument was set at 40 °C for 1.0 min with total experimental time of 30 min. Temperature increased up to 300 °C at a heating rate of 10 °C min⁻¹. Elite 5 MS column (0.250 µm diameter and 30 m length) was used to identify bio-oil constituents. Bio-oil was diluted with dichloromethane (DCM HPLC grade), and 1.0 µL of this diluted sample was then injected into the column. Helium was used as the carrier gas at a flowrate of 0.6 mL min⁻¹. MS spectra were collected at different retention times and further analysed using the NIST MS library as reference.

3. Results And Discussion

3.1. Fast Pyrolysis Experiments

Non-catalytic and CFP experiments were performed under the temperature of 400 °C, biomass particle size of 1.5 mm, and nitrogen gas flowrate of 200 mL min⁻¹ for both biomasses. The maximum bio-oil yield of 48.60% (Fig. 2) from PM was reached during NCFP. This result agreed with the literature where the bio-oil yield decreased when catalyst was used during fast pyrolysis [33, 34]. For example, the bio-oil yield from NCFP of PM (48.60%) was higher than that of CFP using ZSM-5 (41.93%). Paysepar et al. [9] have already reported that the application of ZSM-5 as catalyst during fast pyrolysis decreased the bio-oil yield. The highest bio-oil yield during CFP was found when CeO₂ was applied. Unlike bio-oil, the biochar yield increased with the use of catalysts. Indeed, the biochar yield rised from 25.93% during NCFP to 31.73% when Na₂CO₃ was applied for PM. As expected the lowest biochar yield was obtained during CFP with CeO₂. The gas yield showed different trends compared to the bio-oil and biochar yields which decreased or increased respectively with the catalysts. The gas yield increased after the applications of ZrO₂ and ZSM-5, and decreased with CeO₂, ZnO, and Na₂CO₃.

The NCFP and CFP experimental results of Sida are illustrated in Fig. 3. As for PM the maximum bio-oil yield of 47.93% was reached during NCFP of Sida. Similar results were reported by Saracoglu et al. [35] and Ateş, et al. [36], where the bio-oil yield decreased when catalyst was used. Additionally, the bio-oil yield from NCFP of Sida (47.93%) was higher than that of CFP using Na₂CO₃ (43.27%) as the lowest bio-oil yield compared to the other catalysts. The bio-oil yield obtained by using ZSM-5 was found to be 45.60%. Similar results were reported by Maisano et al. [37] during CFP of the Mediterranean Sea plant by using ZSM-5. Contrary to the bio-oil, the biochar yield increased with the use of catalysts. Catalysts can be ordered in terms of the biochar yield in the ascending order as ZSM, CeO₂, ZnO, Na₂CO₃, and ZrO₂. Unlike in PM, catalyst with the lowest bio-oil yield did not have the highest biochar yield. The gas yield indicated different trends compared to the bio-oil and biochar yields. The gas yield increased with the use of CeO₂, Na₂CO₃, and ZSM-5 and decreased for the ZrO₂ and ZnO compared to the NCFP gas yield.

3.2. Bio-oil Characterization

3.2.1. Elemental Analysis

The results of ultimate analysis of different bio-oil samples obtained from fast pyrolysis of PM and Sida with and without catalysts are tabulated in Table 3. The non-catalytic bio-oil from PM contained 42.34% of C which was lower than that reported by Mohan et al. (2006) [38] for typical pyrolysis oil as 54–58%. Moreover, O content (49.94%) of this bio-oil sample was higher than the typical O content of bio-oil which varied between 35 and 40%. However, H content (7.21%) of the sample agreed with the literature [39]. In general, it can be seen that O content of bio-oil samples increased during CFP except for Na₂CO₃, while H content decreased. In O content point of view, the results of this study were opposite to the literature [38],

where the application of catalyst led to decrease in O content of bio-oil. This difference can be due to the fact that in our study bio-oil samples were analyzed directly without any fractionation. The C content increased or decreased depending on catalysts type, where it increased when Na_2CO_3 was applied. The N and S contents of bio-oil samples highly depend on the raw biomass content. The HHV of bio-oil samples were calculated by using the ultimate analysis results. Since the HHV is highly influenced by O content, sample with high O content showed low HHV. The bio-oil sample obtained with ZnO had the highest O (62.71%) and lowest C and H contents, thus showed the lowest HHV of 12.01 MJ kg^{-1} among the six samples. When ZSM-5 was applied the corresponding bio-oil sample with O content of 51.32% and the highest H content (8.26%) had the highest HHV compared to the other samples. The HHV of non-catalytic bio-oil sample (18.11 MJ kg^{-1}) was higher than that obtained by using ZnO, CeO_2 , and ZrO_2 , and lower than that obtained with Na_2CO_3 and ZSM-5.

Table 3
Elemental analysis of bio-oil produced from non-catalytic and catalytic fast pyrolysis.

Biomass	Bio-oil Sample	%					HHV (MJ kg^{-1})
		C	H	O	N	S	
Pearl Millet	Non-catalytic	42.34	7.21	49.94	0.47	0.04	18.11
	CeO_2	35.80	7.03	56.78	0.35	0.04	14.91
	ZnO	30.25	6.73	62.71	0.27	0.04	12.01
	ZrO_2	41.57	7.06	50.87	0.44	0.07	17.57
	Na_2CO_3	43.36	7.03	49.03	0.49	0.09	18.35
	ZSM-5	39.96	8.26	51.32	0.34	0.13	18.38
<i>Sida cordifolia</i>	Non-catalytic	37.70	7.39	53.47	1.29	0.15	16.34
	CeO_2	27.79	7.78	63.41	0.97	0.05	12.29
	ZnO	32.90	7.77	58.10	1.16	0.06	14.60
	ZrO_2	32.47	7.59	58.82	1.07	0.06	14.18
	Na_2CO_3	21.84	7.71	69.09	1.27	0.09	9.54
	ZSM-S	26.08	7.83	65.16	0.86	0.08	11.55

Ultimate analysis of bio-oil samples obtained from CFP and NCFP of *Sida* presented different trends compared to PM, probably due to the initial composition of each biomass. The C content of bio-oil sample from *Sida* was lower than that of PM, while H content showed the opposite except for ZSM-5. Also, O content was higher in bio-oil sample from *Sida* which led to the low HHV observed for these samples. During fast pyrolysis of *Sida*, C and S contents of bio-oil samples decreased when catalysts

were applied, whereas O and H contents increased. Bio-oil sample obtained by using Na_2CO_3 had the lowest C but highest O content, and thus the lowest HHV. According to HHV, samples can be ordered as $\text{Na}_2\text{CO}_3 < \text{ZSM-5} < \text{CeO}_2 < \text{ZrO}_2 < \text{ZnO} < \text{no catalyst}$. As for PM, N contents of all bio-oil samples from Sida were almost zero while S content was around 1%. For both biomasses CFP with ZSM-5 produced bio-oil with the highest H content.

3.2.2. GC-MS Analysis of Bio-oil

GC-MS analysis was performed in order to determine different chemical compounds contained in bio-oil samples. Bio-oil from fast pyrolysis of biomass is known as a very complex liquid containing up to 400 chemical compounds [9]. Bio-oil samples obtained from fast pyrolysis of PM and Sida also contained a multitude of compounds which can be grouped as acids, ketones, hydrocarbon, aromatics (phenol, benzene), and others (amine, alcohol, aldehyde ether, ester). The proportions of these chemical groups in bio-oil varied with the initial biomass structural composition and pyrolysis operating parameters. It is well known that feedstock with high lignin content produces bio-oil with high aromatic contents [40]. The use of catalysts having the aim of enhancing the quality of bio-oil, the proportions of chemical groups in bio-oil are also affected by the presence or absence of catalyst. Five different catalysts used in this study influenced bio-oil composition. Due to the large number of chemical compounds in bio-oil, only chemicals with the peak areas $\geq 1\%$ were examined in this study. Acids, ketones, alkanes, aromatics (phenol, toluene, benzene), and others (alcohols, amines, aldehydes) contents of bio-oil samples were examined to determine the best catalyst for the production of each compound from fast pyrolysis of PM and Sida, and the results are presented in Figs. 4 and 5.

Effects of catalysts on acids production

Acids contents of bio-oil samples were examined in order to determine the most suitable catalyst for acids production from fast pyrolysis of PM and Sida. Due to its high corrosivity, acids are mainly considered as undesired products in bio-oil [35]. Acetic, propanoic, and butanoic acids were found as the main carboxylic acids in bio-oil samples. Acetic acid resulted from the removal of acetyl groups contained in xylose unit [41]. Rasrendra et al. [42] produced acetic acid through alcohol carbonylation. Carboxylic acids contents of bio-oil samples from fast pyrolysis of PM increased with catalyst application except for Na_2CO_3 . When ZnO, ZSM-5, and ZrO_2 were used, acids contents initially 9.47% in non-catalytic bio-oil sample rised to 13.60, 14.05, and 14.45%, respectively. The highest acids contents were reached with CeO_2 , while the lowest was observed with Na_2CO_3 . Among carboxylic acids, acetic acid was the most represented in all bio-oil samples. For example, by using ZSM-5, the proportion of acetic, propanoic, and butanoic acids were 6.59, 5.11, and 2.35%, respectively. Bio-oil with the lowest acid content (Na_2CO_3) and the highest acid content (CeO_2) did not contain butanoic acid. In bio-oil from CeO_2 , pentanoic acid (2.26%) and octadecenoic acid (3.50%) were also detected. In general, CeO_2 was found to be the most suitable catalyst for carboxylic acid production from fast pyrolysis of PM. However, for specific production of acetic acid non-catalytic bio-oil sample with 7.04% was the best.

Acids contents of bio-oil samples from fast pyrolysis of Sida showed variable trends compared to PM. In fact, acids contents decreased with the application of catalyst except for CeO_2 which produced the highest acids contents. From the point of view of acids contents, bio-oil samples from Sida can be ordered as $\text{Na}_2\text{CO}_3 < \text{ZrO}_2 < \text{ZnO} < \text{ZSM-5} < \text{no catalyst} < \text{CeO}_2$. Bio-oil samples from Sida contained more carboxylic acids types than that from PM. Indeed, it contained acetic, octadecenoic, n-hexadecanoic, propanoic, butanoic, benzoic, and valeric acid which proportions changed with catalysts. For example, acetic acid from the application of Na_2CO_3 decreased from 7.73% in non-catalytic bio-oil to 2.20% and then increased to 8.13% by using ZSM-5. This change can be due to the nature of catalyst and its chemical composition [16, 43]. The highest acid content of 16.28 and 15.39% in bio-oil samples from PM and Sida respectively were observed with CeO_2 application. Thus, it can be said that CeO_2 was the best catalyst to produce carboxylic acids from fast pyrolysis of PM and Sida.

Effects of catalysts on ketones production

A ketone is a compound containing a carbonyl functional group bridging two groups of atoms [44]. Ketones can be obtained by careful oxidation of a secondary alcohol using a strong oxidant. In industry, ketones are mainly synthesized by oxidation of hydrocarbons by oxygen in the air. This is how cyclohexanone, a precursor to nylon, is made from cyclohexane. Acetone or propanone is the simplest component of ketones. Thus, ketones are very important in the plastics production industries [45].

Ketones contents of bio-oil samples from NCFP of PM was found as 17.38%. After the application of CeO_2 it was still substantially equal (17.35%) and then decreased with ZrO_2 application (16.44%). The ketones contents of 22.71, 25.07, and 28.46% were reached with ZSM-5, ZnO and Na_2CO_3 , respectively. Among ketones compounds, butanone and pentanone were the most represented in all bio-oil samples. For bio-oil samples from Sida, ketones contents decreased from 29.30% in non-catalytic bio-oil to 19.61, 23.67, 24.51, and 28.34% during CFP with Na_2CO_3 , ZrO_2 , ZnO, and ZSM-5, respectively but increased with CeO_2 (31.33%). It can be seen that like acids, ketones also showed varying trends from PM to Sida. For a high production of ketones, Sida seemed to be the most promising than PM, even without catalyst bio-oil sample from Sida contained more ketones than that from PM.

Effects of catalysts on hydrocarbons production

Hydrocarbons are highly desirable for fuels and valuable chemicals productions from fast pyrolysis oil [46]. Bio-oil from fast pyrolysis of biomass contained mainly carboxylic acids and oxygenated compounds which limit its direct use as fuel [16]. In this study, alkanes contents of bio-oil samples from fast pyrolysis of PM and Sida were examined. Alkanes contents of bio-oil samples from fast pyrolysis of PM increased during CFP. The highest alkanes content of 12.92% was reached with CeO_2 , while the lowest was observed with ZnO (4.54%). Zeolite is known as the most suitable catalyst to produce high hydrocarbons yields at a low cost. Bio-oil obtained by using ZSM-5 had 5.15% of alkanes. It is important to note that the selectivity of zeolite depends on its pore structure and acidic sites. Acidic site concentration in zeolite maximizes the level of aromatic compounds in bio-oil because Brønsted acidic

sites produce aromatics, while Lewis acidic sites produce alkanes [47]. Alkanes proportion of bio-oil samples from fast pyrolysis of Sida increased with catalyst application except ZnO, where it decreased from 8.01 (non catalytic) to 6.43%. Unlike bio-oil sample from PM, here the highest alkanes content of 14.15% was observed in bio-oil from Na₂CO₃ catalyst. In point of view of alkanes contents, catalysts can be ordered as Na₂CO₃ > ZSM-5 > ZrO₂ > CeO₂ > ZnO. When comparing two biomasses alkanes production was found to be more suitable from fast pyrolysis of Sida than PM.

Effects of catalysts on aromatics production

Aromatics such as phenols, benzenes, and toluenes in pyrolysis oil have already been reported in the literature [43]. Among all bio-oil chemicals phenolic compounds are important industrial ones and could be used to produce solvents or phenolic-based adhesives i.e. novolac and resole resins. Aromatics are important in chemical industry for plastics production and value-added chemicals [35]. It was also reported that bio-oil could substitute for fossil phenol (up to 25 wt%) in the synthesis of phenolic resins. Bio-oil samples from NCFP of PM contained 26.27% of aromatics which increased during CFP. Jeong et al. [40] reported that phenols contents of bio-oil increased with catalyst application. In fact, it rised from 26.27 to 47.30% when ZrO₂ was applied. Nair and Vinu [48] reported that ZrO₂ application during fast pyrolysis improved the guaiacol content of bio-oil sample. The lowest aromatics content of 26.39% was observed with Na₂CO₃. The CeO₂, ZSM-5, and ZnO catalysts enhanced the proportions of aromatics in bio-oil with the yields of 29.77, 30.68, and 39.10%, respectively. The aromatics contents of bio-oil samples from fast pyrolysis of Sida also increased with catalyst application except ZnO, where the lowest percentage was observed. The CeO₂ and ZSM-5 with 25.11 and 23.56% respectively represented the most important proportions of aromatics. Compared to bio-oil from PM, bio-oil from Sida contained less aromatics. Thus, PM was the most suitable biomass for aromatics production through fast pyrolysis specially by using ZrO₂.

Effects of catalysts on the other compounds

Alcohols, amines/amides, aldehydes, ethers, and esters were considered as the other compounds due to their low percentages in bio-oil samples. Alcohols are highly desirable for valuable chemicals and fuels productions from fast pyrolysis of biomass [49]. Amides may be used to form resilient structural materials (e.g., nylon, Kevlar). Among amides dimethylformamide is one of the most important organic solvents usually used in drug production [44]. An ether is an organic compound that contains two alkyl or aryl groups by an oxygen atom and used in medicine [50]. Alcohols such as methanol and ethanol from bio-oil of PM were improved by using Na₂CO₃, ZnO, and CeO₂. Amines contents of bio-oil samples increased significantly with Na₂CO₃ and ZSM-5 and decreased with the other catalysts. Aldehydes contents increased only when CeO₂ was applied. During fast pyrolysis of Sida, alcohols contents of bio-oil samples increased with Na₂CO₃, ZnO, and ZrO₂ and decreased with ZSM-5 and CeO₂. Amines contents increased during CFP regardless of catalyst type. The highest amines content was observed in bio-oil sample from Na₂CO₃.

4. Conclusions

In this study, fast pyrolysis of PM and Sida was performed with and without catalyst to investigate the most suitable catalyst for the productions of different chemicals such as carboxylic acids, ketones, alkanes, aromatics (phenol, benzene, toluene), and the others (alcohols, aldehydes, amines). Pyrolysis experiments were conducted under the temperature of 400°C, nitrogen gas flowrate of 200 mL min⁻¹, biomass particle size of 1.5 mm, and five different catalysts such as ZSM-5, ZrO₂, ZnO, Na₂CO₃, and CeO₂.

Products distributions were affected by catalyst application. Indeed, the bio-oil yield decreased during CFP for all catalysts, while biochar and gas yields increased/decreased depending on catalyst. The proportions of chemicals groups in bio-oil samples from PM and Sida were also affected by catalyst. For the production of carboxylic acids, CeO₂ was found to be the most promising with 16.28 and 15.39% respectively for PM and Sida. The maximum ketones content of bio-oil samples of 28.46 and 31.33% were obtained by using Na₂CO₃ and CeO₂ respectively from CFP of PM and Sida. Alkanes contents were high with CeO₂ and Na₂CO₃ from pyrolysis of PM and Sida. To produce high aromatics from CFP of PM and Sida, ZrO₂ and CeO₂ were found to be the most suitable. Overall, PM and Sida can be used to produce fuels and value-added chemicals through CFP.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

Zakari Boubacar Laougé: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft.

Hasan Merdun: Funding acquisition, Investigation, Project administration, Resources, Software, Supervision, Validation, Writing - review & editing.

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Authors' information (optional)

Not available

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Figures

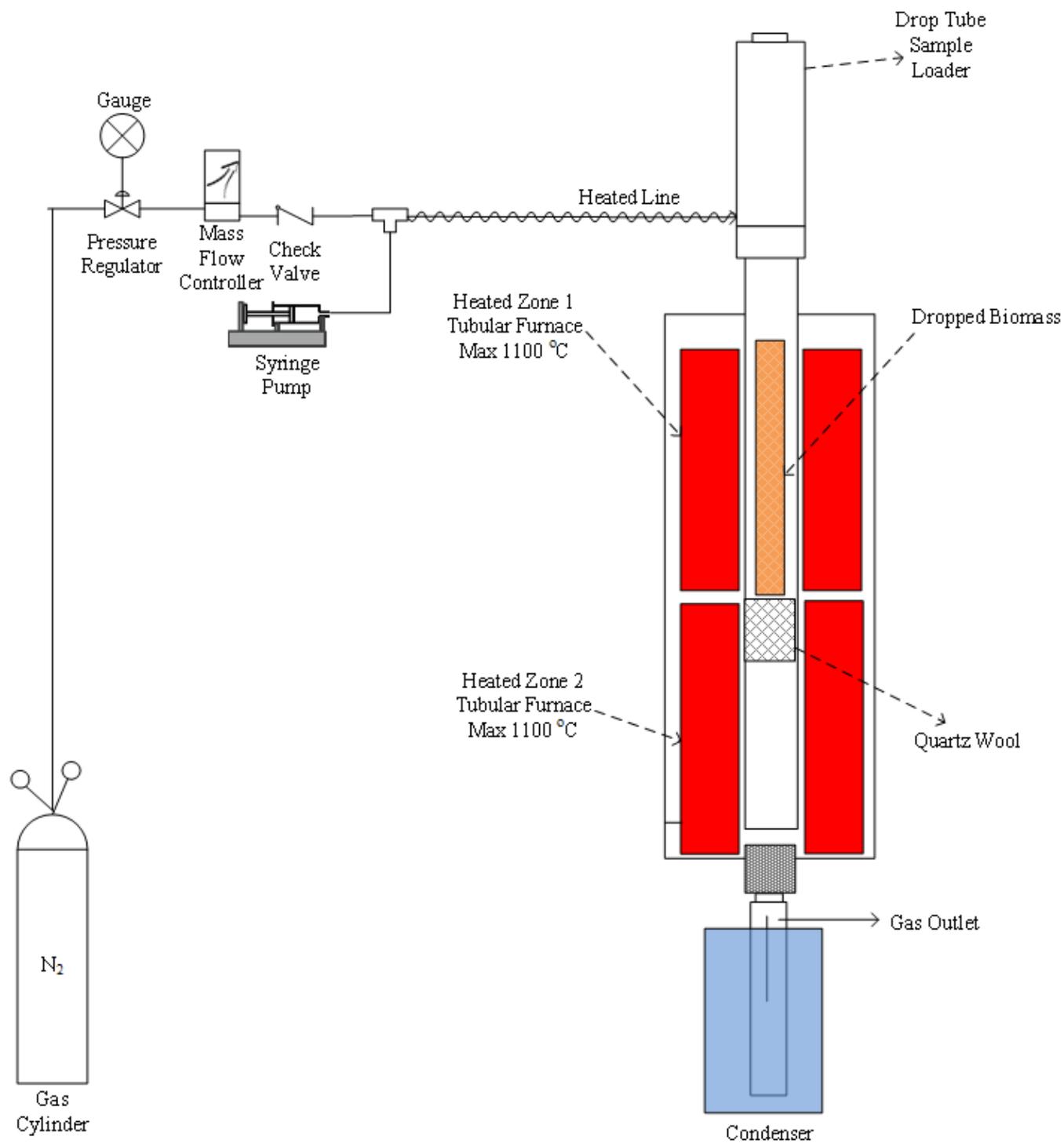


Figure 1

Fast pyrolysis experimental system.

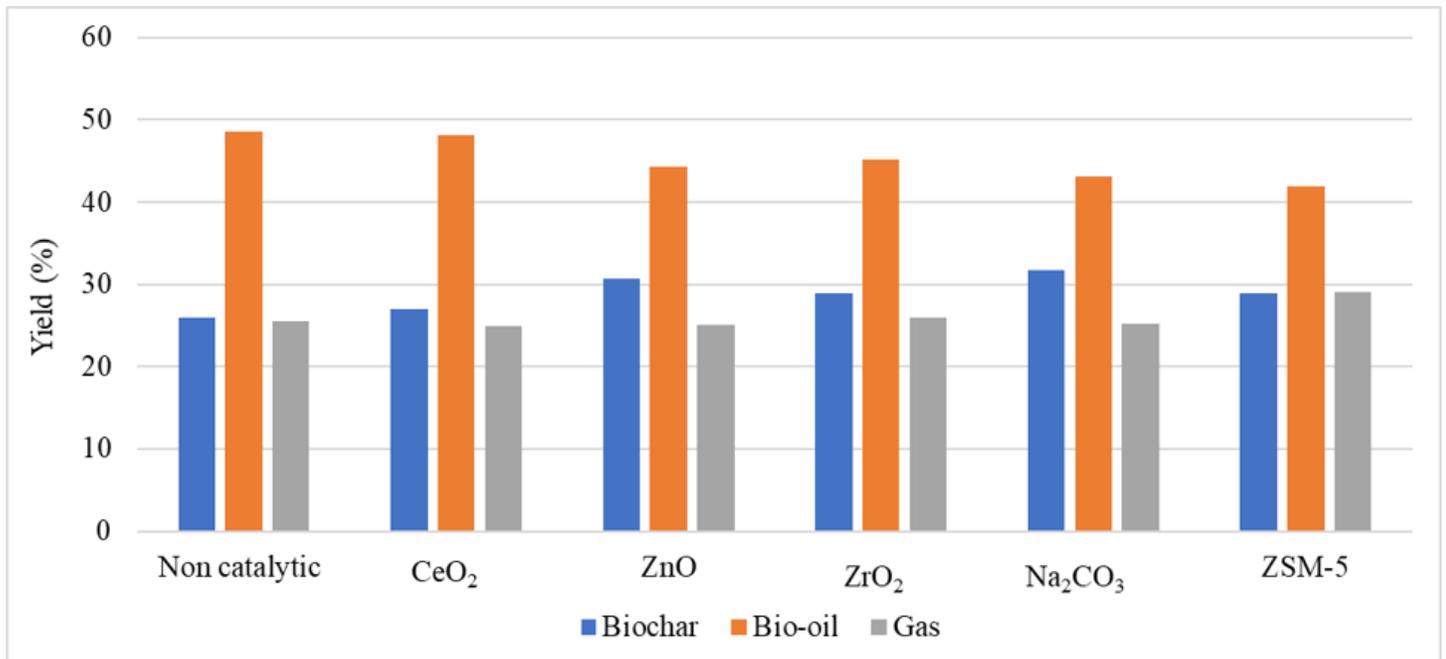


Figure 2

Products yields from non-catalytic and catalytic fast pyrolysis of Pearl Millet.

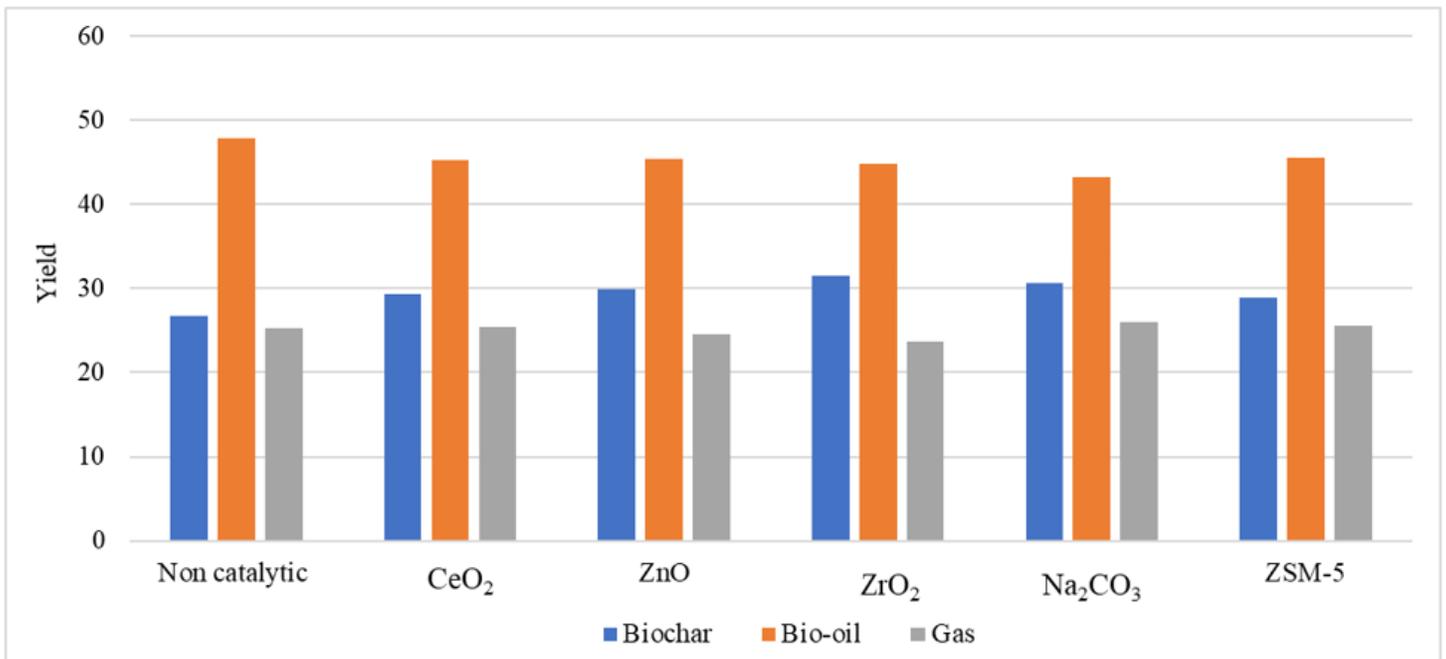


Figure 3

Products yields from non-catalytic and catalytic fast pyrolysis of Sida cordifolia.

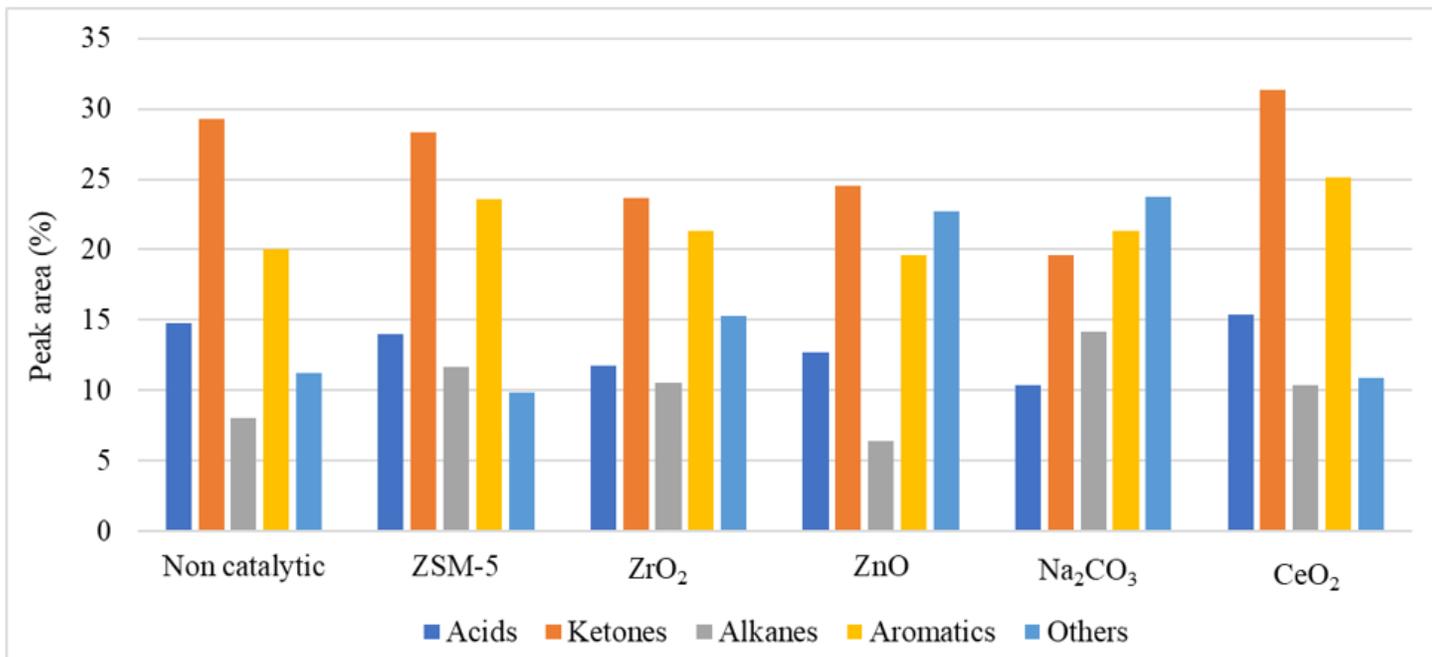


Figure 4

Distribution of chemicals compounds in bio-oil samples of Pearl Millet during catalytic and non-catalytic fast pyrolysis.

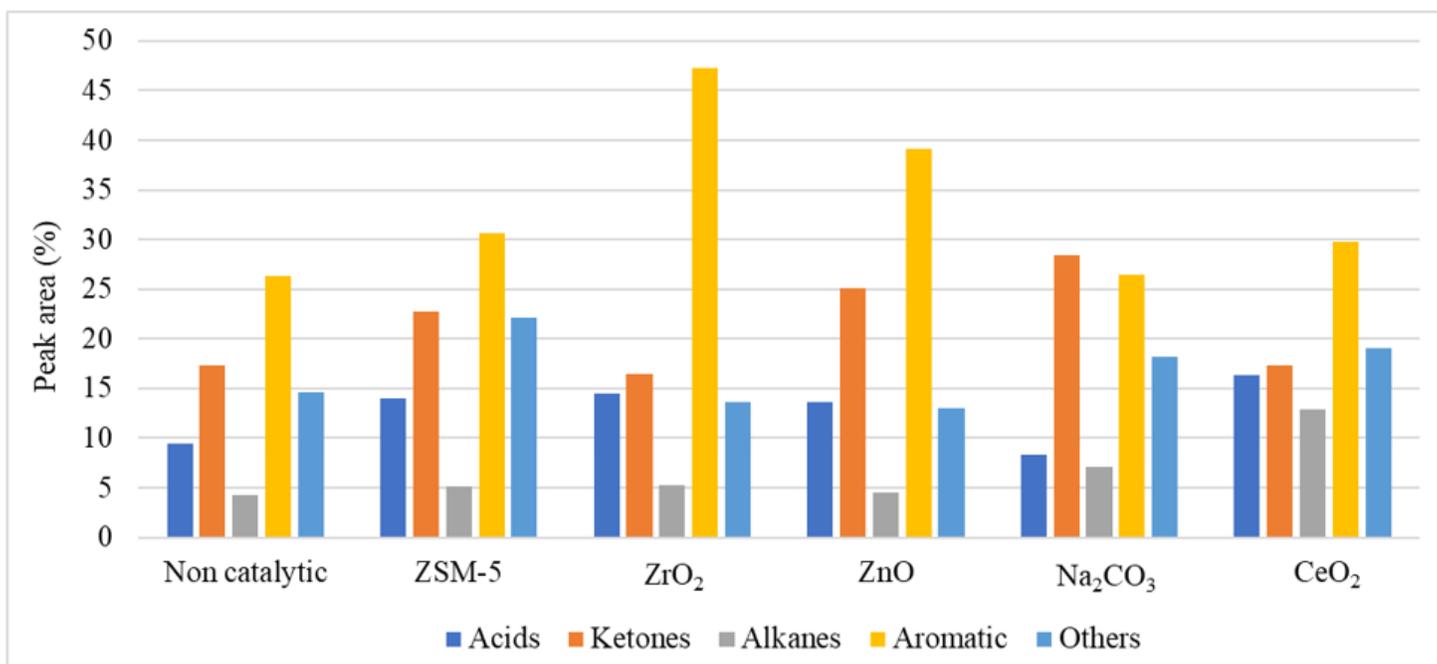


Figure 5

Distribution of chemicals compounds in bio-oil samples of Sida cordifolia during catalytic and non-catalytic fast pyrolysis.

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