

Journal of Scientific & Industrial Research Vol. 80, February 2021, pp. 172-180



# Combination of Woody and Grass type Biomass: Waste Management, Influence of Process Parameters, Yield of Bio-oil by Pyrolysis and its Chromatographic Characterization

C Sowmya Dhanalakshmi<sup>1</sup>\*, P Madhu<sup>1</sup>, A Karthick<sup>2</sup> and R Vignesh Kumar<sup>3</sup>

<sup>1</sup>Department of Mechanical Engineering, SNS College of Technology, Coimbatore, Tamilnadu, India 641 035

<sup>2</sup>Department of Electrical and Electronics Engineering, KPR Institute of Engineering and Technology, Coimbatore, Tamilnadu, India 641 407

<sup>3</sup>Department of Mechanical Engineering, National Engineering College, Kovilpatti, Tamilnadu, India 628 503

Received 25 June 2020; revised 14 October 2020; accepted 01 December 2020

Due to looming demand for fossil fuels and environmental concerns over global warming, extensive attention has been given on the development of renewable energy. Biomass materials are used since millennia for meeting myriad human needs including energy and chemicals. In this study, co-pyrolysis characteristics of woody and grass type agricultural wastes, namely *Borassus flabellifer* and *Cymbopogon flexuosus* were studied in a fixed bed reactor to evaluate their potential use as source of bio-oil. The effects of operating parameters such as temperature, particle size and heating rate were investigated. In this co-pyrolysis process, the maximum yield of pyrolysis bio-oil 47.10 wt% can been obtained under the pyrolysis temperature of 500°C, 1.0 mm particle size and at the heating rate of 30 °C/min. The bio-oil product was analyzed for physical, elemental and chemical composition using Fourier transform infra-red (FTIR) spectroscopy and gas chromatography (GC).

Keywords: Agricultural wastes, Chemical compositions, Co-pyrolysis, Energy conversion, Fixed bed

## Introduction

Among various word wide energy resources, biomass has accomplished fourth ranks. Biomass is providing 35 percent of their energy need in developing nations and it is the most significant energy source.<sup>1</sup> As a clean and alternative source of energy, biomass has gained increased attention because it is abundant, renewable, and readily available, and emits relatively low CO<sub>2</sub> content.<sup>2</sup> Numerous biomass feedstocks have been employed in the past ranging from agricultural wastes and residues to energy crops. Waste management through thermochemical conversion process is gaining increasing importance as larger volumes of solid waste are produced yearly.<sup>3</sup> Pyrolysis is the thermochemical process that converts biomass into bio-oil, char and non condensable gases. The liquid produced from pyrolysis is referred to as pyrolysis oil or bio-oil; it is a dark brown organic liquid and has the potential to produce hydrocarbons easily integrated into existing petroleum refineries as fuels for numerous applications.<sup>4</sup>

Co-pyrolysis of biomass is a very effective method to produce the ideal synthetic liquid fuel.<sup>2</sup> It is a process which involves two or more dissimilar materials as a feedstock. This technique has successfully improved the quantity and quality of the bio-oil without any improvement in the system as well as process.<sup>5</sup> It has shown promise for industrial applications because of its attractive performance and cost ratios.<sup>6</sup> Char or pyrolyzed charcoal is the secondary product during pyrolysis. It is a finegrained porous product. It is a main industrial fuel which can be used for the production of activated carbon and other value-added chemicals. Wood, agricultural crops and their residues are the common sources of biomass. Several reviews have focused on the co-pyrolysis of biomass using different types of reactors to produce liquid fuel.<sup>7,8</sup> An excellent feedstock for co-pyrolysis is various kinds of biomass. Agricultural residues, harvested wood, forest residues, municipal and industrial waste, are the various types of biomass materials used for copyrolysis process.<sup>9</sup> A variety of product composition and yields can be achieved depending on the operating conditions of the process. The variations in

<sup>\*</sup>Author for Correspondence E-mail: dr.sowmi100782@gmail.com

the composition of various biomasses also play a major role in the complexity of the final product obtained.<sup>10</sup> As feedstock, co-pyrolysis uses two or more diverse materials and the operations are virtually identical to standard techniques of pyrolysis. In general, co-pyrolysis is performed under moderate operating pressure and temperature at oxygen-free conditions in a closed reactor system.<sup>11</sup> Many researchers have identified and utilized different types of agricultural residues, wood residues Municipal solid wastes and dedicated energy crops for co-pyrolysis process. The feedstock includes pine cone, corn residues, sugarcane bagasse, beech wood, pine wood, firm sawdust, palm shell potato skin, rapeseed, switchgrass and sorghum, etc.<sup>5,12</sup> While numerous researches are carried out on wood as a fuel, there is some growing interest in fast growing plants like grasses. Grasses are local resources and can be supported with local economic models. One of the largest sources of biomass for agricultural residues in India is palmyra fruit bunch: Borassus flabellifer and lemon grass: Cymbopogon *flexuosus*. These are the two biomass samples native to the Indian subcontinents. Palmyra fruit bunch is the woody biomass obtained by removing the palm fruit from the black husk. The empty bunches are usually thrown away and is burnt in an open atmosphere. The open burning of these bunches has a cruel impact on the atmosphere. Lemon grass is widely cultivated in India. A massive grass type biomass available in the solid-waste form after retrieval of the oils from these grasses is mainly used for land-filling and a part is burnt to produce steam for stripping which is creating environmental problems.

The aforesaid literature parts confirmed the importance of co-pyrolysis process. There are a less number of existing researches in the field of co-pyrolysis of woody and grass type biomass materials. Particularly no literature is availed in the combination of palmyra fruit bunch and lemon grass. In this study, the co-pyrolysis characteristics of *Borassus flabellifer* and *Cymbopogon flexuosus* were investigated. Fixed bed slow pyrolysis of the mixture of these two samples was carried out with different temperature ranges, different particle size and at different heating rate to examine their effect on pyrolysis yield. The physical and chemical properties of the bio-oil were analyzed in order to find out the suitable applications by FTIR Spectroscopy and GC-MS.

# **Materials and Methods**

#### Materials

The palm fruit bunches and lemon grass used in this study was sampled from Coimbatore, Tamilnadu, India. Equivalent amounts of woody and grass type biomass were blended with the ratio of 1:1 and experiments were conducted. The blend was prepared by manual mixing of these two waste samples. In order to remove the moisture content of the blend, it was dried in open sunlight for four weeks and further dried in a vacuum oven at 40°C for 6 hours and stored in desiccators. The blended samples were ball milled to homogenize the composition to obtain four different sizes - 0.5, 0.75, 1.0 and 1.25 mm. The proximate and ultimate analysis of the sample is shown in Table 1 along with the protocol used for the analysis. The ultimate analysis of the biomass sample and char has been found by ASTM D5373 by using Vario EL-III (Germany) Elementar analyzer. Lignin, cellulose and hemicellulose content of the woody and grass biomass mixture were measured by using traditional wet chemistry method.<sup>14</sup> From the component analysis, it has been clear that the biomass sample is environmental friendly due to its low fractions of nitrogen and sulfur.

Table 1 — Proximate and ultimate analyses of the biomass mixture					
Parameters	Biomass mixture	Char	Standard		
	Proximate analysi	s in wt%			
Volatile matter	64.64	24.51	ASTM D3175		
Fixed Carbon	24.45	65.18	By difference		
Moisture Content	5.32	4.21	ASTM D3173		
Ash	5.59	6.10	ASTM D3174		
Ultimate analysis in wt%					
Carbon	43.46	56.60	ASTM D5373		
Hydrogen	5.01	5.13	ASTM D5373		
Nitrogen	1.10	5.04	ASTM D5373		
Oxygen	50.42	33.03	By difference		
Sulfur	0.01	0.20	ASTM D5373		
H/C molar ratio	1.3	1.079			
O/C molar ratio	0.871	0.438			
Empirical formula	CH <sub>1.373</sub> N <sub>0.0217</sub>	CH <sub>1.079</sub> N <sub>0.9.9</sub>			
	$O_{0.871}$	O <sub>0.438</sub>			
Lig	ninocellulosic ana	lysis in wt%			
Cellulose ( $\pm 0.05\%$ )	19.43	—			
Hemi-cellulose $(\pm 0.05\%)$	42.16	—	—		
Lignin (± 0.05%)	38.41	—			
dry ash basis					

## **Reactor Setup**

The experiments were carried out in a laboratory scale fixed bed reactor described by Sowmya Dhanalakshmi and Madhu<sup>15</sup> as shown in Fig. 1. The reactor consists of stainless tube of 100 mm inner diameter and 150 mm height was externally heated by an electrical furnace. Temperature of the reactor was measured by two K type thermocouples which were located at two different places inside the reactor. 100 g of the sample with different particle sizes was placed inside the reactor per batch and the temperature was raised at different heating rates. The heating rate and process temperature were controlled by a PID controller. For the efficient conversion and to avoid heat loss, the outside of the reactor is well insulated with mineral wool and Chromel-Alumel. The reaction outcomes including volatile compounds, gas and fine charcoal were quenched by the condenser by the cooled water maintained at 0°C. Experiments have been carried out in a temperature ranges from 350 to 550°C, under normal atmospheric pressure. The bio-oil condensed by the condenser was collected in a conical flask and weighed. The char was collected from the bottom of the reactor and weighed. The mass of the uncondensable during the reaction was found by the remaining material balance.

# *Yield of biofuel (wt%)=*

$$\frac{\text{Desired product (bio-oil/char/gas) in gram}}{\text{Biomass sample fed in gram}} \times 100\%$$

## Experimental Procedure

Three set of experimental works has been carried out. Effect of pyrolysis temperature on the product yield has been analyzed first. For this purpose, the sample is heated to the temperature of 350, 400, 450, 500, 550 °C at the constant particle size of 0.75 mm

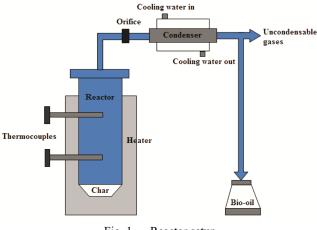


Fig. 1 - Reactor setup

and at the heating rate of 10 °C/min. the biomass samples are heated and held for 25 min for the complete release of volatile products. The next groups of experiments are contacted with the different particle sizes of 0.5, 0.75, 1.0, 1.25 mm at the temperate of 500°C and at the heating rate of 10 °C/min. Last set of experiments has been conducted to determine the effect of heating rate. For this the heating rate has been varied as 10, 20, 30 °C/min at the optimum pyrolysis temperature of 500°C and at the optimum particle size of 1.0 mm. Each experiment was conducted twice and the average was taken to consideration. The average yields are given within the error of less than  $\pm 2$  wt%. The present experimental conditions are given in Table 2.

## **Characterization Methods**

The physical characterizations of the bio-oil were measured by using BROOKFIELD LV-DV-II Pro viscometer and Penskey Martein closed cup apparatus. By weighing known volume of the sample, the density of the oil was measured. Parr-6772 calorimetric thermometer is used to measure the calorific value of the bio-oil. Digital pH meter was used for measuring the pH values of bio-oils. The component analysis of the bio-oil and char was measured by Elementar Vario EL-III Elementar instrumentations with WinWar software. Thermo MS DSQ II gas chromatograph (GC) used to find the various chemical components of the bio-oil. Separation of organic compounds was attained by the capillary column with the dimensions of HP-5, 30 m long  $\times$  0.25 mm diameter  $\times$  0.25 µm. During this analysis Helium was used as a carrier gas with the flow rate of 10 ml/min. The dehydrated liquid product was diluted with diethyl ether to provide the

Table 2 — Experimental conditions				
Case	Temperature in °C	Particle size in mm	Heating rate in °C/min	
	e	111111	C/IIIII	
Run 1	350	0.75	10	
Run 2	400	0.75	10	
Run 3	450	0.75	10	
Run 4	500	0.75	10	
Run 5	550	0.75	10	
Run 6	500	0.5	10	
Run 7	500	0.75	10	
Run 8	500	1.0	10	
Run 9	500	1.25	10	
Run 10	500	1.0	10	
Run 11	500	1.0	20	
Run 12	500	1.0	30	

#### 174

appropriate concentration. Initially the temperature of the oven was set to 25°C for 2 min, thereafter it was increased to 200°C with the interval of 10°C and remained for 15 min and finally it was increased to 350°C and remained for 10 min. Injections were carried out in split stage by using a ratio of 1:10 and the injection temperature portions was 250°C. NIST library G1035A software was preferred in data accomplishment system.

# **Results and discussion**

## **Effect of Temperature on Product Yield**

In pyrolysis, biomass material undergoes end to end crucial and minor reactions relating heat and mass transfer mechanism. The main function of the temperature during pyrolysis is to provide the necessary heat for the decomposition of the biomass. Due to the additional energy obtainable to break the biomass bonds, the biomass conversion increases with increasing temperature. The effect of process temperature on the product yields: bio-oil, char and gas is shown in Fig. 2. The experiments were conducted by varying the temperature values. Observably the optimum temperature for maximum bio-oil is in the range of 500°C. The yield of bio-oil increases from 30.35 wt% to 40.50 wt% when the temperature is increased from 350 to 550 °C. On the other side the char yield decreases from 40.48 wt% to 20.54 wt% and the yield of gas increases from 29.17 wt% to 38.96 wt%. At the temperature of  $< 350^{\circ}$ C, the biomass decomposition mainly takes place at heteroatom within the structure which results in production of char.<sup>16,17</sup> When the temperature reaches about 550°C, huge breakup of biomass species cause the high molecular disordering, producing many types of compounds.<sup>18</sup> At the lower temperature, the

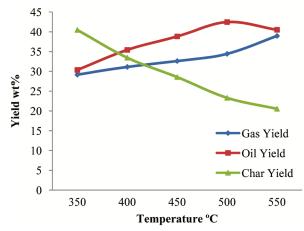


Fig. 2 — Effect of temperature on yield products

conversion efficiency of biomass into bio-oil remained very low and enormous conversion of biomass to its fragments occurs within the range of 400–500°C.<sup>19</sup> Due to the availability of additional energy inputs to break the biomass structure, the conversion efficiency increases with increase in temperature. Due to strong cracking, at the pyrolysis temperature of 500°C the yield of bio-oil passes through a maximum of 42.46 wt%. When the temperature went beyond 500°C, the yield of bio-oil decreased to 40.50 wt%. This is due to the formation of secondary cracking reactions of the pyrolysis vapor. At elevated temperature, the secondary decomposition of the bio-char could produce noncondensable gases contributing an increase in gaseous products.20,21

# Effect of particle size on product yield

Depending upon the type of biomass and type of pyrolyser, the useful size of the biomass particles may vary. The yield of bio-oil, char and gas during pyrolysis by changing its particle sizes are represented Fig. 3. The effect of particle size on yield can be explained by the conductivity of the biomass samples. During pyrolysis, biomass being poor thermal conductor poses heat transfer difficulties. The size of the biomass is considered important on the yield of biofuel products.<sup>22</sup> In this study, the yield of bio-oil is considerably increases as the particle size is increased from 0.5 mm to 1.0 mm. The study found that the biooil yield increases from 39.32 wt% to 45.54 wt% and the char and gas yield decreases from 24.48 wt% to 21.93 wt% and 36.20 wt% to 32.50 wt% respectively when the particle size is increased from 0.5 mm to 1.0 mm. Further increases of particle size from 1.0 mm to 1.25 mm, leads to decrease of the bio-oil yield to 43.36 wt%. The particles with smaller diameter can

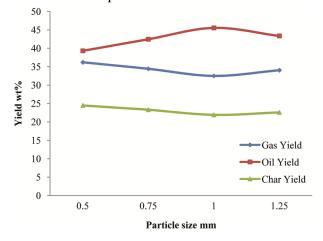


Fig. 3 — Yield of pyrolysis products at difference particle size

be heat up uniformly than larger particles. The poor heat transfer of the larger particles will guide to yield lower bio-oil.<sup>23</sup> From this study, it has been noted that particle size of 1.0 mm seems to be good for the production of higher bio-oil yield. Biomass structure is another important factor to clarify the product distributions. The structure of the cell may affect the process behavior, such as the release of alkaline earth metallic species.<sup>24</sup> Based on these results particle size has significant parameter during pyrolysis product distributions.

## Effect of Heating Rate on Product Yield

The type of decomposition product during pyrolysis is also defined by the rate of biomass heating. Various researchers conducted the effect of heating rate on the yield of bio-oil during pyrolysis.<sup>25</sup> To determine the effect of heating rate, the pyrolysis experiments of mixed biomass were conducted at different heating rates of 10, 20, 30 °C/min with the constant pyrolysis temperature of 500°C and at the particle size of 1.0 mm. The bio-oil yield is low at lower heating rate and increases with the increase of heating rate. At lower heating rate of 10 °C/min, the bio-oil yield is 45.54 wt% and increases to the value of 47.10 wt% at the heating rate of 30 °C/min. At higher heating rates, high bio-oil yield mainly be obliged to short time available for secondary reactions such as tar cracking and repolymerization. However, the higher heating rates always favour the formation of higher gas yield.<sup>26</sup> Rapid heating of the biomass reduces the heat and mass transfer limitations. It improves quantity of the volatiles by fast endothermic decompositions and minimizes the time for secondary reactions yielding lower char yield.<sup>27</sup> In this study, the char yield is found to decrease from 21.93 wt% to 19.31 wt% when the heating rate is increased from 10 °C/min to 30 °C/min. The maximum bio-oil yield of 47.10 wt% was obtained at the heating rate of 30 °C/min, whereas the maximum gas yield of 33.59 wt% was also obtained at the heating rate of 30 °C/min. The maximum char yield about 40.48 wt% was obtained at the lower temperature of 350°C, particle size of 0.75 mm and hating rate of 10 °C/min. The effect of heating rate on pyrolysis yields is shown in Fig. 4.

#### **Product Characterization**

#### **Physical Properties of the Bio-oil**

The obtained bio-oil from this study is highly oxygenated with oxygen content of 38.3 wt%. The

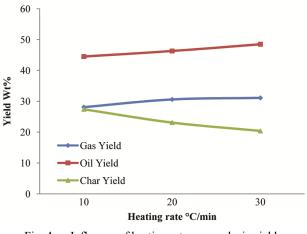


Fig. 4 — Influence of heating rate on pyrolysis yields

density and viscosity of the bio-oil was measured as 1005 kg/m<sup>3</sup> and 7.52 cSt respectively. The root difference between bio-oil and hydrocarbon fuels is the presence of oxygen. Bio-oil usually has an oxygen content of between 35 and 45 %; it is distributed in more than 300 compounds and continues to change according to the source materials as well as the pyrolysis conditions. The high number and concentration of oxygen compounds decreases the energy density to less than half the conventional fossil fuel standard.<sup>28</sup> It leads to several direct combustion problems, such as instability, low heating value, and high corrosivity. The density and viscosity of the biooil are related to the ability to flow. The flash point of the bio-oil is about 150°C indicates that it can be stored safely at room temperature. The pH value of the bio-oil is 3.4 which is also reliable. The low pH value of the bio-oil point out the presence of acidic compounds and it has to be treated before used for the specific applications. The lower pH value often aggravates corrosiveness issues, which can contribute to higher costs of storage and transport.<sup>29</sup> It may be corrosive to steel, aluminum and nickel based materials. The ash content of the bio-oil is less than 0.1 wt%. The calorific value of the bio-oil is 22.52 MJ/kg which is half the value of the diesel fuels. The comparison of various physical properties of the biooil and total available chemical compounds present in the bio-oil and diesel fuel are shown in Table 3.

## Chemical Characterization of the Bio-oil

The chemical composition of the derived bio-oil sample was determined through FTIR and GC analyses. FTIR analysis is a great tool for identifying chemical compositions. It is an analytical technique used to identify organic, polymeric and inorganic

Table 3 — Physical properties of bio-oil						
Property	Value	Neem bark <sup>30</sup>	Hard wood <sup>31</sup>	Diesel <sup>32</sup>	Method	Unit
Density	1005	1015	1220	780 at 15°C	ASTM D1298	kg/m <sup>3</sup>
Viscosity	7.52	8.1	13	1.3-3.3 at 50°C	ASTM D2161	cSt
Flash point	150	155	66	75	ASTM D93	°C
pН	3.4	3.7	#		_	
Carbon	53.36	48.82	55.5	86.58	ASTM 5375	wt%
Hydrogen	8.2	9.1	6.7	13.23	ASTM 5375	wt%
Nitrogen	0.41	0.84	0.1	65 ppm	ASTM 5375	wt%
Oxygen <sup>a</sup>	38.3	0.23	0.0	0.01	By difference	wt%
Sulfur	0.1	41.01	37.7	0.11	IS4668	wt%
H/C molar ratio	1.833	2.223	#	#	#	
O/C molar ratio	0.538	0.630	#	#	#	
Empirical formula	CH <sub>1.83</sub> N <sub>0.016</sub> O <sub>0.538</sub>	CH <sub>2.22</sub> N <sub>0.014</sub> O <sub>0.63</sub>	#	#	#	
Heating value	22.52	22.7	17.5	45-46	ASTM D5468-02	MJ/kg
<sup>a</sup> By difference	#-Not reported					Ũ

materials. This method uses infrared light to scan biooil sample and observe chemical properties and then the absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. The FTIR spectra of the bio-oil sample is shown in Fig. 5 and the absorbance peaks observed in the spectra were listed in Table 4. The OH-stretching, free hydroxyl between 3640 and 3610 cm<sup>-1</sup>, OHstretch, H-bonded between 3500 and 3200 cm<sup>-1</sup> indicates the presence of alcohols and phenols. The C=C stretching vibration between 1675 and 1575  $cm^{-1}$ indicates the presence of Alkanes and aromatics. The absorbance peak between 1500 and 1400 cm<sup>-1</sup> represents C-C stretching (in-ring) indicative of aromatics. The C-H deformation bending between 1445 and 1405 cm<sup>-1</sup> indicates the presence of alkanes group in bio-oil. The skeletal vibration representing the presence of cyclopropanes in the bio-oil appears between 1060 and 1000 cm<sup>-1</sup>. The C-Cl stretch representing alkyl halides appears between 850 and  $550 \text{ cm}^{-1}$ .

The GC analysis shows the various chemical compositions present in the bio-oil. These components are identified with increase in retention time. The most abundant components are phenolics and other aromatic compounds.33 Cellulose and hemicelluloses are the major components of the feedstock material as they are the sources of these aromatic and oxygenated compounds.<sup>34</sup> Different types of compounds such as normal phenols, alkanes, alkenes, fatty acids, esters were identified. Phenol and its compounds were identified as having the total area percentages of 28.09. This is used as an intermediate for industrial synthesis. Phenol is used as a versatile

Table 4 — The FTIR functional group and the indicated compounds of the bio-oil

Frequency Range (cm <sup>-1</sup> )	Group	Class of compounds
3640-3610	OH-stretch, free hydroxyl	alcohols, phenols
3500-3200	OH- stretch, H-bonded	alcohols, phenols
1675–1575	C=C stretching vibration	Alkanes and aromatics
1500-1400	C-C stretch (in-ring)	aromatics
1445-1405	C-H deformation bending	Alkane groups
1060-1000	Skeletal vibration	Cyclopropanes
850-550	C-Cl stretch	alkyl halides
		[ <sup>120</sup>

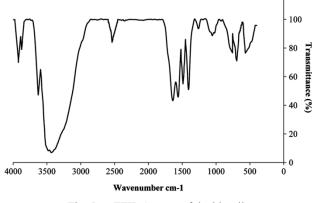


Fig. 5 — FTIR Spectra of the bio-oil

precursor for many herbicides and pharmaceutical drugs.<sup>35,36</sup> It also used in the synthesis of anti-oxidant compounds. The main uses of phenol, consuming two thirds of its production, involve its conversion to precursors for plastics. Asarone is a chemical compounds identified with the bio oil with the area percentage of 4.53. It is a chemical compound of the phenylpropanoid class found in various plants such as Acorus and Asarum. The main clinical symptom of

Table — 5 GC analysis of the bio-oil						
RT/Min	Compound Name	Molecular Formula	Type of Compound	Molecular Weight	% Area	
3	Benzene-1,3,5-D3	$C_6H_3D_3$	NAr	78	6.24	
6.05	Phenol	$C_6H_6O$	ArO	94	13.41	
6.21	Phenol, 2-methyl-	$C_7H_8O$	ArO	108	10.27	
7.10	Phenol, 2,6-dimethyl	$C_8H_{10}O$	ArO	122	3.21	
7.72	Phenol, 2,4-dimethyl	$C_8H_{10}O$	ArO	122	1.20	
7.95	2,5-Diacetylfuran	$C_8H_8O_3$	ArO	152	2.10	
8.01	2-Isopropyl-2,5-dihydrofuran	$C_7H_{12}O$	ArO	112	6.25	
8.56	Phenol, 4-amino-	C <sub>6</sub> H <sub>7</sub> NO	ArO	109	4.33	
9.78	Ethanol	$C_{13}H_{22}O_3$	ArO	226	2.22	
12.21	Kaempferol	$C_8H_8O_4$	ArO	168	1.91	
12.25	2,3,5-Trimethoxytoluene	$C_{10}H_{14}O_3$	ArO	182	2.22	
12.97	Isosorbide	$C_6H_{10}O_4$	ArO	146	0.31	
14.28	Octadecane	$C_{18}H_{38}$	NAr	254	1.11	
17.39	Asarone	$C_{12}H_{16}O_3$	ArO	208	4.53	
18.20	Benzhydryl vinyl ether	$C_{15}H_{14}O$	ArO	210	1.28	
19.33	3,4-Altrosan	$C_6H_{10}O_5$	ArO	162	3.52	
20.45	N-Benzylpiperidone	C <sub>12</sub> H <sub>15</sub> NO	ArO	189	2.33	
21.82	d-Mannose	$C_6H_{12}O_6$	ArO	180	2.91	
23.25	d-Glucoheptose	$C_7H_{14}O_7$	ArO	210	2.49	
23.35	Docosane	$C_{22}H_{46}$	NAr	310	1.81	
25.16	D-Allose	$C_6H_{12}O_6$	ArO	180	5.95	
28.82	3-Acetoxy-24-methyl-5-cholest-5,22-dien-7-one	$C_{31}H_{48}O_3$	ArO	468	4.25	
30.35	Fluprednisolone	C21H27FO5	ArO	378	3.72	
34.42	Di-(2ethylhexyl) phthalate	$C_{24}H_{38}O_4$	ArO	390	4.21	
36.62	Butanoic acid	$C_{24}H_{34}O_{6}$	ArO	418	2.02	
37.65	Nonacosane	$C_{29}H_{60}$	NAr	408	3.33	
38.11	1-Methyl-1,3,3-triphenylindan-2-one	$C_{28}H_{22}O$	ArO	374	0.36	

asarone is extended vomiting that sometimes lasted more than 15 hours. Asarone is not metabolized to trimethoxyamphetamine as has been asserted by online vendors. 4-aminophenol was identified with the area percentage of 4.33. It is the organic compound typically available as a white powder. It was commonly used as a developer for black-andwhite film. 4-Aminophenol is a building block used in organic chemistry. It is the final intermediate in the industrial synthesis of paracetamol. Treating 4aminophenol with acetic anhydride gives paracetamol. One of the other compounds identified in the bio-oil is D-Allose. It is an aldohexose sugar. It is a rare monosaccharide that occurs in the leaves of the African plants. It is soluble in water and practically insoluble in methanol. The various chemical compounds present in the bio-oil identified by GC are given in Table 5.

#### Conclusions

Many researchers have recognized that, the copyrolysis method can greatly improve the quantity

and quality of bio-oil. It is found to be a promising alternative in biomass conversion for the production of bio-oil. Due to the fact that biomass wastes are available in abundant amounts and co-pyrolysis has huge potential for development in many countries. Mixture of Borassus flabellifer and Cymbopogon flexuosus were the promising feedstock for the production of bio-oil. Co-pyrolysis experiments have been conducted for the yield of higher bio-oil. The yield was considered reasonable regarding the previous studies on fixed bed slow pyrolysis. The maximum yield of 47.10 wt% was obtained under the pyrolysis temperature of 500°C, particle size of 1.0 mm and the heating rate of 30 °C/min. In this study temperature was the most significant parameter to determine the product distributions. The calorific value of the bio-oil was more than half the value of diesel fuel which is good enough for an agricultural waste. The GC analysis showed that the bio-oil contained significant amounts of complex organic mixtures containing hydrophilic and carbonyl structures, resulting in low pH values and high

oxygen contents. The chemical elements present in the bio-oil can be used as a feedstock for the chemical industries. Using this co-pyrolysis method, the volume of biomass wastes can be easily controlled. In addition, it can also be noted that this is an optional strategy to enhance the energy security and decrease the dependency on fossil fuels.

## References

- Arulkumar R, Kanagasabapathy H & Manickam I N, Combination of agricultural waste and saw dust into biomass material for briquette, *Indian J Ecol*, 46(1) (2019) 188–191.
- 2 Sudalaiyandi K, Karthick A, Kumar R V, Manoj P V J & Madhu P, Performance and emission characteristics of diesel engine fueled with ternary blends of linseed and rubber seed oil biodiesel, *Fuel*, **285** (2021) 119255.
- 3 Adeniyi A G, Ighalo J O, Onifade D V & Adeoye S A, Modeling the valorization of poultry litter via thermochemical processing, *Biofuel, Bioprod Biorefin*, **14(2)** (2020) 242–248.
- 4 Pecha M B & Garcia-Perez M, Pyrolysis of lignocellulosic biomass: oil, char, and gas, in *Bioenergy* (2020) (pp. 581–619), Academic Press.
- 5 Abnisa F & Daud W M A W, A review on co-pyrolysis of biomass: an optional technique to obtain a highgrade pyrolysis oil, *Energy Convers Manag*, **87** (2014) 71–85.
- 6 Baysal M & Yürüm Y, Characterization of bio-oils and biochar obtained from the pyrolysis of a mixture of *Lolium* perenne, Festuca ovina, Festuca rubra and Poa pratensis grasses, Biofuels, 7(2) (2016) 181–189.
- 7 Abnisa F & Daud W M A W, Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire, *Energ Convers Manag*, **99** (2015) 334–345.
- 8 Mushtaq F, Mat R & Ani F N, A review on microwave assisted pyrolysis of coal and biomass for fuel production, *Renew Sust Energ Rev*, **39** (2014) 555–574.
- 9 Huang Y F, Chiueh P T, Kuan W H & Lo S L, Microwave pyrolysis of lignocellulosic biomass: heating performance and reaction kinetics, *Energy*, **100** (2016) 137–144.
- 10 Adeniyi A G & Ighalo J O, ASPEN Plus predictive simulation of soft and hard wood pyrolysis for bio-energy recovery, *Int J Environ Waste Manag* **26(2)** (2020) 234–244
- 11 Chen W, Shi S, Zhang J, Chen M & Zhou X, Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization, *Energ Convers Manag*, **112** (2016) 41–48.
- 12 Hassan H, Lim J K, & Hameed B H, Recent progress on biomass co-pyrolysis conversion into high-quality biooil, *Bioresour technol*, 221 (2016) 645–655.
- 13 Demirbas M F & Balat M, Biomass pyrolysis for liquid fuels and chemicals: A review, J Sci Ind Res, 66(10) (2007) 797–804
- 14 Dhanalakshmi C S, Madhu P, Karthick A, Mathew M & Kumar R V, A comprehensive MCDM-based approach using TOPSIS and EDAS as an auxiliary tool for pyrolysis material selection and its application, *Biomass Convers Biorefin*, (2020) DOI: 10.1007/s13399-020-01009-0

- 15 Sowmya Dhanalakshmi C & Madhu P, Utilization possibilities of Albizia amara as a source of biomass energy for bio-oil in pyrolysis process, *Energ Source, Part A: Recover, Utiliz Environ Effect*, **41(15)** (2019) 1908–1919.
- 16 Tsai W T, Lee M K & Chang Y M, Fast pyrolysis of rice husk: Product yields and compositions, *Bioresour technol*, 98(1) (2007) 22–28.
- 17 Dave P N & Joshi A K, Plasma pyrolysis and gasification of plastics waste-a review, *J Sci Ind Res*, **69(03)** (2010) 177-179.
- 18 Gercel H F, The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake, Biomass Bioenerg, **23(4)** (2002) 307–314.
- 19 Madhu P, Kanagasabapath H & Manickam I N, Flash pyrolysis of palmyra palm (*Borassus flabellifer*) using an electrically heated fluidized bed reactor, *Energ Source, Part A: Recover, Utiliz Environ Effect*, 38(12) (2016) 1699–1705
- 20 Karthikeyan S, Sathiskumar C, & Moorthy R S, Effect of process parameters on tire pyrolysis: A review, *J Sci Ind Res*, 71(05) (2012) 309–315
- 21 Sohaib Q, Muhammad A & Younas M, Fast pyrolysis of sugarcane bagasse: Effect of pyrolysis conditions on final product distribution and properties, *Energ Source, Part A: Recover, Utiliz Environ Effect*, **39(2)** (2017) 184–190.
- 22 Madhu P, Kumar C N, Anojkumar L & Matheswaran M, Selection of biomass materials for bio-oil yield: a hybrid multi-criteria decision making approach, *Clean Technol Environ Policy*, 20(6) 2018) 1377–1384.
- 23 Şensöz S & Angin D, Pyrolysis of safflower (*Charthamus tinctorius* L.) seed press cake: Part 1, The effects of pyrolysis parameters on the product yields, *Bioresour Technol*, **99(13)** (2008) 5492–5497.
- 24 Madhu P, Livingston T S & Kanagasabapathy H, Flash pyrolysis of lemon grass (*Cymbopogon flexuosus*) for bio-oil production in an electrically heated fluidized bed reactor, *Waste Biomass Valorization*, **9(6)** (2018) 1037–1046.
- 25 Debdoubi A, El Amarti A, Colacio E, Blesa M J & Hajjaj L H, The effect of heating rate on yields and compositions of oil products from esparto pyrolysis, *Int J Eenerg Res*, **30(15)** (2006) 1243–1250.
- 26 Madhu P, Matheswaran M M & Periyanayagi G, Optimization and characterization of bio-oil produced from cotton shell by flash pyrolysis using artificial neural network, *Energ Source, Part A: Recover, Utiliz Environ Effect*, **39(23)** (2017) 2173–2180.
- 27 Strezov V, Moghtaderi B & Lucas J, Thermal study of decomposition of selected biomass samples, *J Therm Anal Calorim*, **72(3)** (2003) 1041–1048.
- 28 Chen H, Lignocellulose biorefinery conversion engineering, in *Lignocellulose Biorefinery Engineering*, (2015) 87–124.
- 29 Wang S, High-efficiency separation of bio-oil, in *Biomass* now-sustainable growth and use, Intech Open, (2013) DOI:10.5772/51423.
- 30 Sowmya Dhanalakshmi C & Madhu P. Biofuel production of neem wood bark (*Azadirachta indica*) through flash pyrolysis in a fluidized bed reactor and its chromatographic characterization, *Energ Source, Part A: Recover, Utiliz Environ Effect,* (2019), DOI:10.1080/ 15567036.2019.1624893

- 31 Solantausta Y, Nylund N O, Westerholm M, Koljonen T & Oasmaa A, Wood-pyrolysis oil as fuel in a diesel-power plant, *Bioresour Technol*, 46(1–2) (1993) 177–188.
- 32 Islam M N, Beg M R A & Islam M R, Pyrolytic oil from fixed bed pyrolysis of municipal solid waste and its characterization, *Renew Energ*, **30(3)** (2005) 413–420.
- 33 Gaurh P & Pramanik H, In-situ production of valuable aromatics via pyrolysis of waste polypropylene using commercial catalyst ZSM-5, *Indian J Chem Technol*, 27 (2020) 144–152
- 34 Toraman H E, Vanholme R, Borén E, Vanwonterghem Y, Djokic M R, Yildiz G & Marin G B, Potential of genetically engineered hybrid poplar for pyrolytic production of bio-based phenolic compounds, *Bioresour technol*, 207 (2016) 229–236.
- 35 Madhu P, Manickam I N & Kanagasabapathy H, Production and characterization of phenolic compounds by flash pyrolysis of palmyra palm, *Energ Source, Part A: Recover*, *Utiliz Environ Effect*, **38(15)** (2016) 2161–2169.
- 36 Dhanalakshmi C S & Madhu P, Recycling of wood bark of *Azadirachta indica* for bio-oil and chemicals by flash pyrolysis, *Indian J Ecol*, 46(2) (2019) 347–353.