International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.9, No.02 pp 118-135, 2016

Production of chemicals via flash pyrolysis of agricultural biomass

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Abstract: Pyrolysis of biomass is a means to industrially manufacture renewable oil and gas, in addition to biochar for soil amendment and long-term carbon fixation. In this work, bio oil derived from the flash pyrolysis of palmyra palm fruit bunch are analysed using gas chromatography mass spectroscopy technique. The pyrolysis oil fraction exhibits a wide variety of fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidinines, phytol and phenols. In this work the gas chromatography–mass spectroscopy was developed and applied for the analysis of various chemicals present in the pyrolysis bio oil. More than 250 chemical compounds were identified. Most of these compounds have not been reported earlier. The increase in the number of identified chemical products is due to increased separations. The method described in this article is a suitable research tool for the determination of various chemical compounds from pyrolysis bio oil.
Keywords: Biomass, Pyrolysis, Bio oil, GC-MS, Chemicals.

1. Introduction

Cultivating sustainable sources of high volume biomass for the production of fossil fuel alternates is a key challenge to growth of the biofuel industry. Anthropogenic climate change and greenhouse gas emissions and concerns to the side, challenging demand for oilseed crops in global food, feed and fuel markets. These added increasing pressures to commodity prices and this threatens socio-economic stability [1]. Biomass utilization as a source of clean energy and chemicals has attracted many research attentions in recent years among to fossil fuel energy crisis and clean energy drive [2, 3]. Conversion of non-edible biomass such as agriculture residues, wood chips, stalks, and fruit bunches industrial and municipal solid wastes into fuels and useful chemicals would solve energy issues and waste disposal [4]. Pyrolysis is a thermal degradation of biomass in the absence of oxygen under moderate temperature over short residence time. Pyrolysis products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char [5]. It is the most promising and economical process for the conversion of biomass to liquid products. Liquid yields up to 80 wt% have so far been reported at operating conditions (350-550ºC). However, the high oxygen and water content, the low heating value, zero miscibility with petroleum fuels and the instability under storage and heating conditions are the serious obstructions of using biomass pyrolysis liquids in fuel applications. Biomass pyrolysis has so far been studied in various reactor types including: fluidized beds [6-9], ablative reactors [10], cyclonic reactors [11], circulating fluid beds and vacuum pyrolysers. A detailed review of all biomass processes is given in the

literature [12]. In general cellulose, hemicelluloses and lignin are the three major biomass components before the pyrolysis process in order to avail important chemicals [13].

The chemical composition of bio-oils is depended by the nature of the biomass from which they originate and the pyrolysis conditions employed [14, 15]. The pyrolysis oil resulting from the two phases: a lower mainly organic phase and an upper aqueous phase, which is rich in low molecular weight compounds with added value, such as carboxylic acids, phenols, guaiacols, syringols, etc. The chemical composition of this aqueous phase provides it suitable as feedstock for the production of hydrogen or after further extraction of specific chemicals for other applications, since the bio-oil contains both volatile and non-volatile compounds, the bio-oil's complex nature renders essential the use of high resolution chromatographic techniques such as HPLC and GC [16, 17], In GC analysis of the bio oil The increase in the number of identified products is due to increased number of separations [18]. At present, analysis by GC-MS is essential for the identification of natural organic. Usually, determination of various chemical compounds, such as aromatic compounds, fatty acids, general hydrocarbons, and hydroxy or amino metabolites is achieved using GC-MS techniques.

Borassus flabellifer is a robust tree and can live more than 100 years and reach a height of 30 metres (98 ft), with a canopy of green-bluish leaves with several dozen fronds spreading 3 m (9.8 ft) across. The very large trunk resembles that of the coconut tree and is ringed with leaf scars. Young palmyra palms grow slowly in the beginning but then grow faster with age. The fruit measures 4 to 7 inches in diameter, has a black husk, and is borne in clusters. The top portion of the fruit must be cut off to reveal the three sweet jelly seed sockets. The jelly part of the fruit is covered with a thin, yellowish-brown skin. These are known to contain watery fluid inside the fleshy white body. After consuming the fruit, the top portions were thrown out and it is burning in the open atmosphere.

In this research work the flash pyrolysis of palmyra palm fruit bunch have been carried out in a fluidized bed pyrolyser. Further detection of a wide range of chemicals from the pyrolysis bio oils has been carried out.

2. Experimental set up

2.1 Flash Pyrolyser

The experimental set up used for the present study is same as that used in previous paper by the literature [19] and further is explained in this section. The pyrolysis experiments conducted in the reactor is made up of stainless steel tube of internal diameter 50 mm. The reactor is filled with sand of particle size of 0.71 mm supported with the perforated base for enabling fluidization. The reactor is heated using 2 kW electrical heater with ammeter and voltmeter setup to measure the power input and is controlled by an autotransformer and temperature cut off unit. Pyrolysis experiments were carried out under nitrogen atmosphere at the temperatures of 500 °C and at the particle size of 0.71-1.0 mm. The temperatures of the reactor are measured with the help of thermocouple located at five different points along the reactor. The biomass particles are kept in the hopper and are fed into the reactor through screw feeder. Fluidization is first done by air till the reactor reaches the uniform temperature and then in inert atmosphere using nitrogen gas. The flow rate of the nitrogen was measured with the help of a rotameter. The flow rate was maintained to 1.75 m^3/h.

The rising gas from the reaction first passes through the cyclone separator thereby preventing char from reaching the condensing unit. The vapours and the gases are passed through a water cooled condenser to entrap the derived bio oil.

2.2. Apparatus and chromatography conditions

Gas chromatography Mass spectroscopy is a technique that can be used to characterize the structure and composition of the various components of the bio oil. For the identification and quantitative measurement of volatile and semi-volatile organic compounds in the pyrolysis bio oil was performed on a GC-MS equipment (South Indian Textile Research Association) THERMO GC-TRACE ULTRA VER: 5.0, THERMO MS DSQ II were used for the analysis under the following experimental conditions: A capillary column coated with a 0.25 µm film of DB-35 with length of 30 m and diameter 0.25 mm. The GC was equipped with Helium gas as carrier gas was set at the flow rate of 10 ml/min. The oven initial temperature was set to 70 °C for 2 min and then

increased to 250 °C at a rate of 10 °C/min. Mass spectrometer was operated at an interface temperature with ion source temperature of 200 °C. The sample was run fully at a range of 40–650 m/z.

3. Results and discussions

3.1. Characterization of biomass

The proximate and ultimate analysis of the dried pamyra palm fruit bunch was carried out and presented. The result confirmed that the biomass restrained maximum volatile matters (69.1%), fixed carbon (20.4%) contents and ash (2.2%) with lower percentage of moisture (8.3%). More amount of volatile matter produces more liquid and gaseous fuel during pyrolysis. The ultimate analysis determined the presence of carbon (52.15%), oxygen (44.31%), hydrogen (3.35%), nitrogen (0.12%) and sulfur (0.07%). Lower sulfur content in the raw materials makes them suitable feed for pyrolysis to produce good quality of liquid and gaseous fuels. The presence of volatiles determines the combustibility of biomass. Initially, moisture and more volatile compounds were removed within 150 °C and after that the thermal degradation of biomass started and proceeded followed by two steps such as degradation of hemicelluloses and cellulose. At higher temperature lignin degrades. Hemicelluloses degrade at lower temperature than cellulose. At higher temperature lignin degrades slowly till the end stage of degradation. At the end of pyrolysis, residue of biomass remained as char. It was observed that maximum degradation occurred during second and third stage in the temperature range between 150 and 450 °C. This temperature range was considered as active pyrolytic zone for biomass where maximum volatilization took place.

3.2. Compound analysis of bio oil

The results pertaining to GC-MS analysis of the pyrolysis oil lead to the identification of a number of compounds. These compounds were identified through mass spectrometry attached with GC. The increase in the number of identified products is due to increased separations. A number of compounds can be identified and listed in Table 1. They include acids, alcohols, aldehydes, ketones, phenols, esters, sugars, furans, guaiacols and multifunctional compounds. These compounds are also found in other bio-oils produced from different biomass resources [20]. Cellulose and hemicelluloses are the major components of the biomass feedstock as they are the sources of these aromatic and oxygenated compounds [21]. This class of compounds abundantly occurs in bio-oil since they are present as the monomeric units and oligomers from the lignin in the biomass feedstock. Some of these compounds have beneficial applications in the medical, industrial, and agricultural fields.

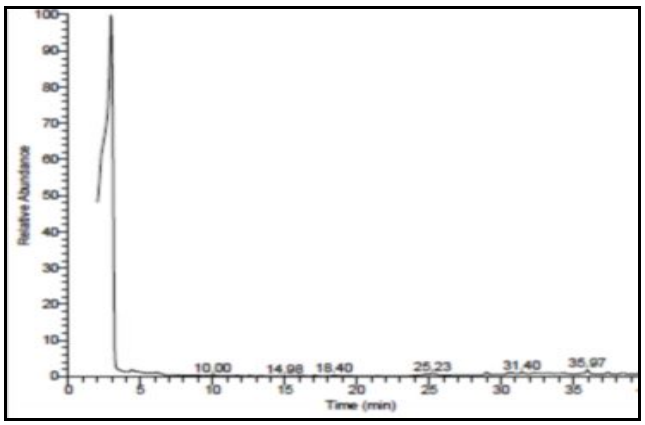

Figure 1: GC-MS analysis of the pyrolysis oil

Gas chromatography–mass spectrometry was developed and applied for the analysis of various chemical compounds derived from pyrolysis oil. Most of these compounds have not been reported earlier. Bio-oil consists mostly of phenolic and oxygenated compounds with aliphatic compounds in significant amounts. The elements and its derivatives found in the GC–MS analysis are used medicinally and also feed for the chemical industries. Table 1 shows the various chemicals identified during the chromatographic analysis.

Table 1: GC-MS analysis of the pyrolysis oil

S.N	RT/ min	Compound Name	Probability	Molecular Formula	Molecular Weight	Area %
1	4.39	Ethanol, 2-[2-(4-pyridyl)ethylamino]-	11.20	$C_9H_{14}N_2O$	166	9.84
2		6-Pyridin-4-ylhexan-1-ol	10.33	$C_{11}H_{17}NO$	179	
3		N-cyclohexyl-N'-[2-(4-pyridinyl)ethyl]urea	8.73	$C_{14}H_{21}N_3O$	247	
4		2-Pyridineethanamine, N-methyl- (CAS)	7.71	$C_8H_{12}N_2$	136	
5		Betahistine	7.71	$C_8H_{12}N_2$	136	
6		N-[3-[N-Aziridyl]propylidene]-2-[2-pyridyl]ethylamine	6.81	$C_{12}H_{17}N_3$	203	
7		Urea, 1-cyclohexyl-3-(2-pyridin-4-yl-ethyl)-	6.28	$C_{14}H_{21}N_3O$	247	
8		5-Cyano-4-oxo-2-phenylcarbamoylmethyl s ulfanyl-3-aza-spiro[5.5]undec-1-ene-1-carboxylic acid ethyl ester	3.81	$C_{22}H_{25}N_3O_4S$	427	
9		1-Benzyl-2,3,3-trimethyldiaziridine	2.84	$C_{11}H_{16}N_2$	176	
10	5.58	(3R,5Z)-3-hydroxyhept-5-enoic acid	60.21	$C_7H_{12}O_3$	144	0.70
11		Dodecane, 2,2,4,9,11,11-hexamethyl- (CAS)	14.88	$C_{18}H_{38}$	254	
12		Furan, tetrahydro-2-methyl-(CAS)	4.29	$C_5H_{10}O$	86	
13		Oxazolidine, 4,4-dimethyl-	3.37	$C_5H_{11}NO$	101	
14		Furan, tetrahydro-2-methyl-(CAS)	4.29	$C_5H_{10}O$	86	
15		1-Chlorohexylacetate	2.04	$C_8H_{13}ClO_2$	176	
16		Butane, 2,3-dimethyl-(CAS)	1.65	C_6H_{14}	86	
17		Butane, 2,2-dimethyl-(CAS)	1.23	C_6H_{14}	86	
18		3-Hydroxy-2,2-dimethylhexyl ester of butanoic acid	1.08	$C_{12}H_{24}O_3$	216	
19	6.14	BENZENE-1,3,5-D3	32.91	$C_6H_3D_3$	78	8.54
20		3-(Azidomethyl)cyclohexene	8.79	$C_7H_{11}N_3$	137	
21		Cyclohexene, 3-bromo-(CAS)	4.27	C_6H_9Br	160	
22		2,5,5-Trimethyl-cyclohex-3-enone	2.58	$C_9H_{14}O$	138	
23		3-Cyclohexen-1-one, 2,5,5-trimethyl-	2.58	$C_9H_{14}O$	138	

24		1,4-Hexadiene, 5-methyl- (CAS)	2.08	C_7H_{12}	96	
25		2-Pentyne, 4,4-dimethyl-	1.84	C_7H_{12}	96	
26		1,4-Hexadiene, 2-methyl-	1.55	C_7H_{12}	96	
27	7.07	Phenol, 2,6-dimethyl- (CAS)	9.55	$C_8H_{10}O$	122	0.71
28		Phenol, 2,5-dimethyl-	6.36	$C_8H_{10}O$	122	
29						
30		Phenol, 2,4-dimethyl- (CAS)	5.37	$C_8H_{10}O$	122	
31		3 - methyl - anisole and 4 - methyl - anisole	5.16	$C_8H_{10}O$	122	
32		benzeneethanamine, 4-methoxy-à-methyl-	4.76	$C_{10}H_{15}NO$	165	
33		3-Oxo-androsta-1,4-dien-17á-spiro-2'-3'-oxo-oxetane	4.58	$C_{21}H_{26}O_3$	326	
34	7.74	p-Methoxyamphetamine	24.50	$C_{10}H_{15}NO$	165	0.78
35		2-isopropylpyrimidine	6.81	$C_7H_{10}N_2$	122	
36		Phenol, 2,4-dimethyl- (CAS)	5.35	$C_8H_{10}O$	122	
37		Phenol, 3,4-dimethyl- (CAS)	4.73	$C_8H_{10}O$	122	
38		4-Methoxyamphetamine, N-acetyl	4.36	$C_{12}H_{17}NO_2$	207	
39		Phenol, 2,5-dimethyl- (CAS)	3.85	$C_8H_{10}O$	122	
40		Phenol, 3,5-dimethyl- (CAS)	3.55	$C_8H_{10}O$	122	
41		Phenol, 4-ethyl- (CAS)	3.00	$C_8H_{10}O$	122	
42	8.95	ç,ç-Dimethylallenyl - 1-Butynyl Sulfide	50.02	$C_9H_{12}S$	152	1.40
43		2,5-Diacetylfuran	13.09	$C_8H_8O_3$	152	
44		4-isopropenyl-5-methyl-4-hexen-1-al	6.35	$C_9H_{14}O_2$	154	
45		4-Acetyl-1,3,5-trimethylpyrazole	5.86	$C_8H_{12}N_2O$	152	
46		7,7-dimethylbicyclo[3.3.0]octan-2-one	4.61	$C_{10}H_{16}O$	152	
47		5-Methyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one	3.53	$C_9H_{12}O_2$	152	
48		5-tert-Butyl-1,3-dimethylpyrazole	3.25	$C_9H_{16}N_2$	152	
49		3-tert-Butyl-1,5-dimethylpyrazole	3.25	$C_9H_{16}N_2$	152	
50		3-Acetyl-2-amino-1H-pyridin-4-one	3.13	$C_7H_8N_2O_2$	152	
51		1-Methoxy-4-(1'-methylethyl)cyclohexa-1,4-diene	2.14	$C_{10}H_{16}O$	152	

52	10.0	2-Methoxy-3-methylhydroquinone	39.80	$C_8H_{10}O_3$	154	2.95
53		2,4-Dimethoxyphenol	31.28	$C_8H_{10}O_3$	154	
54		Phenol, 2,6-dimethoxy-	16.13	$C_8H_{10}O_3$	154	
55		2-Acetylcycloheptaneone	4.92	$C_9H_{14}O_2$	154	
56		Formic acid, 2,6-dimethoxyphenyl ester	4.73	$C_9H_{10}O_4$	182	
57		Phenol, 2,6-dimethoxy-(CAS)	16.13	$C_8H_{10}O_3$	154	
58		Phenol, 3,4-dimethoxy-(CAS)	1.86	$C_8H_{10}O_3$	154	
59	11.69	Kaempferol	28.00	$C_8H_8O_4$	168	1.12
60		2-Hydroxy-3-methyl-5-methoxy-p-benzoquinone	16.97	$C_8H_8O_4$	168	
61		4,5-Dimethoxy-2-methylphenol	12.32	$C_9H_{12}O_3$	168	
62		4-(1-Hydroxyethyl)-2-methoxyphenol	8.70	$C_9H_{12}O_3$	168	
63		Benzene, 1,2,3-trimethoxy- (CAS)	2.46	$C_9H_{12}O_3$	168	
64		Benzoic acid, 4-hydroxy-3-methoxy-(CAS)	0.72	$C_8H_8O_4$	168	
65		3,5,6-Trimethyl-2-methoxy-4pyrone	0.57	$C_9H_{12}O_3$	168	
66		(1R,4R,6R,9S)-4,9-Dimethyl-7-oxabicyclo[4.3.0]nonan-3 one-	0.45	$C_{10}H_{16}O_2$	168	
67		2-fluoro-4,7,7-trimethyltricyclo [2.2.1.0(2,6)]heptan-3-one	0.29	$C_{10}H_{13}FO$	168	
68	12.57	Octadecane(CAS)	7.11	$C_{18}H_{38}$	254	1.01
69		Hexadecane,2,6,10,14-tetramethyl- (CAS)	6.83	$C_{20}H_{42}$	282	
70		Nonadecane (CAS)	6.57	$C_{19}H_{40}$	268	
71		Hexadecane	6.57	$C_{16}H_{34}$	226	
72		Pentadecane	6.06	$C_{15}H_{32}$	212	
73		Hexadecane (CAS)	6.57	$C_{16}H_{34}$	226	
74		eicosane	6.06	$C_{20}H_{42}$	282	
75		Hexadecane, 2,6,11,15-tetramethyl- (CAS)	5.82	$C_{20}H_{42}$	282	
76		Hexadecane, 2,6,11,15-tetramethyl-	5.82	$C_{20}H_{42}$	282	
77		Tetradecane	5.37	$C_{14}H_{30}$	198	
78	13.27	2,3,5-Trimethoxytoluene	21.85	C10H14O3	182	0.86
79		1-(3,4-Dimethoxyphenyl)-1-ethanol	17.18	$C_{10}H_{14}O_3$	182	
80		1-Methyl-5-t-butyluracil	17.18	$C_9H_{14}N_2O_2$	182	
81		1-(5-Pentyl-2-furyl)ethan-1-ol	14.51	$C_{11}H_{18}O_2$	182	
82		1,2,4,5	9.66	$C_{\ }H_{\ }$	182	

		Tetravinylbenzene				
83		Benzene, 1,1'-ethylidenebis (CAS)	8.16	$C_{14}H_{14}$	182	
84		2-(N-Methylamino)-4,5-dimethoxyanilinemonohydrochloride	3.71	$C_9H_{14}N_2O_2$	182	
85		2,4-Dihydroxy-6-methoxy-acetophenone	1.24	$C_9H_{10}O_4$	182	
86		4,4'-Dimethylbiphenol	1.24	$C_{14}H_{14}$	182	
87		2-Carboxy-4-methylbicyclo[2.2.2]oct-2-en-1-ol	0.92	$C_{10}H_{14}O_3$	182	
88	17.08	Docosane (CAS)	6.30	$C_{22}H_{46}$	310	1.16
89		Docosane, 11-decyl- (CAS)	5.81	$C_{32}H_{66}$	450	
90		Heptadecane, 2,6,10,15-tetramethyl- (CAS)	5.36	$C_{21}H_{44}$	296	
91		Tricosane	5.15	$C_{23}H_{48}$	324	
92		Tetradecane, 2,6,10-trimethyl-	4.75	$C_{17}H_{36}$	240	
93		Eicosane	4.57	$C_{20}H_{42}$	282	
94		Tridecane, 2-methyl-	4.03	$C_{14}H_{30}$	198	
95	18.40	Benzhydryl vinyl ether	19.21	$C_{15}H_{14}O$	210	1.26
96		1,2-Diphenylpropan-2-one	14.33	$C_{15}H_{14}O$	210	
97		N'-(5-Acetyl-6H-thiopyran-2-yl)-N,N-dimethylformamidine	8.68	$C_{10}H_{14}N_2OS$	210	
98		(2R)-2-Cyclopentylmethylhexan-1-ol	8.01	$C_{12}H_{24}O$	184	
99		diphenyldithioessigsaure-methylester	6.29	$C_{15}H_{14}S_2$	258	
100		(E)-3-(4-Biphenylyl)-2-propen-1-ol	6.05	$C_{15}H_{14}O$	210	
101		1,1-Diphenyl-2-methylpropane	3.66	$C_{16}H_{18}$	210	
102		7,7-(2,2 Dimethylpropylidenedioxy)bicyclo[3.3.0]octane-3-one	3.24	$C_{13}H_{20}O_3$	224	
103		4-Butyl-1,1'-biphenyl	2.73	$C_{16}H_{18}$	210	
104		2-Pentanone, 1-(2,4,6-trihydroxyphenyl)	1.93	$C_{11}H_{14}O_4$	210	
105	19.27	2à,10à-Epidioxy-3á-iodo-5,10-secocholestan-5-one	32.05	$C_{27}H_{45}IO_3$	544	0.67
106		6-á-Hydroxy-4-oxa-4a-homo-5ácholest-4a-en-3-one	25.19	$C_{27}H_{44}O_3$	416	
107		1,3-Dimethyl-2,4-dioxo-6-(2-phenylethenyl)-8-phenyl-1,2,3,4-tetrahydro[1.2.4]triazolo[3,4-f]purine	12.99	$C_{22}H_{18}N_6O_2$	398	

108		5,6-Dihydro1-methoxy-3,4-bis(methoxycarbonyl)-12-meth yl-4aH,12H-2,11-dithiachrysene	8.65	$C_{22}H_{22}O_5S_2$	430	
109		N-Benzyl-N-(2-chlorobenzyl)-N-(2-bromo-3-(2-chlorophen oxy)propyl)amine	7.31	$C_{23}H_{22}BrCl_2NO$	477	
110		7-(Trimethylsilyloxy)-3-[4-(trimethylsiloxy)phenyl]-4H-1-b enzopyran-4-one	2.11	$C_{21}H_{26}O_4Si_2$	398	
111		2à,10à-Epidioxy-5,10-secocholest-3-en-5-one	1.65	$C_{27}H_{44}O_3$	416	
112		5,5'-Bis(2-chloroethoxy)-4,4'-dimethoxy-2,2'-dimethylbiphenyl	1.53	$C_{20}H_{24}Cl_2O_4$	398	
113		1-[4'-Chlorobenzyl)(2,5-dimethoxyphenyl)]-2,5-dimethoxbenzene	1.08	$C_{23}H_{23}ClO_4$	398	
114		3-Cyano-2-ethoxy-4-phenyl-6,7-dihydropyrido[3',2':4,5]t hi eno[3,2-b]quinolin-9(8H)-one	0.82	$C_{23}H_{17}N_3O_2S$	399	
115		Eicosane, 2-methyl-	8.14	$C_{21}H_{44}$	296	
116		Docosane (CAS)	7.19	$C_{22}H_{46}$	310	
117		Nonane, 5-methyl-5-propyl-	5.51	$C_{13}H_{28}$	184	
118		Heptacosane	5.08	$C_{27}H_{56}$	380	
119	21.42	2-methyloctacosane	4.10	$C_{29}H_{60}$	408	0.87
120		Docosane, 11-decyl-(CAS)	2.89	$C_{32}H_{66}$	450	
121		Hexadecane, 1-iodo-	2.78	$C_{16}H_{33}I$	352	
122		Tridecanol, 2-ethyl-2-methyl-	2.67	$C_{16}H_{34}O$	242	
123	24.80	(10RS,2E,6E)-and(10S,2E,6E)-10-(1',3'-Dioxolan-2'-yl)-3,7,11-trimethyl-1-(tert-butyldimethylsiloxy)dod eca-2,6-diene	72.46	$C_{24}H_{46}O_3Si$	410	4.24
124		3,3',5,5'-tetrakis(t-Butyl)-1,1',4,2'-tetrahydro-diphenylene-2,4'-dione	10.09	$C_{28}H_{40}O_2$	408	
125		3-(4'-Acetanilido)-5,6-diphenylimidazo[2,1-b]thiazole	9.70	$C_{25}H_{19}N_3OS$	409	
126		3-Acetoxy-24-methyl-5-cholest-5,22-dien-7-one	4.71	$C_{31}H_{48}O_3$	468	
127		2,3,6,7-Tetrahydro-3	0.86	$C_xH_yN_zO$	409	

		methyl-5-piperidyl-2-phenyl-1H-naphth[1,2-e]indazol-1-one				
128		7-(4-Dimethylaminophenyl)-3,3,12-trimethyl-3,12-dihydro-6H-pyrano[2,3-c]acridin-6-one	0.83	$C_{27}H_{26}N_2O_2$	410	
129		2,3,4,5,6-Pentakis(pyrazol-1'-yl)pyridine	0.67	$C_{20}H_{15}N_{11}$	409	
130		3-Chloro-4-oxo-2-(2'-benzothiazolyl)pyrazolo[3',4' : 4,5]pyrimido[2,1-b]benzothiazole	0.38	$C_{18}H_8ClN_5OS_2$	409	
131		2-(1'-Naphthyl)-4-[2"-oxo-1"-(ethoxycarbonyl)cyclopent- yl]-1" quinoline	0.08	$C_{27}H_{23}NO_3$	409	
132		(2S,5R,6S,8R,9R)-5,6-Diphenyl-8,9-dicarbomethoxy-1-az a-4-oxabicyclo[4.3.0]nonan-3-one	0.07	$C_{23}H_{23}NO_6$	409	
133	25.23	Dicyano[2.4]-2-methyl-4-t-butylmetacyclophan-1-ene	40.71	$C_{30}H_{36}N_2$	424	7.04
134		9-Diethylamino-1,2,3,4,6-pentafluoro-5H-benzo[a]phenoxzin-5-one 12- oxide	26.30	$C_{20}H_{13}F_5N_2O_3$	424	
135		7-Methoxymethyl-1-(trimethylsilyl)-1-[1,1-bis(trimethylsilyl)ethyl]-2-oxa-1-silaindane	24.26	C20H40O2Si4	424	
136		7-(4-Dimethylaminophenyl)-3,3,12-trimethyl-3,12-dihydro-6H-pyrano[2,3-c]acridin-6-one	3.30	$C_{27}H_{26}N_2O_2$	410	
137		(10RS,2E,6E)-and(10S,2E,6E)-10-(1',3'-Dioxolan-2'-yl)-3,7,11-trimethyl-1-(tert-butyldimethylsiloxy)dodeca-2,6-diene	2.53	$C_{24}H_{46}O_3Si$	410	
138		N,N'-Dicyano-2,3-diphenylpyrazino[2,3-b]naphthoquinodimine	0.92	$C_{26}H_{14}N_6$	410	
139		7-Ethoxymethyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)methyl]-2-oxa-1-silaindane	0.72	$C_{20}H_{40}O_2Si_4$	424	
140		3à-H-2'-	0.15	$C_{...}H_{...}O_{...}$	442	

		Oxofurano[2,3]cholestan-5à-ol				
141		3-(4'-Acetanilido)-5,6-diphenylimidazo[2,1-b]thiazole	0.12	$C_{25}H_{19}N_3OS$	409	
142		3á(-Dimethylphenylsiloxy)-5à,13à-androstane-17-one	0.09	$C_{27}H_{40}O_2Si$	424	
143		Cholestan-26-oic acid, 3,7,12,24-tetrakis(acetyloxy)-,methyl ester, (3à,5á,7à,12à)- (CAS)	10.07	$C_{36}H_{56}O_{10}$	648	
144		à-D-Galactopyranoside, methyl2-(acetylamino)-2-deoxy-6-O-methyl-3,4-bis-O-(trimethylslyl)-	4.89	$C_{16}H_{35}NO_6Si_2$	393	
145	26.66	24,28-methylene-fucosterol;2nd24,28-diastereomer	4.51	$C_{30}H_{50}O$	426	2.66
146		Gorgosterol	4.33	$C_{30}H_{50}O$	426	
147		Prosta-5,11-dien-1-oic acid, 9-oxo-11,15bis[(trimethylsilyl) oxy], trimethylsilyl ester,(5Z,11à,13E,15S)-	4.33	$C_{29}H_{56}O_5Si_3$	568	
148		Progesterone	3.66	$C_{21}H_{30}O_2$	314	
149		ç-Lactone of 18-hydroxydeoxycortexone	3.37	$C_{20}H_{26}O_3$	314	
150		pregn-4-ene-3,20-dione	3.66	$C_{21}H_{30}O_2$	314	
151	28.97	2,7-Di-tert-Butyl-3,6-diphenylbiphenylene	26.16	$C_{32}H_{32}$	416	6.77
152		16-(Acetoxymethyl)-21-oxobenzo[g]indolo[2,3-a]quinolizne-19-yl acetate]	21.08	$C_{24}H_{20}N_2O_5$	416	
153		(1R*,2R*,5R*,6S*)-2-(3,4-Dimethoxy)phenyl-6-(3,4,5-tri methoxy)phenyl-3,7-dioxabicyclo[3.3.0]octane	18.63	$C_{23}H_{28}O_7$	416	
154		(5à,6à)-4,5-Epoxy-17-methyl-3-phthalimidomorphinan-6-ol	13.15	$C_{25}H_{24}N_2O_4$	416	
155		2,14-dimethoxycarbonyl-6,9-dimethoxy-2-thia[3.2]methacclophenane	5.59	$C_{22}H_{24}O_6S$	416	
156		15-Deoxy-12-hydroxy-10-(trifluoromethyl)ë(7)-PGA(1) methyl ester	3.61	$C_{22}H_{31}F_3O_4$	416	

157		4-Ethylenedioxy-3,5-difluoro-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4b']dithiophene	3.40	$C_{17}H_{22}F_2O_2S_2Si_2$	416	
158		5-(2-Methoxyphenyl)porphyrin	2.38	$C_{27}H_{20}N_4O$	416	
159		1,5-Dimethyl-6-(1,5-dimethylhexyl)-18oxatetracyclo[9.6.1.0(2,10).0(5,9)]octdecane-13,15-dione	2.01	$C_{27}H_{44}O_3$	416	
160		(3á-5Z,7E,24R)-9,10-Secocholesta-5,7,10(19)-triene-3,24,25-triol [24R,25-dihydroxyvitamin D3]	1.15	$C_{27}H_{44}O_3$	416	
161		6a,14a-Methanopicene, perhydro-1,2,4a,6b,9,9,12a-heptamethyl-10-hydroxy-	4.90	$C_{30}H_{50}O$	426	
162		Acetic acid,	4.90	$C_{32}H_{52}O_2$	468	
163		17-(1,5-dimethyl-hexyl)-4,4,10,13,14-pentamethyl-2,3,4,5,8,10,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]penanthren-3-ol (ester)	4.90	$C_{32}H_{52}O_2$	468	
164	30.50	(acetylacetonato)[(1S,9S)-5-cyano-1,9-bis(methoxycarbonyl)semicorrinato]copper(II)	4.71	$C_{30}H_{50}O$	426	4.19
165		9,19-Cyclolanost-7-en-3-ol	4.71	$C_{30}H_{50}O$	426	
166		Lup-20(29)-en-3-ol, acetate, (3á)-	4.35	$C_{32}H_{52}O_2$	468	
167		Lupeyl acetate	4.35	$C_{32}H_{52}O_2$	468	
168		6a,14a-Methanopicene, perhydro-1,2,4a,6b,9,9,12a-heptamethyl-10-hydroxy-	4.18	$C_{30}H_{50}O$	426	
169		Toosendanin	3.28	$C_{30}H_{38}O_{11}$	574	
170		13,27-Cycloursan-3-ol, acetate, (3á,13á,14á)-	2.77	$C_{32}H_{52}O_2$	468	
171	30.75	2,2-Dimethyl-9-methoxy-10-hydroxy-bis-2H-chromeno[bepyran-12(6H)-one	66.00	$C_{22}H_{18}O_6$	378	3.72
172		5,6,8-Trimethoxy-7-	13.05	$C_{23}H_{26}N_2O_3$	378	

		pyrrolidinyl)-4-phenylquinoline				
173		Fluprednisolone	3.70	$C_{21}H_{27}FO_5$	378	
174		11-(2,4,6-cycloheptatriene-1-yl)-5,12-dimethoxynaphth[2,-a]azulene	3.41	$C_{27}H_{22}O_2$	378	
175		Ergosta-5,7,22-trien-3-ol, (3á,22E)- (CAS)	2.68	$C_{28}H_{44}O$	396	
176		5-t-Butyldimethylsilyloxy-1,2,3,4,5,6-hexahydro-9-methoxy-3,8,11-trimethyl-10-nitro-1,5-imino-3-benzazocin-4-one	2.47	$C_{21}H_{33}N_3O_5Si$	435	
177		Demethyl-Calabaxanthone	1.99	$C_{23}H_{22}O_5$	378	
178		1,4,9(11)-Pregnatriene-3,20-dione, 21-acetoxy-17-hydroxy-	1.14	$C_{23}H_{28}O_5$	384	
179		1,3-Bis(4-methylbenzylidene)-4-phenylcyclohexan-2-one	1.05	$C_{28}H_{26}O$	378	
180	31.40	Di-(2-ethylhexyl)phthalate	29.47	$C_{24}H_{38}O_4$	390	3.97
181		1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester(CAS)	29.47	$C_{24}H_{38}O_4$	390	
182		Phthalic acid, di(2-propylpentyl) ester	17.86	$C_{24}H_{38}O_4$	390	
183		1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester(CAS)	29.47	$C_{24}H_{38}O_4$	390	
184		1,2-Benzenedicarboxylic acid, dioctyl ester (CAS)	8.67	$C_{24}H_{38}O_4$	390	
185		1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	7.66	$C_{16}H_{22}O_4$	278	
186		1,2-Benzenedicarboxylic acid, dioctyl ester (CAS)	8.67	$C_{24}H_{38}O_4$	390	
187		1,2-benzenedicarboxylic acid	29.47	$C_{24}H_{38}O_4$	390	
188		Diisooctyl phthalate	4.64	$C_{24}H_{38}O_4$	390	
189	32.28	Nonacosane (CAS)	15.87	$C_{29}H_{60}$	408	3.30
190		Octadecane, 3-ethyl-5-(2-ethylbutyl)-	14.02	$C_{26}H_{54}$	366	
191		Heptadecane, 9-hexyl-	4.12	$C_{23}H_{48}$	324	
192		Dotriacontane (CAS)	2.83	$C_{32}H_{66}$	450	
193		Octacosane (CAS)	2.50	$C_{28}H_{58}$	394	
194		Tetratetracontane (CAS)	2.40	$C_{44}H_{90}$	618	
195		Nonadecane (CAS)	2.31	$C_{19}H_{40}$	268	
196	33.30	2,9-bis(2',6'-	60.16	$C_{28}H_{24}N_2O_4$	452	1.95

		phenanthroline				
197		3-(3",5"-Dimethoxy-4"-hydroxyphenyl)diosmetin	14.87	$C_{24}H_{20}O_9$	452	
198		(R)-[4,4'-bis(dimethylamino)-6,6'-dimethylphenyl-2,2'-diyl]bis(diphenylphosphine)	10.20	$C_{42}H_{42}N_2P_2$	636	
199		1,3-Bis(4-nitrobenzyl)-5,6-dihydrobenzo[f]quinazoline	8.61	$C_{26}H_{20}N_4O_4$	452	
200		1,3-Dimethyl-2,4-dioxo-6-(phenylcarbamoyl)-8-(p-chloro phenyl)-1,2,3,4-tetra hydro[1.2.4]triazolo[3,4-f]purine	1.50	$C_{21}H_{16}ClN_7O_3$	449	
201		(RS)-[4,4'-bis(dimethylamino)-6,6'-dimethylphenyl-2,2'-diyl]bis(diphenylphosphine)	1.21	$C_{42}H_{42}N_2P_2$	636	
202		2-Bromo-8,9-dihydro-4,6,7a-trihydroxy-5-methoxy-1,8,8, 9-tetramethyl-3H-phenaleno[1,2-b]furan-3,7(7aH)-dione	0.69	$C_{20}H_{19}BrO_7$	450	
203		N-fluoresceinylbenzamide	0.58	$C_{27}H_{17}NO_6$	451	
204		4,6-Dimethoxy-3-methyl-2,7-di(3'-phenylprop-2'-enoyl)inole	0.46	$C_{29}H_{25}NO_4$	451	
205		(1R,6S,7S)-7-[(2S)-2-(Methoxymethyl)pyrrolidino]-11-eth oxy-8-ethoxycarbonyl-9-phenyltricyclo[5.2.2.0(1,6)]undeca-8,10-diene	0.37	$C_{28}H_{37}NO_4$	451	
206	33.87	N-Methoxycarbonyl-2,3-bis(bromomethyl)indole	6.94	$C_{12}H_{11}Br_2NO_2$	359	0.86
207		2-(4-Ethoxy-phenyl)-4,4-diethyl-1,4-dihydro-2H-benzo[d][,3]oxazine	6.13	$C_{20}H_{25}NO_2$	311	
208		1,9-Bis(trimethylsiloxy)nonane	4.26	$C_{15}H_{36}O_2Si_2$	304	
209		2-Methoxy-6-(quinolin-2-yl)pyridino[4,5-b]indole-8-carb oxylic acid	3.93	$C_{22}H_{15}N_3O_3$	369	
210		1,3-Bis(dibromomethyl)-2-methoxybenzene	3.77	$C_9H_8Br_{4O}$	448	

211		(13R,14R)-13,14-Dihydroxyretinol	2.97	$C_{20}H_{32}O_3$	320	
212		b-nitroisoeugenol-trifluoroacetyl derivative	2.73	$C_{12}H_{11}F_3NO_5$	306	
213		á-Nitroisoeugenol - trifluoroacetyl derivetive	2.73	$C_{12}H_{10}F_3N\ O_5$	305	
214		15-exo-acetoxy-3-acetyl-3,4,4A-endo,5,6,10B-hexahydro-6,10B-ethano-dibenzo (A,K)phenanthridine	2.31	$C_{27}H_{25}NO_3$	411	
215		2,6-Di-t-butyl-4-(2-methylphenyl)aniline	7.38	$C_{21}H_{29}N$	295	
216		3-Acetyl-1-ethyl-6-hydroxy-2-(p-methoxyphenyl)indole	5.36	$C_{18}H_{17}NO_3$	295	
217		2-(2'-Methylpiperidino)naphtho [2,3-b]furan-4,9-dione	5.15	$C_{18}H_{17}NO_3$	295	
218		3-Acetyl-1-ethyl-5-hydroxy-2-(p-methoxyphenyl)indole	4.95	$C_{18}H_{17}NO_3$	295	
219		2,5,8-Trimethoxy-4-phenylquinoline	4.95	$C_{18}H_{17}NO_3$	295	
220		1-Isocyano-2-[1-(2,4,6-rimethoxyohenyl)ethenyl]benzene	4.37	$C_{18}H_{17}NO_3$	295	
221		3-Octyl-2,4,5-trimethoxyaniline	4.03	$C_{17}H_{29}NO_3$	295	
222	34.34	1-methyl-4-phenyl-5,8-dimethoxy-2(1H)-quinolinone	4.03	$C_{18}H_{17}NO_3$	295	2.56
223		4-Octadienoic acid, 9a-(acetyloxy)-1a,1b,4,4a,5,7a,7b,8,9,9a-decahydro-4a,7b-dihydroxy-3-(hydroxymethyl)-1,1,6,8-tetramethyl-5-oxo-1	3.72	$C_{30}H_{40}O_8$	528	
224		H-cyclopropa[3,4]benz[1,2-e]azulen-9-yl ester, [1aR-[1aà,1bá,4aá,7aà,7bà,8à,9á(2Z,4E),9aà]]-1-(2-Hydroxy-3,4-dimethoxybenzyl)isoquinoline	3.57	$C_{18}H_{17}NO_3$	295	
225	35.52	Spirost-8-en-11-one, 3-hydroxy-, (3á,5à,14á,20á,22á,25R)-	9.58	$C_{27}H_{40}O_4$	428	0.68
226		Butanoic acid, 1a,2,5,5a,6,9,10,10a-	7.72	$C_{24}H_{34}O_6$	418	

		methyl)-1,1,7,9-tetramethyl-11-oxo-1H-2,8a-methanocycl openta[a]cyclopropa[e]c yclodecen-6-yl ester,[1aR-(1aà,2à,5á,5aá,6á,8aà,9à,10aà)]-				
227		3Beta,17beta-diacetoxy-5-chloro-6beta-nitro-5alpha-androstane	7.72	$C_{23}H_{34}ClNO_6$	455	
228		17á-Acetoxy-1',1'-dicarboethoxy-1á,2á-dihydrocycloprop[1,2]-5à-androst-1-en-3-one	7.12	$C_{28}H_{40}O_7$	488	
229		Pregn-4-en-18-al, 11,21-dihydroxy-3,20-dioxo-, (11á) (CAS)	4.32	$C_{21}H_{28}O_5$	360	
230		Stigmast-5-en-3-ol, (3á,24S)- (CAS)	3.39	$C_{29}H_{50}O$	414	
231		Pregnane-3,11,20-trione, (5á) (CAS)	2.73	$C_{31}H_{50}O_3$	470	
232		13,14-Epoxyursan-3-ol, acetate	2.73	$C_{31}H_{50}O_3$	470	
233	35.97	Ergost-5-en-3-ol, (3á,24R)- (CAS)	20.29	$C_{28}H_{48}O$	400	10.26
234		ERGOST-5-EN-3á-OL	20.29	$C_{28}H_{48}O$	400	
235		Campesterol	20.29	$C_{28}H_{48}O$	400	
236		(E)-5,10-secocholest-1(10)-en-3,5-dione	12.29	$C_{27}H_{44}O_2$	400	
237		5-Cholestene-3-ol, 24-methyl-	8.92	$C_{28}H_{48}O$	400	
238		Ergost-5-en-3-ol, (3á,24R)- (CAS)	20.29	$C_{28}H_{48}O$	400	
239		Ergost-5-en-3-ol, (3á)-	20.29	$C_{28}H_{48}O$	400	
240		7á-Methylcholesterol	5.94	$C_{28}H_{48}O$	400	
241	37.40	Stigmasta-5,22-dien-3-ol, (3á,22E)- (CAS)	26.90	$C_{29}H_{48}O$	412	4.95
242		Stigmasterol	26.90	$C_{29}H_{48}O$	412	
243		Hexadecanoic acid, 2-(octadecyloxy)ethyl ester (CAS)	7.91	$C_{36}H_{72}O_3$	552	
244		D-prim-cortisone	6.99	$C_{21}H_{28}O_5$	360	
245		Stigmasta-5,22-dien-3-ol, (3á,22E)- (CAS)	26.90	$C_{29}H_{48}O$	412	
246		Pregna-1,4-diene-3,11,20-trione, 17,21-dihydroxy- (CAS)	6.72	$C_{21}H_{26}O_5$	358	
247		Pregnenolone	5.94	$C_{21}H_{32}O_2$	316	
248		Bufa-20,22-dienolide, 3-(acetyloxy)-14,15-epoxy-16-oxo-, (3á,5á,15á)-	4.55	$C_{26}H_{32}O_6$	440	
249	38.42	2,6,10,14,18,22-	10.46	$C_{30}H_{48}$	408	4.03

		2,6,10,15,19,23-hexamethyl-, (all-E)-, didehydro deriv.,				
250		(14-methoxy-5,13,13-trimethyl-8-oxo-9,15-dioxapentacycl o[12.2.2.1(2,6).0(1,2).0(10,19)]nonadec-11-en-5-yl)methymethylcarbonate	5.39	$C_{24}H_{34}O_7$	434	
251		Carbonate(methyl), (14-methoxy-5,13,13-trimethyl-8-oxo-9,15-dioxapentacycl o[12.2.2.1(2,6).0(1,2).0(10,19)]nonadec-11-en-5-yl)methyl	4.97	$C_{24}H_{34}O_7$	434	
252		Octanoic acid, 2-methylcyclohexyl ester, trans- (CAS)	3.61	$C_{15}H_{28}O_2$	240	
253		Pregnan-20-one, 5,6-epoxy-3-hydroxy-, (3á,5à,6à)- (CAS)	2.62	$C_{21}H_{32}O_3$	332	
254		Desacetylcinobufotalin	2.52	$C_{24}H_{32}O_6$	416	
255		Pregn-4-ene-3,20-dione, 17,19,21-trihydroxy-	2.32	$C_{21}H_{30}O_5$	362	
256		Pregnan-20-one, 3-hydroxy-, (3à,5à)- (CAS)	2.32	$C_{21}H_{34}O_2$	318	
257	39.84	(R)-(-)-2-Amino-2'-(diphenylphosphino)-1,1'-binaphthyl	33.30	$C_{32}H_{24}NP$	453	6.93
258		2,8-Dichloro-3,7-dihydroxy-5-methoxy-4,6-diphenyldibenophosphol e 5-Oxide	13.16	$C_{25}H_{17}Cl_2O_4P$	482	
259		7-(2"-Hydroxyisopropyl)-4,5-epoxy-18,19-dihydro-3,6-di methoxy-17-(3',3'-dimethylallyl)-6,14-ethenomorphinane	3.94	$C_{28}H_{39}NO_4$	453	
260		Methyl(3aS*,10bR*)-2-(Bromomethylene)-10-methyl-10b-phenyl-2,3,4,5,10,10b-hexahydro-3aH-furo[2,3-a]carbazole-3a-carboxylate	3.79	$C_{24}H_{22}BrNO_3$	451	
261		Carotene	3.49	$C_{40}H_{56}$	536	
262		6-Methoxy-4-(4'-methoxyphenyl)-9-(2',4',6'-trimethylphen yl)-1H,3H-naphtho[2,3-c]furan-1,3-dione	3.36	$C_{29}H_{24}O_5$	452	

263		2-Formyl-3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]ph osphepine 3-oxide	2.10	$C_{33}H_{21}O_2P$	480	
264		10-Hydroxy-neoline	1.77	$C_{24}H_{39}NO_7$	453	
265		7-[(1'-Hydroxy-1'-methyl)ethyl]-4,5-epoxy-18,19-dihydro-,6-dimethoxy-17-(3",3"-dimethylallyl)-6,14-ethenomorphinane	1.70	$C_{28}H_{39}NO_4$	453	
266		6E-Hydroximinogorgost-4-en-3-one	1.70	$C_{30}H_{47}NO_2$	453	

4. Conclusion

In this study, the pyrolysis oil was identified as a biofuel candidate. Analytical methods for the identification of volatile compounds are the key to studying their formation and functions in biological interactions. The present study successfully identified their hydrocarbons and other volatile compounds present in the pyrolysis oil and the GC–MS measurement is achieved in a fully programmed way, the presented approach offers an interesting and powerful tool for the study of the dynamic range of volatile compounds. The application of the method resulted in the identification of more than 250 different volatile compounds.

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