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# Fluids Production from Wood Wastes via Pyrolysis

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Abstract- Woody pruning residues of fast-growing species, namely Casuarina glauca, C. cunninghamiana, Eucalyptus camaldulensis, E. microtheca, Prosopis juliflora, Acacia ampliceps, Ficus retusa, Citrus sinensis, Malus domestica, and Psidium guajava were pyrolyzed at 450°C with 2.5°C/minutes in a flowing N<sub>2</sub>-atmosphere. Properties of the pyrolytic fluidy products, namely distillate and noncondensible gases (NG) were determined. They were species dependent except for the yields of N<sub>2</sub>-liquid trap distillate (NLTD) and NG. The yield of NLTD ranged from 20.37 % to 30.64 % with GHC varying from 3658 to 4923 calories/g for E. camaldulensis and F. retusa, respectively. The range of NG yield ranged from 28.4 % to 38.4%.

Chemical identification of the methylene chloride fraction (MCF) from the NLTD was made using GLC-MS. The highest phenolics content in the MCF was 73.01% for *E.camaldulensis*. Syringol, with the highest yield generally, and guaiacol were detected in all MCF's except for *M. domestica* and *P.guajava* that were free of guaiacol. Further, *C. cunninghamiana* had the highest content of aromatics other than phenolics (48.01 %). The highest heterocyclics content was detected for *E. microtheca* (31.12%) with the predominance of 3-acetyl-6-methyl-pyran-2, 4-dione. *P. guajava* had the highest aliphatics content (80.14%), especially hexadecanoic acid.

**Keywords**- Wood, Pyrolysis, Distillate, noncondensible gases, Gross heat of combustion, GLC-MS.

## I. INTRODUCTION

Agro-biomasses are more challenging feedstocks for energy use due to the high amount of alkali metals and nitrogen in the oil. In addition, they produce more water during pyrolysis, causing phase instability [1].

Biomass can be converted into charcoal, pyrolytic distillate, and noncondensable gases by the dry thermal distillation process, namely pyrolysis in absence of air. The proportions of the three pyrolytic products appear to be somewhat related to both type of raw material and process conditions [2].

Considerable efforts have been made to convert wood biomass to liquid fuels and chemicals since the oil crisis in mid-1970s [3].

Chemical fractionation of bio-oil showed that only low quantities of hydrocarbons were present, while oxygenated and polar fractions dominated [4].

The advantages of the pyrolytic distillate are that its easy to handle than raw biomass, its much high energy density, its lower contents of nitrogen and sulphur comparing with other fossil fuels, and its wealthy as a chemical feedstock. On the other hand, its disadvantages are that it may be highly oxyginated, viscous, corrosive, relatively unstable, chemically very complex, and in gasification processes, its tar is considered as very undesirable and likely to cause operating problems (especially condensation in transfer lines). The utilization of the pyrolysis oil is confined now to be a source of energy [2].

The major properties of the pyrolysis oil that can used as a measure of its quality are: chemical propertis, namely acidity, organic fatty acids content, pyrolytic alcohol content, phenolic content, polycyclic aromatic hydrocarbons content, and ash content, and physical propertis, namely the yield, gross heat of combustion, viscosity, flash point, flame temperature, corrosivity, solidifying point, and pour point.

Since the evolved noncondensable gases have medium calorific values, they are used for drying wood and heating processes of the charge during pyrolysis as well as steam production [2].

The oils produced by slow pyrolysis had lower oxygen content due to secondary reactions of dehydration, decarboxylation and condensation [5]

It has been indicated by [6] and [7] that the liquid phase should be optimized by removing the condensible volatiles from the heated zone as rapidly as possible to prevent secondary reactions to occur. They suggested two possible explanations for occurrence of Pyrolytic distillate. The higher flow rate of an inert gas used may reduce yield of distillate be removing volatiles which have not had adequate time to form condensible compounds. The second possibility is concerned with this particular reactor and the size of the liquid nitrogen trap. Perhaps some of the less condensible compounds are removed before they are adequately cooled for condensation to occur and, consequently, lower yield of distillate is obtained.

Isolation of phenols from *Eucalyptus* wood pyrolysis tar was carried out with the objective of recovering valuable pure phenols, such as phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol [8]

Ghetti et al [9] pyrolyzed different biomass materials at 450°C in a flowing helium gas. They found that the quality of biomass-derived oil depending on the lignin content of the starting material. Thus, with a lower lignin content, as in *Triticum aestivum*, *Sorghum bicolor* and *Hibiscus cannabinus*, a lighter pyrolysis product was obtained, while biomass with higher lignin content, such as *Miscanthus siensis*, *Cynara cardunculus*, *Populus nigra* and *Pinus pinea*, produced a heavier tar

It was found that the chemical composition of the biomass samples influenced the distribution of the pyrolysis products [10]. An aqueous smoke flavouring from oak (*Quercus* sp.) sawdust contained aldehydes, ketones, diketones, esters, alcohols, acids, furan and pyran derivatives, syringol, guaiacol, phenol and pyrocatechol derivatives, alkyl and aryl ethers. In addition, some furan and pyran derivatives is noteworthy, as well as a significant number of lignin dimers in low proportion, a considerable number of anhydrosugars in very high proportion and some nitrogenated derivatives in low proportions were detected [11].

Raveendram et al [12] found that the liquid yields from different biomass types varied from about 22 % for wood to almost double that figure for groundunt shell and rise husk.

It was indicated that removing ash increases the rate of releasing of volatiles and the residence time available for volatiles inside the biomass particle decreases that allowing volatiles to escape rapidly without condensation or cracking. Thus, higher molecular weight-compounds being accumulated in liquids, consequently, the heating value of the liquids increase [13]. Furthermore, it was found that the guaiacol-type and syringol-type compounds as the primary products of lignin pyrolysis are predominant in bio-oil, acting as the significant precursors for the formation of the derivatives such as the phenol-, cresol- and catechol-types. A series of freeradical chain-reactions, concerning the cracking of different side-chain structures and the methoxy groups on aromatic ring, are proposed to demonstrate the formation pathways for the typical compounds in bio-oil by closely relating lignin structure to the pyrolytic mechanisms. The methoxy group is suggested to work as an important source for the formation of the small volatile species (CO, CO<sub>2</sub> and CH<sub>4</sub>) through the relevant free radical coupling reactions [14].

In general, softwood pyrolysis oil is higher in calorific value, presumably due to the resin content in the wood. Furthermore, extremely good yields of tar and naval stores (turpentine and pine oil) can be extracted from these oils, which make them a valuable fuel [15]. It was found by Raveendran and Ganesh [16] that heating values of liquids are comparable with those of oxygenated fuel such as methanol and ethanol which are much lower than those of petroleum fuels. Further, the heating value is a function of the initial composition of biomass (celulose, lignin and silica-free ash content).

This study was initiated to evaluate the properties of the pyrolytic distillate as well as yield of noncondensible gases produced in the laboratory from ten species of timber and fruit trees grown in Egypt and study the chemical composition of the methylene chloride fraction (MCF) obtained from  $N_2$ -liquid trap distillate (NLTD) from each species which is an indicator of the aromatic compounds content resulted mainly from thermal degradation of lignin and chemical recovery.

## II. MATERIALS AND METHODS

#### 2.1. Raw materials

There are large quantities of wood branches resulted annually in Egypt from prunning processes of timber trees specially *Ficus retusa* and the common fruit trees such as *Citrus sinensis, Malus domestica* and *Psidium guajava*. Accordingly, the main raw material used for charcoal production is wood from timber trees specially casuarina and eucalypt and old or non-productive fruit trees as well as the prunnings yield [17].

Branches of ten hardwood species, namely Casuarina glauca Sieb., Casuarina cunninghamiana Miq., Eucatyptus camaldulensis Dehn., Eucalyptus microtheca F.V.M., Prosopis juliflora D.C., Acacia ampliceps MSLN, Ficus retusa Linn., Citrus sinensis Osbeck, Malus domestica Borkh. and Psidium guajava Linn. were used. Three trees were selected from each species from the same location. The ages of the selected trees ranged from 11-15 years old. The ages of the chosen branches were nearly similar in all species and varied from 6 to 8 years. The diameter outside bark of the selected trees ranged from 15-45 cm. From each of the selected trees, one of the primary branches was selected. Accordingly, three branches were selected from each species. The diameter outside bark of the selected branches ranged from 8-15 cm. Each of the selected branches was cut at height of 10 cm above its base at about 140-170 cm above ground level for C. glauca, C. cunninghamiana, and F. retusa, and 40-90 cm for the other species. From each isolated branch, one disc of about 20 cm along the grain was cut at height of 10 cm above the branch base that was specified for the determinations of wood properties. Furthermore, subsequent disc, about 30 cm thick along the grain, was cut and used for pyrolysis process and consequently for the determinations of pyrolytic products properties. For the disc specified for pyrolysis process, one bolt (about 1.8 cm tangentially and 30 cm long) from heartwood was cut longitudinally. A diametric strip (nominal 1.8 cm tangentially and radially, and 30cm longitudinally) was removed and subsequently crosscut into 12 cubic samples free of visible defects that were specified for each run.

# 2.2. Pyrolysis

The pyrolysis runs were carried out with a bench scale reactor [18] which consists of an electric tube furnace (carbolite furnace modle MTF 12/338) controlled by a microprocessor temperature programmer with an error of  $\pm 5^{\circ}$ C with an accuracy of 1°C and heating rate of 0.01°C/min., digital thermometer with a chromel alumel thermocouple (type K with an error of  $\pm 1^{\circ}$ C), nitrogen regulator system consisted of a regulator and a flowmeter with an accuracy of  $\pm 2\%$  of the full scale and the reactor body made up of Pyrex

glass that consists of the samples tube (with outer diameter of 2.8cm) and the train of traps. This train is consisted of two connected traps: The first one is immersed in covered Dewar flask filled with liquid nitrogen and the second one is simply a water scrubber, held at room temperature. Before starting a pyrolysis run, the samples were centered in the tube furnace with the chromel-alumel thermocouple of the digital thermometer. Nitrogen flow was introduced at 354 ml/minute until a steady gas flow was obtained, increased to 825ml/minutes for 10 minutes and re-adjusted at 354 ml/minute for the duration of the pyrolysis run. Adding the N<sub>2</sub>-liquid to the trap is done at the beginning of each run according to [18]. Then, the furnace was switched on and the temperature program was set on the desired maximum final temperature (MFT) of 450°C with a heating rate (HR) of 2.5°C/min., starting from a room temperature. After the MFT was reached, the heating system was shut off and the samples were allowed to cool to 100°C with maintenance of nitrogen flow at 354 ml/minute.

## 2.3. Determination of pyrolytic distillate properties

The N<sub>2</sub>-liquid trap distillate (NLTD) was rinsed out of the first trap and samples tube with acetone, evaporated under reduced pressure to remove the acetone and weighed frequently until constant weight. The yield of NLTD was measured based on oven-dry weight of the original wood. The yield of water scrubber distillate (WSD) was determined by evaporating the water at and frequent weighing until constant record [2]. The yield of NG was calculated by subtracting the weights of all recovered components from the total weight of the twelve oven-dry wood samples.

## 2.4. Column chromatography fractionation of NLTD

Due to the complexity of the chemical composition of the pyrolytic distillate, a pretreatment or frationation procedure must be done to facilitate its chromatographic analysis [19].

Isolation of the methylene chloride fraction (MCF) from the NLTD was performed according to the procedure suggested by (Pimenta et al [20] using two mini glass columns for each sample. Initially, about 1g of air-dried NLTD was transferred to the 1st column filled with 6g of activated anhydrous sodium sulphate and was eluted with 35ml of methylene chloride (MC). After thermal concentration, the extract was transferred to the 2nd column filled with 9g of activated neutral aluminum oxide that previously conditioned with 10ml of n-hexane. Then, a 15 ml of n-hexane was added

and the resultant aliphatic hydrocarbons fraction was discarded. Consequent elution with 30 ml of a MC/ n-hexane mixture (95:5 V/V) was done and the produced extract was collected and evaporated. During eluting the 2nd column with either n-hexane or MC, consecutive samples were taken by a capillary glass tube, just from beneath the column trap, to determine the presence of aromatic hydrocarbons and to ensure a similarity between the three NLTD samples of the three branches of a certain species by thin layer chromatography (TLC) technique [18] and [20].

#### 2.5. Chemical Constituents of the MCF

Studying the chemical composition of the methylene chloride fraction (MCF) may be useful in one or more of the following reasons: 1) to qualify the utilization of the local hardwood species as raw materials for energy or chemical feedstocks, 2) to provide significant information about the composition and levels of the methylene chloride fraction of N<sub>2</sub>-liquid trap distillate which influence environment and gasification process and 3) to broaden the understanding of thermochemical. The identification of the constituents of MCF from the NLTD was made using HB5890 gas liquid chromatograph (GLC) coupled with HB5890B series mass spectrometer (MS) at Central Lab. Unit in High Institute of Public Health, Alexandria, Egypt. The GLC was equipped with a splitless injector adjusted at 280°C, and a flame ionization detector (FID) held at 300°C using helium as a carrier gas. Samples were separated on a capillary column (30 m long, and 0.25 mm internal diameter) HP-5 (Avondale, PA, USA) of 0.25 µm film thickness. The temperature of the GLC column was programmed from 80°C to 100°C at a HR of 15°C/minute, and then increased to 310°C for 10 minutes at a heating rate of 5°C/minute. The temperature of ion source in the MS was held at 200°C. All mass spectra were recorded in the electron impact ionization made at 70 eV. The MS was scanned from m/z 40 to 410 at a rate of two scans per second. Peaks areas were automatically calculated by an integrator. Concentration of such compound was calculated as a percentage of its peak area based on whole peak areas for the detected compounds in a MCF. Interpretation the resultant mass spectra were made using a computerized library searching program and by studying the fragmentation pattern of such compound resulted form MS analysis and were confirmed by those obtained from other studies carried out similar circumstances.

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## 2.6. Statistical Analysis

The results of the properties of pyrolytic products were statistically examined by analysis of variance according to randomized complete block design with multiple observations per a species per a block. The least significant difference at 95% level of confidence (LSD $_{0.05}$ ) method was used to compare the differences between species means for properties studied [21] and [22].

#### III. RESULTS AND DISCUSSION

Pyrolytic products, namely distillate, and non-condensible gases produced from the ten wood species were characterized and were found to be species dependent except for the yields of NLTD and NG whereby they were species independent (Table 1).

Table 1. The analysis of variance for yields of  $N_2$ -liquid trap distillate (NLTD), water scrubber distillate (WSD) and nocondensable gases (NG) produced from the pyrolyzed wood of the ten species.

Source of Variation	Yield d.f of NLTD		Yield of WSD	Yield of NG		
		Mean Squares				
Replications	2	7.0256	0.00332	14.518		
Species	9	32.4233 <sup>N.S</sup>	3.79268**	34.831 <sup>N.S</sup>		
Experimental Error	18	23.9685	0.006868	20.859		
Total	29	25.4239				

<sup>\*\*</sup> Significant at 1% Level.

## 3.1. Yield of NLTD

The mean values for the yield of NLTD ranged from 20.37 to 30.64% (Table 2) reflecting the statistical similarity between the species. This result was agree with that reported by Emrich [15] who reported that there is no significant differences exist between pile wood and the residues of forestry and the primary and secondary wood industry. On the other hand, the result differed from those obtained by Shafizadeh and Chen [23] and Raveendran et al [12] as well as that reported by anonymous [24] who found a significant differences between species in their productivity of the pyrolytic distillate using different species.

Further, water scrubber distillate (WSD) varied from 0.54-2.99% for *Casuarina cunninghamiana* and *Psidium guajava*, respectively (Fig. 8). However, this product is less importance than the NLTD one due to its lower value and the energy needed for drying the water.

# 3.2. Gross Heat of Combustion of NLTD

The differences between species in their GHC of NLTD may be illustrated by their differing in the initial composition of biomass [12] and [15]. Since correlation analysis in this study did not produce meaningful relationship between the GHC of NLTD and lignin content of wood, a possible lignin effect can be seen in the case of *Ficus retusa* with the highest

Table 2. Mean Values <sup>1,2,3</sup> for Yield and Gross Heat of combustion (GHC) Of N<sub>2</sub>-Liquid Trap Distillate (NLTD), and Yields of Water Scrubber Distillate (WSD) and Non-condensable Gases (NG) Produced from the Pyrolyzed Wood of the Ten Species

		~ F		
Species	NLTD Yield	GHC of NLTD	WSD Yield	NG Yield
	%	Cal/g	%	%
Casuarina glauca	25.2 <sup>ABC</sup>	4108 <sup>BC</sup>	0.6 <sup>F</sup>	38.4 <sup>A</sup>
Casuarina cunninghamiana	28.5 <sup>ABC</sup>	4735 <sup>AB</sup>	0.5 <sup>F</sup>	34 <sup>ABC</sup>
Eucalyptus camaldulensis	29.5 <sup>AB</sup>	3658 <sup>C</sup>	1.5 <sup>D</sup>	29 <sup>C</sup>
Eucalyptus microtheca	29.5 <sup>AB</sup>	3819 <sup>C</sup>	1.8 <sup>C</sup>	28.4 <sup>C</sup>
Prosopis juliflora	20.9 <sup>C</sup>	4260 <sup>ABC</sup>	3.9 <sup>A</sup>	30 <sup>BC</sup>
Acacia ampliceps	27.2 <sup>ABC</sup>	3812 <sup>C</sup>	0.8 <sup>E</sup>	33.7 <sup>ABC</sup>
Ficus retusa	22.2 <sup>BC</sup>	4923 <sup>A</sup>	1.8 <sup>C</sup>	$37^{AB}$
Citrus sinensis	30.6 <sup>A</sup>	4391 <sup>ABC</sup>	$0.8^{E}$	33.2 <sup>ABC</sup>
Malus domestica	27.3 <sup>ABC</sup>	4005 <sup>BC</sup>	$0.9^{E}$	36 <sup>ABC</sup>
Psidium guajava	29.2 <sup>ABC</sup>	$4642^{AB}$	$3^{\mathrm{B}}$	31.5 <sup>ABC</sup>

<sup>&</sup>lt;sup>1</sup> Means with the same letter are not differed significantly at 5% Level.

lignin content of wood (29.49 %) gave the highest GHC of NLTD (4923 cal/g). These results were agree with that reported by other researchers [13], [15] and [16].

## 3.3. Chemical Constituents of MCF of NLTD

Examining the results of MWR of MCF from the ten species presented in Tables 7- 16 revealed that it varied from 82 to 390 among the species. This reflects the complexity of their chemical compositions. Further, this MWR was found to be more wider for the timber than the fruit tree species studied. Furthermore, it can be concluded that MWR of the phenolic content of MCF constituted a small part of the total MWR of MCF although the phenolic compounds represented the major class in MCF of many of the species studied except for *Psidium guajava* whereby it had the lowest phenolics content.

## 3.3.1. Chemical composition of NLTD within species

Comparing the chemical constituents within species by using the results of GLC/MC presented in Tables 7-16 is necessary to know the importance of such species as a chemical feedstock or a source of energy, for improving gasification process, and/or study the influence of these compounds on the environment. These results are presented below:

N.S Not significant.

<sup>&</sup>lt;sup>2</sup> Each value is an average of 3 samples, GHC of NLTD is an average of 9 samples.

<sup>&</sup>lt;sup>3</sup> Based on original oven-dry weight.

## 3.3.1.1. Casuarina glauca

It can be seen from Table 3 that the phenolic derivatives content constituted about one half of the MCF sample (47.55%) based on the total peaks detected. Syringol was the highest phenolic (23.58% of MCF), while 4-ethyl-2-methoxyphenol was the lowest (7.3% of MCF). In between, guaiacol and 2-methoxy-4-methylphenol were yielded in yields of 8.42 and 8.25%, respectively.

Table 3. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of  $N_2$ -Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of Casuarina glauca at 450°C.

Compound	RT (min.)	M W	Formula	Yield %
Guaiacol	4.39	124	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	8.4
2-Methoxy-4-methylphenol.	6.0	138	$C_8H_{10}O_2$	8.3
4-Ethyl-2-methoxyphenol.	7.6	152	$C_9H_{12}O_2$	7.3
Syringol.	9.2	154	$C_8H_{10}O_3$	23.9
4-Hydroxy-3-methoxybenzoic acid.	11.2	168	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	15.2
3,5-Trimethoxytoluene.	12.9	182	$C_{10}H_{14}O_3$	11.9
3-Crotyl-5- methyl-4-thiouracil.	14.8	196	$C_9H_{12}N_2OS$	4.5
Hexadecanoic acid.	22	256	$C_{16}H_{32}O_2$	3.9
1,2- Benzenedicarboxylic acid, bis (2-ethyl hexyl ester), or	32	390	$C_{24}H_{38}O_4$	17.0
,2- Benzenedicarboxylic acid, diisoctyl.		390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	
Total phenolics con	tent, %			47.55

<sup>&</sup>lt;sup>a</sup> Based on total areas of the identified peaks.

It was also found that this MCF was free of any monoterpenes as well as cresols. In addition, some aromatics other than phenolics were detected in the MCF, namely 4-hydroxy-3-methoxybenzoic acid, 2,3,5-trimethoxytoluene and 1,2-benzenedicarboxilic acid, [bis(2-ethylhexyl ester) or diisoctyl] with the highest yield for the latter (17 % of MCF).

Furthermore, 3-crotyl-5-methyl-4-thiouracil was the unique heterocyclic compound detected in this MCF with a concentration of 4.53 %. Hexadecanoic acid (palmetic acid) was the unique aliphatic found (3.87 % of MCF).

## 3.3.1.2. Casuarina cunninghamiana

The phenolics content was about MCF (38 % of the MCF) as shown in Table 4. However, the other chemical classes shared in the reminder part of MCF, syringol was the highest phenolic compound in yield (20.59 % of MCF), while 2,6-

dimethylethyl-4-methylphenol was the lowest (0.93 % of MCF). In between, guaiacol, 4-methoxy-2-methylphenol and 4-Ethyl-2-methoxyphenol were probably present in the MCF in yields of 6.30, 5.51 and 4.67%, respectively.

Table 4. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Casuarina cunninghamiana* at 450°C.

from the r yroryzed wood o	Cusuurin	curinti	isnamana at -	150 C.
Compound	RT	M	Formula	Yielda
	(min.)	W		%
Limonene.	3.7	136	$C_{10}H_{16}$	2.5
Guaiacol	4.4	124	$C_7H_8O_2$	6.3
4-Methoxy-2-methylphenol	6	138	$C_8H_{10}O_2$	5.5
4-Ethyl-2-methoxyphenol.	7.6	152	$C_9H_{12}O_2$	4.7
Syringol.	9.1	154	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	20.6
3-Acetyl-6-methyl-5H- -2,4- (3H)-dione.	11.2	168	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	8.2
2,6-Dimethylethyl-4-methyl phenol.	12.7	192	$C_{13}H_{20}O$	0.9
2,3,5-Trimethoxytoulene.	12.9	182	C <sub>10</sub> H <sub>14</sub> O	7.4
2-Ethyldiphenylmethane.	14.8	196	$C_{15}H_{16}$	1.7
Hexadecanoic acid.	22	256	C <sub>16</sub> H <sub>32</sub> O	3.3
1,2-Benzene dicarboxylic (2-ethyl hexyl ester), or	32	390	C <sub>24</sub> H <sub>38</sub> O 4	38.9
2-Benzendicarboxylic acid, diisoctyl.		390	C <sub>24</sub> H <sub>38</sub> O 4	
Total phenolics co	ontent, %			38

<sup>&</sup>lt;sup>a</sup> Based on total areas of the identified peaks.

Further, limonene, the unique monocyclic terpene found (2.47 %). In addition, some aromatics other than phenolics was found in the MCF, namely 2, 3,5-trimethoxytoluene (7.35%), 2—ethyldiphenylme-thane (1.74%), and 1,2-benzenedicarboxylic acid, [bis (2-ethylhexyl ester) or diisoctyl] with the highest cocentration for the latter (38.92 % of MCF). Also, one of the heterocyclics, namely 3-acetyl-6-methyl-5H-pyran-2,4(3H)-dione was detected in this MCF (8.22 %). Also, hexa-decanoic acid with a low concentration of 3.3 % was detected representing the aliphatic acids class alone.

## 3.3.1.3. Eucalyptus camaldulensis

The chemical composition of MCF presented in Table 5 indicated that it contained the highest phenolics yield (73.01%) of the MCF. Syringol was found to be the highest phenolic in yield (32.08  $\,\%$  of MCF) follow-ed by 4,5-dimethoxy-2-methylphenol (19.31%) and guaiacol (11.20%).

On the other hand, the lowest phenolic compound was 4-ethyl-2-methoxyphenol.

M-or p- cresol was probably constituted about 1.7 % of MCF. It should be referred to that this species was free of any monoterpenes. Furthermore, three minor peaks representing aromatics other than phenolics were detected in this fraction, namely 2, 3, 5- trimethoxytoluene, 4-ethyldiphenylmethane,

1,2-benzenedicarboxylic acid, bis (2-ethylhexyl ester) in weak concentrations of 0.69, 2.94, and 3.82 %, respectively.

Table 5. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Eucalyptus camaldulensis* at 450°C.

	риз син		
	MW	Formula	Yield (%)
	92	CH	_ ` _
			2.1
			1.7
4.66	124	$C_7H_8O_2$	11.2
6.51	138	C <sub>0</sub> H <sub>10</sub> O <sub>2</sub>	6.6
0.01	100	08111002	0.0
8.40	152	C <sub>2</sub> H <sub>4</sub> ,O <sub>2</sub>	3.7
0.40	132	C911 <sub>12</sub> O <sub>2</sub>	3.1
10.66	154	$C_8H_{10}O_3$	32.3
11.51	102	CILO	0.7
11.51	102	$C_{10}\Pi_{14}O_3$	0.7
12.12	168	$C_9H_{12}O_3$	10.2
13.12			19.3
15.00	100	G 11 0	10.5
15.20	182	$C_{11}H_{18}O_2$	13.5
17.13	167	C <sub>8</sub> HN <sub>5</sub>	1.7
17 29	196	$C_{15}H_{16}$	
17.27			2.9
		CH ON	2.7
	196		
		-	
24.96	256	$C_{16}H_{32}O_2$	0.7
38 38	390	C.H.O.	3.8
50.50	370	C241138C4	3.0
6.			53.70
	RT (min.) 4.08 4.46 4.66 6.51 8.40 10.66 11.51 13.12	RT (min.) MW  4.08 82  4.46 108  4.66 124  6.51 138  8.40 152  10.66 154  11.51 182  13.12 168  15.20 182  17.13 167  17.29 196  24.96 256  38.38 390	(min.)         MW         Formula           4.08         82         C <sub>6</sub> H <sub>10</sub> 4.46         108         C <sub>7</sub> H <sub>8</sub> O           4.66         124         C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> 6.51         138         C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> 8.40         152         C <sub>9</sub> H <sub>12</sub> O <sub>2</sub> 10.66         154         C <sub>8</sub> H <sub>10</sub> O <sub>3</sub> 11.51         182         C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> 13.12         168         C <sub>9</sub> H <sub>12</sub> O <sub>3</sub> 15.20         182         C <sub>11</sub> H <sub>18</sub> O <sub>2</sub> 17.13         167         C <sub>8</sub> HN <sub>5</sub> 17.29         196         C <sub>15</sub> H <sub>16</sub> 196         C <sub>9</sub> H <sub>12</sub> ON <sub>2</sub> -S         S           24.96         256         C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> 38.38         390         C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>

<sup>&</sup>lt;sup>a</sup> Based on total areas of the identified peaks.

For the heterocyclic compounds found in the MCF (3-crotyl-5-methyl-4-thiouracil and tetracyanopyrrole were present in concentrations of 2.94 and 1.66 %, respectively (Table 9 and Fig. 27). In addition, the results showed the presence of three aliphatic hydrocarbons, namely 2-hexyne, 2,4-dimethyl-3- (methoxycarbonyl)-5-ethyl-5-pentadiene, and Hexadecanoic acid with concentrations of 2.04, 13.46, and 0.68 %, respectively.

## 3.3.1.4. Eucalyptus microtheca

The results of GLC/MS presented in Table 6 show that the phenolic derivatives constituted 55.27 % of the total compounds detected.

The highest yield among the phenolics detected was for syringol (28.34 %) followed by guaiacol (9.53%), 2-methoxy-4-methylphenol and 4-ethyl-2-methoxyphenol. Contrarily, the lowest phenolics yield was detected to be 2,3-or 2,6-dimethoxyphenol and 2,6-dimethoxy-4- (2-propenyl) phenol.

In addition, m- or p- cresol was probably present in the MCF in a yield of 7.13%. Further, the only monocyclic terpene found in the MCEF sample was limonene (3.32 %). For the aromatics other than phenolics, they were found in low yields such as 2,4- or 2,5- dihydroxy-propiophenone, 4-hydroxy-3-methoxybenzeneacetic acid, 2-ethyldiphenylmethane and 1,2-benzenedicarb-oxylic, [bis (2-ethylhexyl ester) or diisoctyl].

Further, three heterocyclic aromatics, namely 3-acetyl-6-methyl-5H-pyran-2,4 (3H)-dione, 2-methylimino-3-methyl-2,3,4,5,6,7-hexahydrobenzothiazole and 3-crotyl-5-methyl-4-thiouracil were found in good observable concentrations (15.74, and 11.28 %, respectively). Further, the absence of aliphatic hydrocarbons in the MCF sample reflects the high efficiency of the fractionation procedure.

Table 6. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of  $N_2$ -Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Eucalyptus microthica* at 450°C.

from the Tytoryzed Wood of Euchtypius microunica at 450 C.					
Compound	RT (min.)	MW	Formula	Yield (%)	
Limonene.	3.66	136	C <sub>10</sub> H <sub>16</sub>	3.32	
M- or P-Cresol.	4.1	108	C <sub>7</sub> H <sub>8</sub> O	7.1	
Guaiacol	4.4	124	$C_7H_8O_2$	9.5	
2,3- or 2,6- Dimethylphenol.	5.2	122	$C_8H_{10}O$	1.3	
2-Methoxy-4- methylphenol.	6.1	138	$C_8H_{10}O_2$	8.3	
4-Ethyl-2-methoxy-phenol.	7.7	152	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	4.8	
Syringol	9.3	154	$C_8H_{10}O_3$	28.3	
2,4-or2,5-Dihydroxy-propiophenone.	9.6	182	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	1.2	
3-Acetyl-6-methyl-5H-pyran-2,4(3H) dione.	11.4	168	$C_8H_8O_4$	15.7	
Methylimino-3- methyl-2,3,4,5,6,7 hexahydro- benzothiazole.	13.1	182	C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> S	11.3	
4-Hydroxy-3 methoxy-benzeneacetic acid.	13.2	182	$C_9H_{10}O_4$	0.8	
2,6-Dimethoxy-4-(2-propenyl) phenol.	14.7	194	$C_{11}H_{14}O_3$	1	
2-Ethyldiphenyl- methane, or	14.9	196	$C_{15}H_{16}$	4.1	
3- Crotyl-5-methyl-4-thiouracil.		196	C <sub>9</sub> H <sub>12</sub> ON <sub>2</sub> S		
1,2-Benzenedi carboxylic acid, bis (2- ethyl hexyl ester), or	22	390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	1.3	
1,2-Benzene di- carboxylic acid,diisoctyl.	32	390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>		
Other minor peaks, %.					
Total phenolics content,	%.			55.3	
<sup>a</sup> Based on total areas of the identified peaks.					

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

## 3.3.1.5. Prosopis juliflora

It can be seen from Table 7 that the total phenolic compounds in the MCF was found to be 67.74% of the sample composition.

Table 7. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of  $N_2$ -Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Prosopis juliflora* at 450°C.

	RT			Yield
Compound	(min.)	MW	Formula	(%)
Limonene.	3.65	136	$C_{10}H_{16}$	3.06
1,3-Bezenediamine.	3.81	108	$C_6H_8N_2$	3.62
O-Cresol.	4.11	108	C <sub>7</sub> H <sub>8</sub> O	4.55
Guaiacol.	4.41	124	$C_7H_8O_2$	19.30
2,4-Dimethylphenol.	5.20	122	$C_8H_{10}O$	2.28
2-Methoxy-4-methyl-	6.02	138	$C_8H_{10}O_2$	15.09
phenol.				
4-Ethyl-2-methoxy-	7.64	152	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	8.13
phenol.	7.04	132	C911 <sub>12</sub> O <sub>2</sub>	0.13
Syringol.	9.15	154	$C_8H_{10}O_3$	20.82
2-Methoxy-4-propyl-	9.50	166	$C_{10}H_{14}O_{2}$	2.12
phenol.	7.50	100	C101114O2	2.12
3-Acetyl-6-methyl-				
5H-pyran-2,4	11.23	168	$C_8H_8O_4$	9.68
(3H)-dione.				
2,3,5-Trimethoxy-	12.98	182	$C_{10}H_{14}O_3$	4.97
toluene.	12.70	102	010111403	1.27
2-Ethyldiphenyl-	14.82	196	C <sub>15</sub> H <sub>16</sub>	1.86
methane.			10 10	
Tetradecanoic acid.	22.01	228	$C_{14}H_{28}O_2$	2.73
1,2-Benzenedi-		390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	
carboxylic acid,bis (2-ethyl		370	C241138C4	1.79
hexyl ester), or	31.98			1.77
1,2-Benzendi-carboxylic		390	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	
acid, diisoctyl.		370	C241138O4	67.74
Total phenolics content, %.				

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

Furthermore, the highest yield was found for syringol (20.82%) and guaiacol (19.30%) in the MCF. On the other hand, the lowest phenolic yield was for 2-methoxy-4-propylphenol and 2,4-dimethylphenol (2.12 and 2.28%, respectively). In between, 2-metoxy-4-methylphenol (15.09%) and 4-ethyl-2- methylphenol (8.13%).

Cresols were represented here by o-cresol in a yield of 4.55%. It was also found the monocyclic terpene, d1-limonene, in the MCF in a weak concentration. Further, aromatics other than phenolics, namely 1,3-benzene-diamine, 2,3,5-trimethoxy-toluene, 2-ethyldiphenyl-methane, and 1,2-benzenedicarboxylic acid, [bis (2-ethylhexyl ester) or diisoctyl] were detected in the MCF. The unique heterocyclic aromatic compound detected was 3-acetyl-6-methyl-5H-pyran-2,4 (3H)-dione (9.68%). Further, tetradecanoic acid represented the unique aliphatic acid in this fraction.

## 3.3.1.6. Acacia ampliceps

It can be seen from Table 8 that the MCF sample contained high content of the phenolics (62.47 %).

Table 8. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of Acacia amplicans at 450°C

from the Pyrolyzed Wood of <i>Acacia ampliceps</i> at 450°C.					
Compound	RT (min.)	MW	Formula	Yield (%)	
Limonene.	3.60	136	$C_{10}H_{16}$	1.16	
O- or M-Cresol.	4.1	108	C <sub>7</sub> H <sub>8</sub> O	8.24	
Guaiacol.	4.4	124	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	15.04	
2,3-or2,4-Dimethyl	5.2	122	C <sub>8</sub> H <sub>10</sub> O	3.14	
phenol.					
2-Methoxy-4-methyl-	6	138	$C_8H_{10}O_2$	11.49	
phenol.					
4-Ethyl-2-methoxy-	7.7	152	$C_9H_{12}O_2$	6.61	
phenol.					
Syringol.	9.2	154	$C_8H_{10}O_3$	23.79	
2-Methoxy-4-propyl-	9.5	166	$C_{10}H_{14}O_2$	1.44	
phenol.					
2,5-Dimethoxybenzyl	11.3	168	$C_9H_{12}O_3$		
alcohol, or				10.16	
4-Hydroxy-3-methoxy-		168	$C_8H_8O_4$	10.10	
benzoic acid.					
1,1`-Dimethylethyl-	12.7	180	$C_{12}H_{20}O$	0.96	
phenol.				0.70	
7,8-Dimethylbenzo-		188	$C_{14}H_{20}$	7.78	
cyclooctene, or	13			7.76	
Mono-TMS-hydro-	13	182	$C_9H_{14}O_2S_i$		
quinone.					
2-Ethyldiphenyl-	14.8	196	$C_{15}H_{16}$	2.28	
methane.				2.20	
1-(2,4,6-Trihydroxy-3-	18.3	210	$C_{11}H_{14}O_4$		
methylbenzene)1-				1.08	
butanone.					
Hexadecanoic acid.	22	256	$C_{16}H_{32}O_2$	2.42	
1,2-Benzenedi-	32	390	$C_{24}H_{38}O_4$		
carboxylic acid,bis(2-				2.69	
ethylhexyl ester) bis (2-					
ethylhexyl ester).					
Other minor peaks, %.				1.7	
Total phenolics content, %.			-	62.5	
3D 1 1 C.1 11	( C 1				

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

Also, the highest yield of phenolic constituents in the MCF was 23.79 % for syringol, whereas the lowest value was 0.96 % for 1,1`-dimethyethylphenol. In between, guaiacol (15.04%), 2-methoxy-4-methylphenol (11.49%), 4-ethyl-2- methylphenol (6.61%) and 2,3- or 2,4-dimethylphenol (3.14%).

O- or m-cresol probably present in a yield of 8.24%. Further, The monocyclyclic terpene (limonene) studied was detected in a low yield (1.16%). From the same presentations, some aromatics other than phenolics were detected in the MCF, namely 2,5-dimethoxybenzyl alcohol or 4-hydroxy-3-methoxybenzoic acid (10.16%), 7,8-dimethy-lbenzocyclooctene (7.78%), 2- or 4-ethyldiphenylmethane, 1- (2,4,6-trihydroxy-3-methylbenzene) 1-buta-none (1.08%), and 1,2-benzenedi-carboxylic acid, bis (2-ethylhexyl ester) in a concentration of 2.69%. Further, the concentration of hexadecanoic acid was 2.69% of the total peaks.

#### 3.3.1.7. Ficus retusa

Table 9 shows that the overall content of phenolics in the MCF sample was 48.22 %. Syringol was the highest one (22.93 % of MCF). Contrarily, the lowest phenolic concentration was found to be 11.29 % for 2-methoxy-4-methylphenol. In between, guaiacol was detected in a yield of 14% of MCF.

Table 9. Important Chemical Constituents Propably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Ficus retusa* at 450°C.

Compound	RT (min.)	MW	Formula	Yield (%)
Guaiacol.	4.41	124	$C_7H_8O_2$	14
2-Methoxy-4-methyl	6.00	138	$C_8H_{10}O_2$	11.29
phenol.				
2,5-Dimethoxy-toluene.	7.62	152	$C_9H_{12}O_2$	11.55
Syringol.	9.12	154	$C_8H_{10}O_3$	22.93
3-Acetyl-6-methyl-5H-	11.20	168	$C_8H_8O_4$	13.56
pyran-2,4-(3H) dione.				
2,3,5-Trimethoxy-toluene.	12.97	182	$C_{10}H_{14}O_3$	9.51
5H-Indeno[1,2-b]	14.80	171	$C_{12}H_{13}N$	2.97
pyridine.				
Tetradecanoic acid.	22.03	228	$C_{14}H_{28}O_2$	5.86
1,2-Benzenedi-carboxylic	31.98		$C_{24}H_{38}O_4$	
acid, bis (2-ethyl hexyl				
ester), or		390		8.33
1,2-Benzendi-carboxylic		370	$C_{24}H_{38}O_4$	0.55
acid,				
diisoctyl.				
Total phenolics contents, %.				48.22

<sup>&</sup>lt;sup>a</sup> Based on total areas of the identified peaks.

In addition, the MCF was found to be free of monoterpens as well as cresols. Furthermore, three aromatics other than phenolics, namely 2,5-dimethoxytoluene, 2, 3, 5-trimethoxytoluene 1,2-benzene-dicarboxylic acid, [bis (2-ethylhexylester), or diisoctyl] with yields of 11.55, 9.5, and 8.33 %, respectively. It was also detected two heterocyclic aromatics, namely 3-acetyl-6-methyl-5H-pyran-2,4 (3H)-dione, and 5H-Indeno [1,2-b] pyridine (13.56 and 2.97 %, respectively). Aliphatic hydrocarbon acids was represented in this case by tetradecanoic acid (5.86 %).

#### 3.3.1.8. Citrus sinensis

Studying the chemical results presented in Table 10 indicated that the sample of MCF contained 61.39 % of phenolic compounds based on the total peaks area. It can be also seen that the highest phenolic in yield was syringol (23.65 % of MCF) followed by guaiacol(14.08%), 2-methoxy-4-methylphenol (9.80%) and other phenolicsin low yields. On the other hand, the lowest compound within the phenolic constituents were 2,6-dimethoxy-4- (2-propenyl) phenol (0.76 %). In addition, this species had one of the three isomers of cresols (5.13%). It was found that this species was free of any monoterpenes. Two aromatics other than phenolics, namely 2,3,5-trimethoxybenzene, 2,3,5-trimethoxytoluene, 4-hydroxy-

Table 10. Important Chemical Constituents Probably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of Citrus singusts at 450°C

Produced from the Pyrolyzed Wood of <u>Citrus sinensis</u> at 450°C.					
Compound	RT (min.)	MW	Formula	Yield (%)	
O- ,M- or P-Cresol.	4.21	108	C <sub>7</sub> H <sub>8</sub> O	5.13	
Guaiacol.	4.52	124	$C_7H_8O_2$	14.08	
3,5-Dimethylphenol, or	5.37	122	$C_8H_{10}O$	1.68	
3,4-Dimethyl-,acetate-phenol.		164	$C_{10}H_{12}O_2$		
2-Methoxy-4-Methyl-phenol	6.28	138	$C_8H_{10}O_2$	9.80	
4-Ethyl-2-methoxy-phenol.	8.16	152	$C_9H_{12}O_2$	8.22	
Syringol.	10.06	154	$C_8H_{10}O_3$	23.65	
Eugenol, or		164	$C_{10}H_{12}O_2$		
2-Methoxy-4-(2-propenyl) phenol.	10.14	164	$C_{10}H_{12}O_2$	1.08	
2-Methoxy-4 propyl-phenol.	10.35	166	$C_{10}H_{14}O_2$	2.12	
3-Acetyl-6-methyl-5H-pyran-2,4-(3H)-dione.	12.50	168	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	10.35	
2,3,5-Trimethoxy-benzene, or	14.66	168	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	10.75	
2,3,5-Trimethoxy-toluene.		182	$C_{10}H_{14}O_3$		
4-Hydroxy-3-methoxy-benzene-acetic acid.	14.76	182	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.87	
2,6-Dimethoxy-4- (2propenyl) phenol	16.65	194	$C_{11}H_{14}O_3$	0.76	
2Ethyldiphenylmethane.	16.87	196	$C_{15}H_{16}$	4.85	
Hexadecanoic acid	22	256	$C_{16}H_{32}O_2$	4.58	
Total phenolics content, %.				61.39	
åD d + - t - 1					

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

3-methoxyb-enzeneacetic acid and 2-ethyldiphenylmethane with the highest yield for the former(10.75 %).

From the same presentations, one heterocyclic derivative, 3-acetyl-6-methyl-5H-pyran-2,4 (3H)-dione, was appeared at noticable yield of 10.35 % of the total MCF sample. This is beside the unique aliphatic hydrocarbon acid, namely hexadecanoic acid representing only 4.58 % of the total detected peaks area.

## 3.3.1.9. Malus domestica

From the GLC/MS output shown in Table 11, it can be indicated that phenolic derivatives constituted (35.55 % of MCF). Further, two phenolics were detected with the highest yield for Syringol (30.09 % of MCF) followed by 4-ethyl-2-methoxyphenol (5.46 %).

Table 11. Important Chemical Constituents Probably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD) Produced from the Pyrolyzed Wood of *Malus domestica* at 450°C.

Compound	RT (min.)	MW	Formula	Yield (%)
O-Cresol.	4.11	108	C <sub>7</sub> H <sub>8</sub> O	5.97
Methylthiobenzene.	4.43	124	C <sub>7</sub> H <sub>8</sub> S	12.08
3-Ethyl-5-methyl-	5.21	180	$C_6H_{12}S_3$	4.08
1,2,4trithiolane.				
4,5-Dimethyl-1,3-	6.03	138	$C_8H_{10}O_2$	5.32
benzenediol				
4-Ethyl-2-methoxy-phenol.	7.66	152	$C_9H_{12}O_2$	5.46
Syringol	9.14	154	$C_8H_{10}O_3$	30.09
4-Hydroxy-3	11.21	168	$C_8H_8O_4$	13.07
methoxybenzoic acid.				
3-Acetyl-6-methyl-5H-	12.98	168	$C_8H_8O_4$	12.72
pyran-2,4-(3H) dione.				
2,3,5-Trimethoxy-toluene.		182	$C_{10}H_{14}O_3$	
3-Methyl-2,4-	14.82	156	$C_7H_8O_4$	2.72
hexadienedioic acid.				
Hexadecanoic acid.	22	256	$C_{16}H_{32}O_2$	5.71
Other minor peaks, %.				
Total phenolics content, %.				
3-Acetyl-6-methyl-5H-	12.98	168	$C_8H_8O_4$	12.72
pyran-2,4-(3H) dione.				

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

O-cresol represented the cresols class alone in a yield of (5.46%). Whereas, this species was free of monoterpenes. Aromatics other than phenolics were detected, namely methylthiobenzene,3-ethyl-5-methyl-1,2-trithiolane, 4,5-dimethyl-1,3-benzendiol, 2,3,5-tri-methoxytoluene and 4-hydroxy-3-methoxybenzoic acid with concen-trations of 12.08, 4.08, 5.32, 12.72 and 13.07 % of MCF, respectively (Table 15 and Fig. 33). Further, the more frequently present heterocyclic in this study was detected to be 3-acetyl-6-methyl-5H-pyran-2,4 (3H)-dione (12.72 %).

In addition, the alkanoic compound, namely hexadecanoic acid was also observed in a concentration of 5.71 % of the total MCF sample. The alkeneoic acid (3-Methyl-2,4-hexadienedioic acid) was detected (2.73 %).

## 3.3.1.10. Psidium guajava

Examining Table 12 revealed that the phenolics content in the MCF sample was the lowest among the ten species (7.98%). Uncommonly, syringol content of the MCF sample lowered to be 7.98% and was the unique phenolic derivative in this fraction. Further, limonene was found in a low yield of 3.31% of the MCF this species, while it was free of any cresols.

Also, the unique aromatic derivative other than phenolics was found to be mono-TMS-hydroquinone that appeared in a low concentration of 3.21 % of MCF. It can be also seen that some heterocyclics may be present, namely 3-acetyl-6-methyl-5H-pyran-2,4(3H)-dione (5.22% of MCF), and 2-thiopheneacetic acid or 3-[(furan-3-yl) hydroxymethyl] 4-isopropylcyclohexane (3.36% of MCF-)were probably present

Table 12. Important Chemical Constituents Probably Present in Methylene Chloride Fraction (MCF) of N<sub>2</sub>-Liquid Trap Distillate (NLTD)

Produced from the Purplyand Wood of Poidium aurigus at 450°C

Produced from the Pyrolyzed Wood of <i>Psidium guajava</i> at 450°C.				
Compound	RT (min.)	MW	Formula	Yield (%)
Limonene.	3.6	136	$C_{10}H_{16}$	3.31
Syringol.	9.1	154	$C_8H_{10}O_3$	7.98
3-Acetyl-6-methyl-5H-pyran-2,4 (3H)-dione.	11.2	168	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	5.22
Mono-TMS-hydro- quinone,or	12.9	182	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub> Si	3.21
1-(2,6-Dihydroxy-4-methoxy) ethanone.		184	$C_9H_{12}O_4$	
2-Thiopheneacetic acid, or		236	$C_6H_6O_2S$	3.36
3-[(Furan3yl) hydroxyl- methyl] 4- isopropyl- cyclohexane.	16.8	236	$C_{14}H_{20}O_3$	
Hexadecanoic acid.	22.3	256	$C_{16}H_{32}O_2$	51.07
Cis-9-Octadecenoic acid	25.5	282	$C_{18}H_{36}O_{2}$	16.39
Octadecanoic acid	25.8	284	$C_{18}H_{36}O_{2}$	9.47
Total phenolics contents, %	).			7.98

<sup>&</sup>lt;sup>a</sup>Based on total areas of the identified peaks.

in the MCF sample in a yield of 5.22 and 3.36 %), respectively).

For the aliphatic acids detected, hexadecanoic acid was found to be account for 51.06 %, cis-9-octadecenoic acid was 16.39 %, and octadecanoic acid was 9.47 % of the total fraction. Unexpectedly, the aliphatic acids constituted about two thirds of the total methylene chloride fraction.

## 3.3.1.11. Chemical composition difference between species

Comparing the chemical constituents of MCF between the species (Tables 3-12) revealed that limonene was the unique monterpene detected and was present in a half of the ten wood species. This result is confirmed by Shafizadeh [25] who indicated that volatile extractives like monoterpenes could evaporate without major change. Furthermore, cresols were probably present in the MCF of the species studied except for the two species of casuarina and *Pisidium guajava*.

Regarding to the phenolics content in Figure 1, it was observed to be different between species. The highest phenolic content value was observed for *Eucalyptus camaldulensis* whereas *Psidium guajava* had the lowest value (73.01 and 7.98%, respectively).

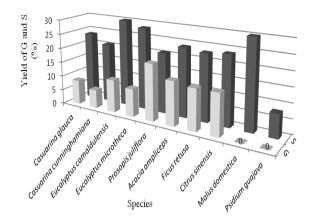


Figure 1. Yields of guaiacol (g) and syringol (s) of the methylene chloride fraction (MCF) of liquid trap distillate (NLTD) produced from the ten species.

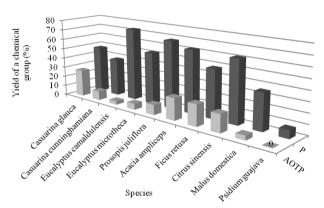


Figure 2. Yields of phenolics (P) and aromatics other than phenolics (AOTP) of the methylene chloride fraction (MCF) of liquid trap distillate (NLTD) produced from the ten species.

The presence of syringol and guaiacol, the monomers consitituting lignin, in all MCF from the ten species studied, except for Malus domestica and Psidium guajava that were free of guaiacol, is an indicator to the participation of lignin on their phenolic content. In addition, syringol was found in the MCF of all the ten wood species with the highest concentration, except for Psidium guajava that contained low quantity of it. The highest content of the syringol comparing with guaiacol can be explained by the illustration offered by Beaumont [26] that the syringyl-propane units are not so linked to the lignin skeleton as the less substituted units: guaiacylpropane and phenyl-propane. As the aromatic rings of lignin are substituted only at carbons 1,2,4 and 6, the syringyl units encounter three sites that are already occupied (1, 2 and 6); so they can be linked to the lattice only by the propane chain in position 4. On the other hand, the guaiacyl-propane and above all phenyl-propane units can be linked at two points: at the carbon atom no. 6 of the phenyl ring and by the propane chain in position 4. So, during pyrolysis, these two products will yield charcoal, whereas the former will escape more easily.

According to this theory as well as the reults of this study, comparing the role of both guaiacol and syringol in pyrolytic products yields and qualities, guaiacol participates to the charcoal skeleton more than the other, while syringol gives pyrolytic distillate higher than guaiacol.

Despite of phenolic compounds derive from lignin by cracking of phenyl-propane units of the macromolecule lattice [26], the differences between species in their contents of phenolic derivatives can not be attributed directly to their differences in lignin content in the present study. Accordingly, it can be thought that the nature and complexity of the lignin skeleton wherein the manner and the kind of linkages between its monomers as well as the degree of their interferring with extractives may played a role on the thermal degradation of lignin and consequent production of phenolic derivatives.

The content of AOTP was found to be different between species (Figure 2). It differed between 48.01 and 6.76% for *Casuarina cunninghamiana* and *Eucalyptus camaldulensis*, respectively. Furthermorem, 2,3,5-trimethoxytoluene, 1,2-benzenedi-carboxylic acid [bis- (ethylhexyl ester)] or 1,2-benzenedicarboxylic acid, diisocty, and 1 and 2 ethyldiphenylmethane were detected frequently in most of the species studied (Tables 3-12).

For the heterocyclics content, it ranged from 31.12 to 4.53 % for *Eucalyptus microtheca* and *Casuarina glauca*, respectively. The 3-acetyl-6-methyl-5H- pyran-2, 4 (3H)-dione was the most appearance heterocyclic in the MCF of the species studied (Tables 3-12). This result is attributed to that this compound is resulted from the thermal degradation of wood hemicelluloses, which constitute a valuable part of wood structure.

In addition, the aliphatics content in the MCF was observed to be different among the species. It differed between 80.14 and 2.42 % for *Pisidium guajava* and *Acacia ampliceps*, respectively. Hexadecanoic acid was found to be the most presence aliphatic detected in the study (Table 17).

It should be mentioned that results of the chromatographic analysis of the present investigation are in agreement with those done by many researchers [5], [26], [27], [28], [29], [30], [31], and [32].

## 3.3.12. Yield of Water Scrubber Distillate

It is indicated from the analysis of variance in Table 4 that the water scrubber distillate (WSD) was affected statistically according to species. Based on the above-mentioned result, it can be seen from Table 6 that the highest yield value of WSD was obtained form *Prosopis juliflora* (3.93 %). On the other hand, the lowest WSD yield was obtained from both species of casuarina, namely glauca and cunninghamiana (0.61 and 0.54 %, respectively). These results of WSD are agree with those obtained by Elder (1984) from pyrolyzed southern pine.

## 3.3.13. Yield of Noncondensable Gases

Table 1 indicates that there is no significant difference between species in the resulted yield of the noncondensable gases (NG). From the results of yield of NG in Table 2, the mean values of NG yield ranged from 28.38 to 38.36 %. This result situated within the range of nonrecovered percentage

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found by Elder [7] from pyryolyzed southern pine. In addition, this result is in agreement with that reported by Emrich [15]. On the other hand, it differed from those obtained by Bilbao et al [33], and Raveendran et al [12] who found a differences in the NG yield produced from the types of biomass used in their investigations.

## Reasons of absence of levoglucosane in all the MCF's

- I. Atmospheric pressure played an important role in decomposition of levoglucosan and accordingly its absence from the MCF samples. This illustration is confirmed by Shafizadeh [23], [25], [34] and who stated that the yield of levoglucosan drops shaply due to further decomposition for pyrolysis of cellulose at atmospheric pressure other than under vacuum. Similarly, a strong confirmation was offered by Beaumont [26] in which this compound has not been isolated yet from oils of atmospheric pyrolysis.
- II. The lower heating rate  $(2.5\ ^{\circ}\text{C/min.})$  as well as the relatively lower flow rate of  $N_2$ -gas (334 ml/min.) used in this study forced levoglucosan to still an adequate time inside the heat zone of the tube furnace and degraded to lighter compounds due to secondary reactions domained [26] since it has a heavy molec-ular weight and accordingly a moderate volatility.
- III. The fractionation procedure used and nature of levoglucosan.
- IV. The fractionation method was done using methylene chloride. Since levoglucosan dissolves better in higher polarity- solvents, it dessolved to a relatively lower extent in CH<sub>2</sub>Cl<sub>2</sub>. Therefore, the compound did not appear by GLC/MS analysis.
- V. Injection the MCF samples in GLC column without derivation it as a triacetylated or trisilylated levoglucosan that made to increase its volatility. Thus, it could be unable to reach to the FID detector although it may be present on the GLC column.

This finding was conflicted with that reported by Steinbeiss et al [35] in which 2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4*H*)-pyrane-4-one and levoglucosane were found to represent the isotopic signature from cellulose upon Pyrolysis.

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