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Characterisation of Liquid Derived from Pyrolysis Process of Charcoal Production in South of Thailand

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Abstract: Pyrolysis liquid obtained from local suppliers in Phatthalung Province, Thailand was separated in conventional vacuum distillation into light and heavy fractions. The physiochemical characteristics and thermal behaviour of the fractionated pyrolysis liquid were investigated. It was found that light fraction had higherwater content and stronger acidity than heavy fraction and pyrolysis liquid. The heating value of light fraction was lower than those of the pyrolysis liquid and'heavy fraction. The heating value of heavy portion was almost double that of the light fraction. The thermal behaviours of the pyrolysis liquid and the two fractions were determined. The light fraction had the highest decomposition rate and the lowest residual yield; in contrast to heavy fraction had slow weight loss through a wide range of temperatures and it had the highest residual yield. The chemical composition of the pyrolysis liquid and the two fractions'were analysed by GC-MS. The chemical distribution differed for the fractions and the pyrolysis liquid. The light fraction was dominated by acetic acid and the heavy fraction was mainly composed phenolic compounds.

INTRODUCTION

Biomass represents a potential alternative source of energy to replace fossil fuels. It has'attracted great attention as a renewable energy source after the global oil crisis in 1970s [1, 2]. In addition, biomass is considered the only current sustainable source to produce energy-related'products, including electricity, heat and valuable chemicals, such as resins, flavourings and other materials [3, 4]. Furthermore, biomass is an environmentally-friendly candidate because it contains a low content of sulphur [5, 6].

The pyrolysis of biomass has been used for ages to produce charcoal and currently the slow-pyrolysis process is widely used for producing so-called biochar [7, 8]. However, extensive attention has been focused recently on fast pyrolysis to obtain pyrolysis liquid (pyrolysis oil) [9]. Pyrolysis oil is a complex, oxygenated compound with a wide range of boiling temperatures that contains nearly 400 known compounds, primarily of phenolic compounds, organic acids, aldehydes, ketones, esters and water [10, 11].

Currently, pyrolysis oil has attracted considerable interest due to its several applications in industry. Althoughit has been proven to be a promising alternative to petroleum fuels, it also has potential for use in producing value-added chemicals for the pharmaceutical, food and paint industries [2, 12].

The pyrolysis oil mixture is quite complex and there has been significant interest in studying its chemical composition and thermal behaviour. Hence, its chemical and physical properties have been extensively discussed in literature [13-15].

A great deal of work has been done on fractionation and characterization of pyrolysis oil and different methods and techniqueshave been used. Garcia-Perezet *et al*. [16] used different solvents to fractionate'pyrolysis oil into six fractions, which were'characterized by GC-MS,

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hermogravimetric techniques (TG) and gel permeation chromatography (GPC). A similar investigation was conducted by Sipila *et al*. [17] and they have reported the physiochemical properties and fuel characteristics of the water-soluble and water-insoluble fractions of flash pyrolysis oil. They also compared the properties and characteristics of these two fractions with those of the whole pyrolysis oil.

Apart from solvent extraction techniques, Wang, *et al*. [18-20] used molecular distillation techniques to separate pyrolysis oil into several fractions using different operational parameters and then studied the physiochemical characteristics of the fractions.

To a great extent, Thailand is an agriculture-based country and it has the potential for producing energy from biomass equivalent to about 25-30% of its primary energy needs; in addition, rubber wood is regarded as one of the most important sources of biomass and it is planted extensively in the peninsular area in southern Thailand [21]. Rubber wood has been utilised to a great extent by local farmers and small plants to produce charcoal, which is carried in conventional, slow-pyrolysis process. The pyrolysis liquid, called 'wood vinegar' locally, is produced as a by-product from the production of charcoal and it is used extensively by farmers in growing and protecting plants as well as to improve the quality of the soil [22].

To the best of our knowledge, few studies have been conducted on the physiochemical properties of pyrolysis liquid produced from the slow pyrolysis of wood in the process of charcoal production. Most of the studies focused on the fast pyrolysis oil; hence, the purpose of our work was to use vacuum distillation to separate the liquid produced by the slow pyrolysis of wood into fractions and then determine the chemical and physical properties of the fractions.

Pyrolysis liquid was collected from different producers in Phatthalung, one of the southern provinces in Thailand and conventional vacuum distillation was conducted to fractionate the liquid into two fractions.

The pyrolysis liquid and its fractions were analysed using GC-MS. The physical properties of the pyrolysis liquid and its two fractions were investigated, including heating value, pH, colour and thermal stability.

MATERIALS AND METHODS

Crude Pyrolysis Liquid: The crude pyrolysis liquid was obtained from local suppliers in Phatthalung Province. The suppliers produced the liquid as a by-product from the slow pyrolysis of wood in the process of making charcoal. The biomass source they used for making charcoal was mainly rubber wood. First, the crude pyrolysis liquid was treated to reduce water and remove the fine particles using evaporation and filtration, respectively.

Pyrolysis Liquid Fractionation: After the crude pyrolysis liquid was treated as described, the treated liquid was fractionated into two fractions. The fractionation was conducted in a conventional, vacuum-distillation facility at 60-70°C and 60-10 mmHg. The fractions collected from the distillation process were labelled as the light fraction (LF) and the heavy fraction (HF). The LF, which contained the light components, was vaporized, condensed and collected at room temperature. The HF, which contained the heavy components, could not be vaporized and collected as a residual fraction.

GC-MS Analyses: The compounds in the pyrolysis liquid and its fractions were identified with a Trace GC Ultra/ISQMST equipped with a capillary column of 30 m long×0.25 mm × 0.25"µm film thickness. The oven temperature was programed to increase from 35 to 245°C. The data were acquired with Xcalibur software using the Wiley mass spectra library's.

Thermogravimetric Analysis and Physical Characteristics: The physical properties were measured to determine heating value, pH, water content

Table 1: Analysis methods and instruments used for physical characterisation

Physical Property	Method and Instrument
Heating value	CHNS/O Analyser, Flash EA 1112 Series
	Automatic calculation of GHV (Gross Heat Value) and NHV (Net Heat Value) using Eager 300 software.
pH	pH meter
	Water content Coulometric Karl Fischer titration method
	First, the sample was diluted with methanol and then analysed using a Karl Fischer titrator. A mass balance was
	used to determine the water content of the sample.
Appearance	Visual observation

and appearance of the pyrolysis liquid, light and heavyfractions. They were analysed according to the methods listed in Table 1. Thermogravimetry (TG) and Derivative'thermogravimetric (DTG) profiles of the pyrolysis liquid, light fraction and heavy fraction were assessed by a thermogravimetric analyser (Perkin Elmer TGA 7). The conditions were controlled under a nitrogen purge gas at temperatures ranging from 50 to 1000°C with a heating rate of'10°C/min.

RESULTS AND DISCUSSION

GC-MS Characterization of the Pyrolysis Liquid and its Fractions: Several compounds were identified by the GC-MS analyses. The total ion chromatogram of the pyrolysis liquid in Figure 1 and Table 2 show the top 20 compounds of the pyrolysis liquid. Acetic acid had the highest concentration and it was followed by a group of abundant phenolic compounds. Among the phenolic compounds, syringol was the most abundant and it was followed by ketones, pyridines, sugars and acids in that order. Generally, the chemical composition was almost in agreement with that reported by Branca e*t al.* [23] for pyrolysis liquid. In addition, Noor et al. conducted similar work using slow'pyrolysis of cassava wastes for biochar production [8].

Figure 2 shows the GC-MS total ion chromatograms of the two fractions obtained from the vacuum distillation of the pyrolysis liquid. It was obvious that the distributions of the components differed in the two fractions and in the pyrolysis liquid. As illustrated in Figure 3, the compounds in the fractions were classified into different groups, such as acids, esters, phenols and ketones, according to their chemical structures.

Table 3 shows that the light fraction was dominated by acetic acid, followed by acetol. Some phenols were partially distilled during the distillation process and they were present in trace amounts in the light fraction, although the rest of the phenolic compounds were not present. Table 4 shows that the heavy fraction was composed mainly of 2, 6-dimethoxyphenol, followed by high-molecular weight phenols, ketones, pyridines, sugar and some acids.

Furthermore, it was noted that more compounds were detected in the two fractions than in the pyrolysis liquid due to thermal cracking process of conventional distillation that had a long'residence'time and a relatively high temperature. As a result, the thermo-sensitive pyrolysis liquid was not completely vaporized and as a result, some compounds reacted, producing additional compounds [24].

Physical Characteristics of the Pyrolysis Liquid and its Fractions: Table 5 presentsthe principal physical properties of the pyrolysis liquid and its fractions. The pyrolysis liquid was a light-black liquid with a 30% water content, a pH value of 3.72 and a heating value of about 21'MJ/kg. The light fraction, which had good fluidity, was dark yellow with a high water content of 60%; in contrary, the heavy fraction had poor fluidity, was dark black with a relatively low water content of 1.5%. Moreover, the heating value of the light fraction was much lower than that of the heavy fraction. The heating value heavy fractionwas almost double that of the light fraction. Earlier work has proven that the heating value depends mostly on the chemical composition and the water content [5]. In addition, it was noted that the light fraction had the lowest pH value due to its content of acids, particularly acetic acid, which had the highest concentration among all of the components in the light fraction.

Thermogravimetric Analysis: In our study, we used thermogravimetric analysis (TGA) to investigate the thermal stability of the pyrolysis liquid and its fractions. The results of TGA were useful in studying and predicting the properties of the pyrolysis liquid and its fractions. Figure 4 shows the thermal behaviour of the pyrolysis liquid and its fractions at a heating rate of 10°C/min. The pyrolysis liquid was evaporated and decomposed over the temperature range of 25-1004°C; it had its maximum weight loss at 120°C (DGT plot) and its final residue yield at 1004°C was 2%. However, the light fraction, which had the highest rate of decomposition, evaporated mostly in the range of 25-186°C; its maximum weight loss occurred at 161°C (DGT plot) due to the release of water vapour (moisture content was 60%) and compounds that had low boiling points. The yield of the final residue was 0.1% at 1004°C. The heavy fraction had a different thermal behaviour from the light fraction. It had slow weight loss over a wide range of temperatures, *i.e.*, 35-110°C, due to the presence of compounds with higher boiling points and it had its maximum weight loss at 227°C (DGT plot). The yield of the final residue was 20% at 110°C.
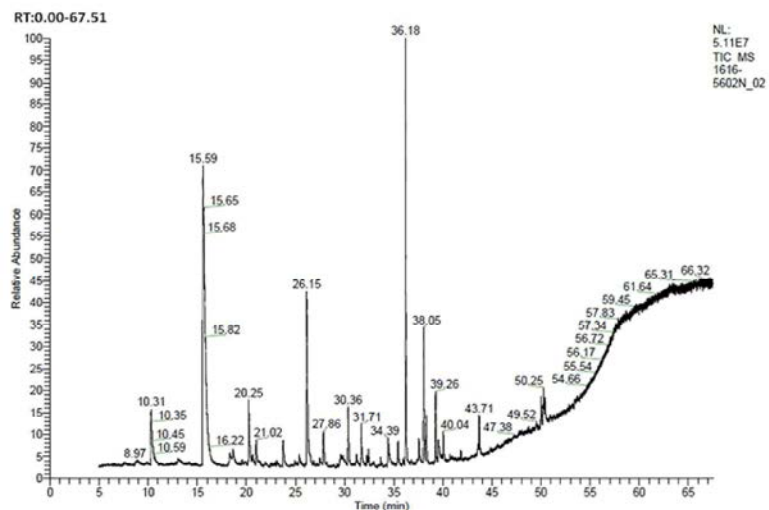
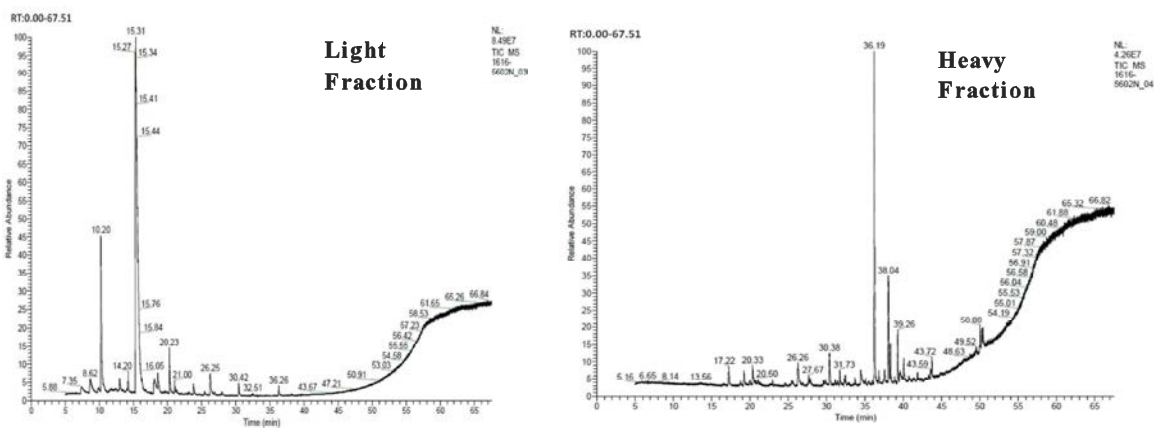Fig. 1: Total ion GC-MS chromatograms of the pyrolysis liquid

Fig. 2: Total ion GC-MS chromatograms of the two fractions obtained from the pyrolysis liquid using conventional vacuum distillation at 60-70°C and 60-10 mmHg
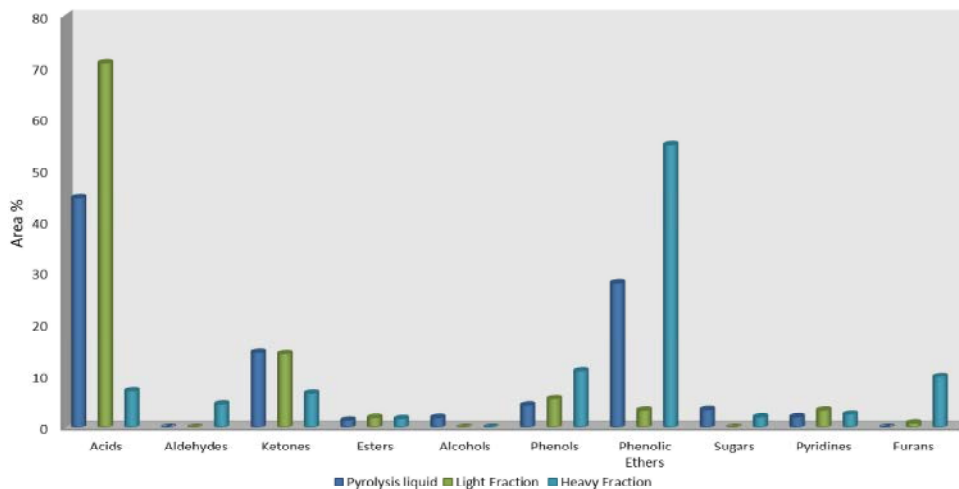

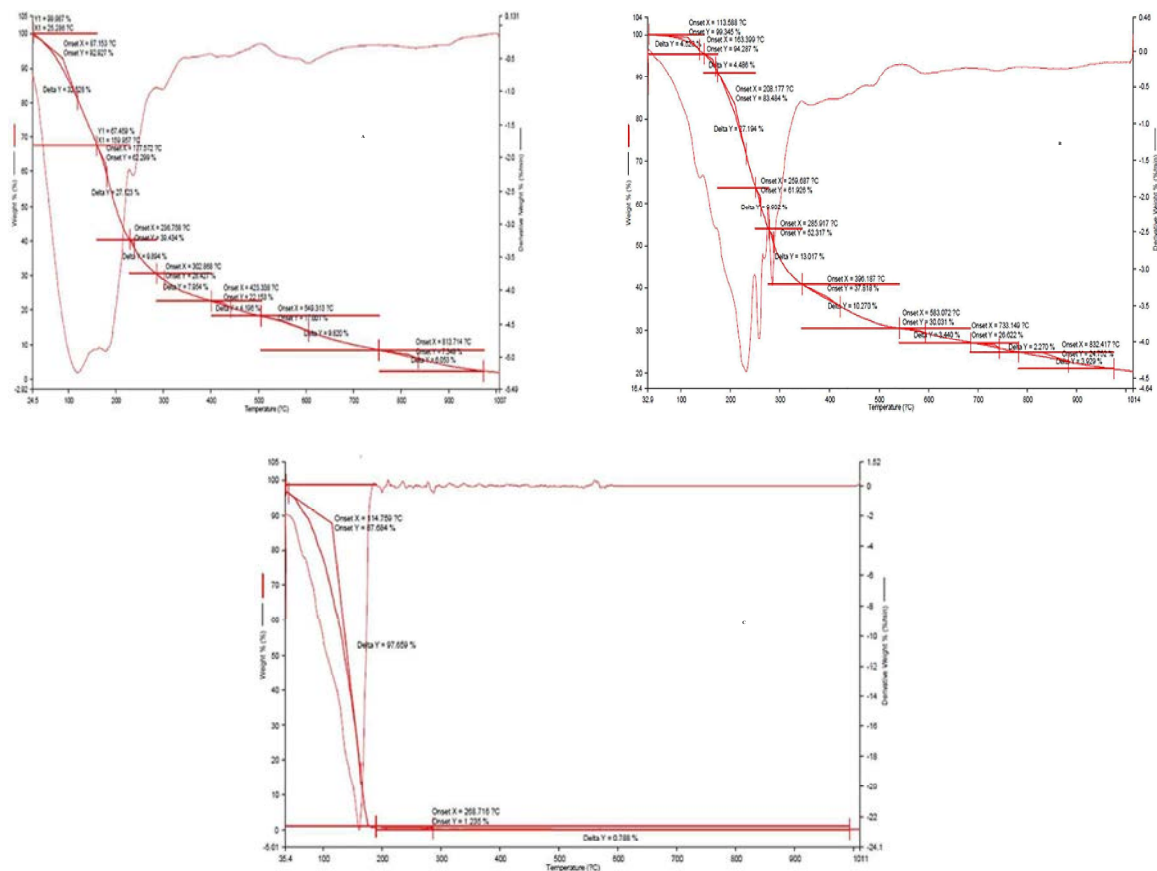Fig. 3: Chemical distribution of the pyrolysis liquid and its two fractions

Fig. 4: TG and DTG at a heating rate of 10°C/min for (A) pyrolysis liquid, (B) heavy fraction and (C) light fraction

Table 2: Main chemical composition of the pyrolysis liquid identified by GC–MS

	Composition	MW	Formula	Peak area %[a]
1	Acetic acid	60	$C_2H_4O_2$	37.30
2	Syringol	154	$C_8H_{10}O_3$	15.27
3	Corylon	112	$C_6H_8O_2$	9.85
4	4-Methoxy-3-(methoxymethyl)phenol	168	$C_9H_{12}O_3$	4.89
5	Acetol	74	$C_3H_6O_2$	4.66
6	4-Chlorobutyric acid	122	$C_4H_7ClO_2$	3.53
7	Phenol	94	C_6H_6O	2.43
8	2,6-Dihydroxy-4-methoxyacetophenone	182	$C_9H_{10}O_4$	2.31
9	Butyryl oxide	158	$C_8H_{14}O_3$	2.19
10	Anhydro - sugar	132	$C_5H_8O_4$	1.96
11	3-Pyridinol	95	C_5H_5NO	1.87
12	3,4,8-Trimethyl-2-none-1-ol	182	$C_{12}H_{22}O$	1.84
13	Syringyl acetone	126	$C_7H_{10}O_2$	1.47
14	Ethyl cyclopentenolone	180	$C_{10}H_{12}O_3$	1.81
15	1-(4-Hydroxy-3-methoxyphenyl)acetone	166	$C_{10}H_{14}O_2$	1.70
16	p-Butoxyphenol	210	$C_{11}H_{14}O_4$	1.55
17	3,4-Anhydro-d-galactosan	144	$C_6H_8O_4$	1.39
18	Levulinic acid	116	$C_5H_8O_3$	1.35
19	à-Furanone	84	$C_4H_4O_2$	1.35
20	2-hydroxy-4 6-dimethoxy acetophenone	196	$C_{10}H_{12}O_4$	1.28

The composition of the pyrolysis liquid estimated by the peak area% of GC-MS

Table 3: Main chemical composition of the light fraction identified by GC–MS

	Composition	Mw	Formula	Peak area %[a]
1	Acetic acid	60	$C_2H_4O_2$	67.96
2	Syringol	154	$C_8H_{10}O_3$	0.48
3	Corylon	112	$C_6H_8O_2$	1.88
4	4-Methoxy-3-(methoxymethyl)phenol	168	$C_9H_{12}O_3$	2.9
5	Acetol	74	$C_3H_6O_2$	11.36
6	4-Chlorobutyric acid	122	$C_4H_7ClO_2$	2.88
7	Phenol	94	C_6H_6O	0.73
8	Pyridine, 4-methyl	93	C_6H_7N	2.67
9	Hydrazine, n-propionyl-N-methyl-	102	$C_4H_{10}N_2O$	1.99
10	Trimethylorthoacetate	120	$C_5H_{12}O_3$	1.11
11	1-Hydroxy-2-butanone	88	$C_4H_8O_2$	1.08
12	4-Hydroxybut-2-enoic acid lactone	84	$C_4H_4O_2$	0.8
13	2-Hydroxyethyl acetate	104	$C_4H_8O_3$	0.74
14	3,5-Dimethylpyridine	107	C_7H_9N	0.37
15	Pyridine	79	C_5H_5N	0.34
16	1,3,5-Trimethyl-2-octadecylcyclohexane	378	$C_{27}H_{54}$	0.26

The composition of the light fraction estimated by the peak area% of GC-MS

Table 4: Main chemical composition of the heavy fraction identified by GC–MS

	Composition	Mw	Formula	Peak area %[a]
1	Syringol	154	$C_8H_{10}O_3$	34.22
2	Corylon	112	$C_6H_8O_2$	4.47
3	4-Methoxy-3-(methoxymethyl)phenol	168	$C_9H_{12}O_3$	11.52
4	4-Chlorobutyric acid	122	$C_4H_7ClO_2$	3.44
5	Phenol	94	C_6H_6O	3.9
6	2,6-Dihydroxy-4-methoxyacetophenone	182	$C_9H_{10}O_4$	5.58
7	Butyryl oxide	158	$C_8H_{14}O_3$	2.61
8	Anhydro– sugar	132	$C_5H_8O_4$	1.76
9	3-Pyridinol	95	C_5H_5NO	2.75
10	3,4,8-Trimethyl-2-none-1-ol	182	$C_{12}H_{22}O$	4.18
11	Syringyl acetone	126	$C_7H_{10}O_2$	2.4
12	Tetrahydro-2-methyl-2-Furanol	102	$C_5H_{10}O_2$	3.66
13	1,4-Benzenediol	110	$C_6H_6O_2$	3.6
14	3,4,5-Trimethoxybenzaldehyde	196	$C_{10}H_{12}O_4$	3.51
15	Dihydro-5-(hydroxymethyl)-2(3h)-furanone	116	$C_5H_8O_3$	2.91
16	Tetrahydrofuran, 2-hexyl-	102	$C_5H_{10}O_2$	2.31
17	Butanoic acid, butyl-1,1-d2 ester	144	$C_8H_{14}D_2O_2$	1.53
18	m-Cresol	108	C_7H_8O	1.21

The composition of the heavy fraction estimated by the peak area % of GC-MS

Table 5: Physical properties of pyrolysis liquid and its fractions

		Heating value (MJ/kg)			
Sample	Appearance	GHV	NHV	Water content (% w/w)	pH value
Pyrolysis liquid	Light black	22	21	30	3.72
Light fraction	Dark yellow	14	12	60	2.67
Heavy fraction	Dark black	28	27	1.5	4.50

CONCLUSIONS

Vacuum distillation was used to fractionate a woody pyrolysis liquid obtained from local suppliers in Phatthalung Province. Fractionation has shown to be a useful technique to assess the whole pyrolysis liquid with respect to physiochemical characteristics of its fractions. The compositions of the pyrolysis liquid, its light fraction and its heavy fraction were experimentally determined and classified into different groups according to their chemical structures. It was obvious that the chemical compositions of the pyrolysis liquid and its two fractions were all different. The light fraction had high water content and strong acidity;

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however, the pyrolysis liquid and its heavy fraction had relatively low acidity and low water content. The heating value of the light fraction was lower than those of the pyrolysis liquid and its heavy fraction, whereas the heavy fraction's heating value was almost double that of the light fraction. The thermal behaviour results that were obtained indicated that the light fraction had the highest rate of decomposition and the lowest residual yield; in contrast, the heavy fraction had a slow weight loss over a wide range of temperatures and it had the highest residual yield.

The results of this study demonstrated that the pyrolysis liquid produced during the process of charcoalproductionhas the potentialfor more extensive and beneficial use. For instance, the light fraction, which has high acetic acid and water contents, can be used as a feedstock for producing pure acetic acid, whereas the heavy fraction can be directed to further processing and upgrading for use as a fuel. It also could be used as the raw material for producing a number of valuable chemicals, which could be more attractive and beneficial than using it to make fuels.

ACKNOWLEDGEMENTS

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Persian Abstract

چکیده

مایع پیرولیز به دست آمده از منابع محلی در ایالت فتالونگ تایلند، بوسیله روش متداول تقطیر جزء به جزء (سبک و سنگین) در خلاء تفکیک گردید. خصوصیات فیزیکوشیمیایی و رفتار حرارتی مایع پیرولیز مورد بررسی قرار گرفت. مشخص شد که جزء سبک تر میزان آب بیشتر و اسیدیته قوی تری از جزء سنگین و مایع پیرولیز دارد. ارزش حراراتی جزء سبک تر کمتر از مایع پیرولیز و جزء سنگین بوده و ارزش حراراتی جزء سنگین تقریبا دو برابر جزء سبک بوده است. رفتار حرارتی مایع پیرولیز و دو جزء سبک و سنگین نیز محاسبه گردیده که جزء سبک دارای بالاترین سرعت تجزیه و پایین ترین بازده مواد باقیمانده بود؛ در مقابل آن، جزء سنگین آهنگ کاهش وزن کند در طیف گسترده ای از دما، و حداکثر بازده مواد باقیمانده را دارد. ترکیب شیمیایی مایع پیرولیز و دو جزء توسط جذب اتمی مورد تجزیه و تحلیل قرار گرفت. توزیع شیمیایی برای دو جزء و مایع پیرولیز متفاوت بوده و جزء سبک تر از اسید استیک و جزء سنگین تر عمدتا از ترکیبات فنلی می‌باشد.