

Pyrolytic Extraction and Characterization of Oil from Waste Recharge Scratch Card Papers for Industrial Application

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Abstract. Oil extracted from mobile phone waste recharge scratch cards paper by thermal pyrolysis was investigated. The oil was characterized by its physical, chemical, and functional groups present. The physicochemical characteristics of the oil determined are density 900 kg/m³, viscosity 1.5 mm²s⁻¹, acid value 1.122 mgKOH/g, saponification value 98.175 mgKOH/g and iodine value 22.84 gI₂/100 g. The pour point and flashpoints are -15 °C and 90 °C respectively. The Fourier Transform Infrared (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS) revealed the presence of aldehydes, ketones, carboxylic acids, esters, alkenes alkanes, ethers, and phenol. This indicates that the oil has industrial applications in chemical, pharmaceutical, and biodiesel production.

Keywords: bio-oil; biomass; pyrolysis; physiochemical.

INTRODUCTION

Pyrolysis is the thermal conversion of organics in the absence of oxygen. It is a promising and environmentally friendly way of energy recovery from biomass as biomass is the only renewable source of fixed carbon. However, among the thermochemical conversion methods, pyrolysis is the most suitable method to produce bio-oil as the main product [19].

Bio-oil obtained by the pyrolysis of biomass is thus emerging as an alternative source of sustainable energy for diesel engines, gas turbines, heating applications, and for use as a chemical feedstock [11]. Bio-oils are highly oxygenated, complex mixtures, viscous, relatively unstable, susceptible, corrosiveness, and poor heating value may present some difficulties on their direct use as conventional fuels [13].

In the pyrolysis process, the volatile components condense to bio-oil or can be subjected to further treatment and processes to produce secondary products such as higher value and quality fuel or chemical products [17]. Biomass utilization gives the possibility of generating value-added products such as chemicals or activated carbons, which means an attractive economic and technological solution [15]. Lignocellulosic biomasses have tremendous potentials in the production of fuels and chemicals. These materials are available in surplus worldwide and do not compete with the food supply [21].

The most important component obtained during pyrolysis is pyrolysis oil. The organic compounds of bio-oil are acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and a large proportion of lignin-derived oligomers [7]. Bio-oils are composed of differently sized molecules derived primarily from the

depolymerization and fragmentation reactions of three key biomass building blocks, i.e., cellulose, hemicellulose, and lignin, resulting in its composition and properties of considerable difference from those of petroleum-based fuel oils [24].

In recent years, the research on bio-oil has been paid more attention due to the property of sustainable, carbon-neutral, and easy to store and transport. Series of methods such as pyrolysis, liquefaction, gasification, hydrotreatment, etc. are developed to prepare and upgrade bio-oil. Pyrolysis is the more efficient method and the pyrolysis process conditions can be optimized to maximize the production of liquids (tar, bio-oil), solids (char), or gases whose distribution depends on the experimental conditions applied especially temperature and heating rate [9].

Pyrolysis has proved itself to be a new type of solid biomass and waste utilization technique that transforms biomass and waste material of low-energy-density into bio-oil of high-energy-density and recover higher-value chemicals. The maximum bio-oil yield of pyrolysis products from the waste paper of 49.13% was achieved at 420 °C and the spectroscopic and chromatographic analysis revealed that bio-oil contained many different chemical classes with anhydrosugars, carboxyl compounds, carbonyl compounds, and aromatic compounds are the four main different compounds in bio-oil [5].

The chemical constituent of biomass contains a different proportion of cellulose, hemicellulose, and lignin substrate. The biomass substrate which contains a greater proportion of lignin derivatives can yield more bio-oils yield [25].

The biomass fast pyrolysis is attractive because the biomass can be readily converted into liquid products. These liquids, such as crude bio-oil, have advantages in transport, storage, combustion, retrofitting as well as flexibility in production and marketing [23].

Recharge card is one of the fastest-selling Global systems for mobile communication (GSM) in most developing countries, especially in Nigeria. Recharge cards are basic top-ups on mobile phones (for calls), tablets, computers, and modems (for internet connection subscription). The printing and usages of recharge vouchers for all networks (MTN, AIRTEL, GLO, ETISALAT, etc.) in Nigeria are increasing because of the high rate of user demand. However, these mobile phone recharge cards have not received the needed safety watch

and attention on the danger it likely poses on the environment [10]. Similarly, commercial available recharged cards in Nigeria are silver coated which is of a health hazard on humans and living creatures due to contamination with heavy metals [2].

This study was aimed at pyrolytic extraction and characterization of oil from mobile phone recharged cards for industrial applications. The recharged cards were selected for this research because it has the potential for bio-oil and bio-chars. Also, the disposal of waste scratch cards paper may cause environmental pollution.

MATERIALS AND METHODS

Sample collection and preparation. Waste recharge card samples were collected from local recharge card vendors within the University of Jos Community. The samples were sun-dried for 48 hrs, cleaned using cotton wool to remove dust particles, and shredded to smaller sizes.

Pyrolysis Process. Ten grams (10 g) of the shredded sample was charged into the boiling tubes. The loaded tube was fitted with a wooden cork that allows for the escape of the syngas and a glass trap used to collect the bio-oil generated in the process. The thermometer was inserted into the point designated for temperature measurement and supported by a retort stand. The dried waste recharge card paper is heated in a pyrolysis reactor gradually at the rate of 30 °C per minute to the temperature of 350 °C and gas was condensed to liquid containing bio-oil and water. The bio-oil was then separated from water in the mixture and purified by filtration using Whatman filter paper 45 µm mesh size. The purified oil was characterized by physical and chemical properties.

RESULTS AND DISCUSSION

The physicochemical characteristics of the waste recharge card bio-oil are summarized in Table 1.

Table 1 – Physiochemical properties of pyrolyzed bio-oil

Parameters	Bio-oil
Density (kg/m ³)	900
Iodine value (gI ₂ /100 g)	22.84
Acid value (mg KOH/g)	1.122
Free fatty acid (wt.%)	0.561
Saponification value (mg KOH/g)	98.175

The density of the oil determined was 900 kg/m^3 and is lower than the density of vegetable oils (930 kg/m^3) and higher than petroleum (881 kg/m^3). The iodine value obtained was $22.84 \text{ gI}_2 / 100 \text{ g}$ (Table 1) and is relatively low compared to the standard values for most oils ranging between 80 and $106 \text{ gI}_2 / 100 \text{ g}$ [1]. The iodine value measures the degree of unsaturation in fat or vegetable oil. It determines the stability of oils to oxidation and allows the overall unsaturation of the fat to be determined qualitatively. Generally, oils having iodine value below $100 \text{ gI}_2 / 100 \text{ g}$ are non-drying, those having values between $100 - 130 \text{ gI}_2 / 100 \text{ g}$ are semi-drying, and those having values above $130 \text{ gI}_2 / 100 \text{ g}$ are termed drying oils [4]. The greater the iodine value, the more unsaturation and the higher the susceptibility to oxidation.

The acid value and free fatty acid of the pyrolytic oil were 1.122 mg KOH/g and 0.561 mg KOH/g respectively. Acid value quantifies the fatty acid found in the oil as it measures the free fatty acids (FFA) of oil. The low value obtained shows that the oil is stable and indicates a maximum purity and suitability for soap production [8]. Oil with high acid value implied high % FFA and will undergo rancidity due to the hydrolysis of the free fatty acids on storage. The low %FFA reduces the tendency of the oil to undergo hydrolytic activities [3].

The saponification value of the oil was 96.175 mgKOH/g and is lower than FAO/WHO standard 181.4 mgKOH/g [1]. This shows that the oil is of lower molecular weight and this property is very important because if it is too high the formation of soap will be more prevalent instead of the desired biodiesel [6]. The saponification value of oil serves as an important parameter in determining the suitability of the oil for soap making.

Table 2 shows a comparison of the fuel properties of the oil and ASTM standard for biodiesel. The density of the oil is within the range of ASTM specification $800-900 \text{ kg/m}^3$. This depicts that the oil can be a raw material for biofuel production. The density of the fuel is an important factor for good engine performance and the higher the density, the more difficult it becomes to pump the fuel. Also, the low value of iodine value ($22.84 \text{ gI}_2 / 100 \text{ g}$) obtained shown in Table 1 indicates that biofuel produced from the oil will be better fuel in terms of oxidative stability and cetane number [18].

Table 2 – Comparison of biofuel properties of oil and ASTM Standard

Parameters	Bio-oil	ASTM Standard for biodiesel
Density (kg/m^3)	900	800-900
Viscosity (mm^2s^{-1})	1.5	1.9-6.0
Pour point ($^{\circ}\text{C}$)	-15	-2
Flash point ($^{\circ}\text{C}$)	90	<130

The viscosity of the oil is close to the ASTM standard for biodiesel. Viscosity plays an important role in the atomization of the fuel when injected into the combustion chamber. High values of viscosity cause inefficient atomization of the fuel and do not contribute to the formation of a good air-oil mixture (resulting in poor combustion) while low values of viscosity cause an average droplet diameter too small, which decreases the reach of the particles within the chamber, and so part of the oil is not burned [14].

Pour point is the lowest temperature at which the product continues to flow when it is cooling, without stirring. The pour point of the oil obtained ($-15 \text{ }^{\circ}\text{C}$) is lower than ASTM for biodiesel and higher than petrol diesel ($-28 \text{ }^{\circ}\text{C}$) indicating that the performance of the biodiesel in cold conditions will be worse than that of petroleum diesel [6]. The flashpoint of the oil was $90 \text{ }^{\circ}\text{C}$ and is between the value of the ASTM standard for biodiesel ($>130 \text{ }^{\circ}\text{C}$) and petrol diesel ($90 \text{ }^{\circ}\text{C}$). This will make the biofuel produced from the oil safe for use and storage as fuels with lower flash points tend to ignite at lower temperatures making it highly dangerous if it is not stored and used properly [12].

The GC/MS analysis of the oil in Figure 1 is summarized in Tables 3. Figure 1 shows the peak number and corresponding retention time while Table 3 displayed % abundance of the various compounds in the oil sample.

Methyl-n-heptanoate, methyl decanoate, and the methyl (10 E)-10-octadecanoate are predominant in the sample with a % abundance of 29.65, 15.6, and 11.38 respectively.

Methyl tetradecanoate (9.6 %) and methyl butanoate (9.36 %) are in a moderate amount and are ester compounds. Also, in moderate quantity are alkanes 2,7-dimethyloctane (8.73 %) and 1cosane (8.54 %). 2-butyl-1-octanol (4.63 %), 2(11-methyl dodecoxymethyl) (3.59 %) and 9-octadecenoic acid (3.51 %) are in minor quantity while in trace amount are methyl 3-methyl pentanoate, 13-methyl oxacyclo tetradecane-2,11-dione and

Methyl decanoate with % abundance 0.78, 0.60 and 0.48 % respectively. The GCMS revealed the presence of ester, alkanes, alcohol, and carboxylic acid in the oil sample.

The FTIR spectrum of the sample is shown in Figure 2 and the corresponding functional group in Table 4.

Name of compound	Formula	% Abundance
Methyl 3-methylpentanoate	C ₇ H ₁₄ O ₂	0.78
Methyl butanoate	C ₅ H ₁₀ O ₂	9.36
2,7-dimethyloctane	C ₁₀ H ₂₂	8.73
Methyl-n-heptanoate	C ₉ H ₁₈ O ₂	29.65
Methyl n-heptanoate	C ₈ H ₁₆ O ₂	0.98
Methyl decanoate	C ₁₁ H ₂₂ O ₂	15.60
Methyl decanoate	C ₁₃ H ₂₆ O ₂	0.48
Ethyl hexadecanoate	C ₁₈ H ₃₆ O ₂	0.91
Methyl tetradecanoate	C ₁₅ H ₃₀ O ₂	9.60
Methyl(10E) -10- octadecanoate	C ₁₉ H ₃₆ O ₂	11.38
2-butyl-1-octanol	C ₁₂ H ₂₆ O	4.63
9-octadecenoic acid	C ₁₈ H ₃₄ O ₂	3.51
13-methyl oxacyclo tetradecane-2,11-dione	C ₁₄ H ₂₄ O ₃	0.60

Table 3 – GCMS analysis of the pyrolyzed oil

Name of compound	Formula	% Abundance
7-ethyl tridecane	C ₁₅ H ₃₂	1.51
1 cosane	C ₂₀ H ₄₂	8.54
2(11-methyl dodecoxymethyl)r	C ₁₆ H ₃₂ O ₂	3.59
1-acetoxyhexdecane	C ₁₈ H ₃₆ O ₂	1.84
Methyl n-hexanoate	C ₇ H ₁₄ O ₂	1.12

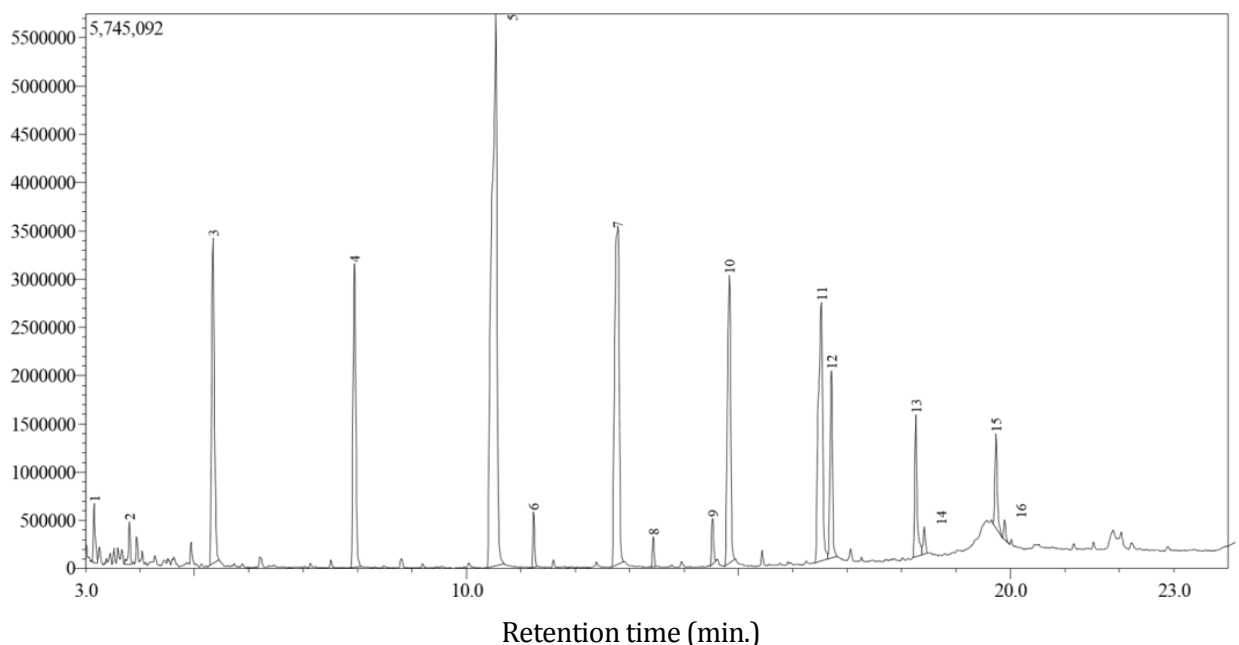


Figure 1 – GCMS Spectra of the pyrolyzed oil

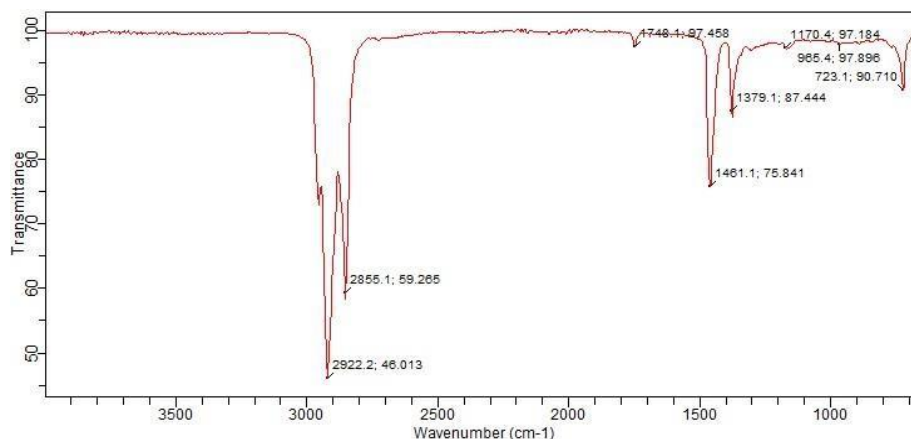


Figure 2 – FTIR of pyrolyzed oil

The O-H stretching vibration at frequency 2922.2 cm^{-1} indicates the presence of phenol and alcohol functional groups [16]. The presence of alkane was detected at 2855.2 cm^{-1} with C-H stretches vibrations. The C=O stretching vibration at 1748.1 cm^{-1} indicates the presence of aldehydes, ketones, carboxylic acids, ester. The presence of alkenes was detected by C=C stretching vibration at 1461.1 cm^{-1} .

Table 4 – FTIR of pyrolyzed oil

Broadband (cm^{-1})	Functional group
1170.4	Esters
2922.2	Alcohol
2855.1	Alkanes
1748.1	Aldehydes, ketones
1379.1	Carboxylic acid
1461.1	Alkenes
765.4	Phenols

The presence of ethers, esters, etc was detected at vibrations stretching 1170.4 cm^{-1} [20]. The compounds detected by their functional groups summarized in Table 3 are ester, carboxylic acids, alkanes, and alkenes. Others are phenols, ketones, and alcohols as revealed by the GCMS.

Generally, cellulose pyrolysis produces mainly three substances (furans, pyrans, and linear small

molecules) and the foremost pyrolysis products include levoglucosan, glycolaldehyde, and 5-hydroxymethyl-furan. The dehydration reaction that is caused by the carbonization of cellulose molecules with increased pyrolysis temperature is indispensable in addition to the depolymerization of cellulose chains and the configuration of various small molecule products [22].

CONCLUSION

Oil was successfully extracted from waste recharge cards by pyrolysis. The physicochemical and fuel properties obtained revealed its suitability for soap making as well as biodiesel production. The GC-MS and FTIR of the samples also showed the presence of many chemical both linear and cyclo-compounds which have wide industrial applications. Although several promising results were obtained, further investigations including quantitative analyses are necessary to determine the desired characteristics for downstream production of fuels or chemicals as well as improve the bio-oil quality for its utilization.

Competing interests

The authors declare that there are no competing interests.

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