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Potato (*Solanum tuberosum*) Peel Waste Utilization for Eco-friendly Bio-oil Production via Pyrolysis

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ABSTRACT

This paper focused upon the production of bio-oil from potato (*Solanum tuberosum)* peel waste (PPW) available in Bangladesh. For the conversion of potato peel into liquid biofuel, the PPW was assessed as received and physico-chemical characterization were carried out. Here, pyrolysis process was performed in a fixed bed horizontal pyrolyzer and the effect of reaction time and temperature on product distribution during pyrolysis and the physio-chemical properties of the produced bio-oil were investigated. The maximum bio-oil yield from PPWs was 32.15 wt.% at 450 °C and 45 min reaction time. Besides bio-oil, non-condensable gases (26.68 wt.%) and bio-char (41.18 wt.%, a porous carbonaceous material) were produced during pyrolysis. Bio-oil produced from PPWs was characterized by conducting various physico-chemical analyses. The fractionation of produced bio-oil gives 68 wt.%medium distillates (80 – 100 °C), 21 wt.% light distillates (below 80 °C fraction) and 11 wt.% residue (heavy fraction; above 100 °C). The use of the produced biofuel in blend with commercial fuel will bring a positive change in fuel economy of the country and will ensure the proper management of potato peel waste and secure a clean environment.

Keywords: Potato peel waste, Pyrolysis, Bio-oil, Parametric study, Bio-char, Fractional Distillation.

1. Introduction

The fossil fuel demand has been consistently increasing with the development of agricultural and industrial sectors. In contrast, the fossil fuel-based economy is not eco-friendly from the point of energy security, environmental impacts and economic development issues. Today, 86% of global energy consumptionis met by fossil fuels. Greenhouse gases (GHGs) emission from the use of conventional fuel endures to generate severe worries due to its effects on the local weather conditions. United Nations (UN) set a goal to bound the global temperature upward push to beneath 2 ° C[1]. Renewable energy could be asubstitute to meet the forthcoming energy demands and to decrease the global problem of environmental pollution. Biomass,one of the oldest sources of world energy supply, is a renewable energy source includes wood, agro-residues, grasses, oil seeds, animal wastes, municipal solid wastes (MSW), algae, industrial wastes, aquatic plants etc.[2]. Biofuel can be solid, liquid (e.g., bio-alcohols, vegetable oils, biodiesels etc.) or gaseous and can be produced from various biomass[3]. Biofuels are non-polluting, easily accessible and reliable fuel for future energy security, green development, GHGs reduction[4]. Biomass conversion to liquid biofuels e.g., biodiesel and bioethanol have been studied in the past but the use of food items for biofuel production raises ethical concern from public. Hence, use of MSW, non-edible seeds, various wastes e.g., potato peels etc. for biofuel production are becoming more attractive as these are waste materials sources and are not used as food item[5].

Pyrolysis, the decomposition of organic substances at relatively high temperatures in absence of oxygen or ominously less oxygen than that required for thorough combustion, is employed to produce liquid, solid or gaseous biofuel from biomass[6]. Among different pyrolysis processes (e.g., flash pyrolysis, fast pyrolysis and slow pyrolysis), fast pyrolysis processes is considered as the most economical and viable which typically produce 60-75 wt.% bio-oil, 10 - 20 wt.% gases and 15-20 wt.% char based on the biomass used[7]. Here, organic components in biomass undergoes thermal decomposition at 350 - 550 °C in the absence of air and sometimes the temperature goes up to 700–800 °C[8]. The decomposition rate depends on various process parameters e.g., reaction temperature, pyrolysis time, heating rate, rector design, types of feedstock used etc. Bio-oil, also termed as pyrolys is oil and bio-crude[9], composed of components including methanol, organic acid (e.g., acetic acid, formic acid), acetone, cyclopentanone, phenol, methoxyphenol, levoglucosan etc.[10],[11]. Bio-oil can be used to generate heat and power in boilers and furnaces as well as to produce various chemicals[12].

Pyrolysis of Napier grass[13], grape bagasse[14], corn stover (leaves, stalks etc.)[15], sewage sludge and wood chip [16] produces bio-oil (35 - 45 wt.%), bio-char (29 - 31 wt.%) and non-condensable gases (14 -26 wt.%). Pyrolysis of rice husk [17], sugarcane waste[18], jute stick [19] gives higher yields of liquid (45 -60 wt.%), considerable amount of biochar (18-25 wt.%) and comparatively small amount of gases (10 -20 wt.%) at 375 - 600 °C. Use of catalyst e.g., 10% of sepiolite[20] increases the bio-oil yield. Few studies on production of bio-oil from potato peel waste (PPW) have been reported[21],[22],[23]. However, an in-depth understanding of bio-oil production from potato peels available in Bangladesh is essential. Hence, this study concentrated on the bio-oil production from PPW collected from Dhaka City of Bangladesh and pyrolysis process parameter optimizations including pyrolysis temperature and time to attain the higher yield (mainly liquid fuel). The physico-chemical characterization of produced bio-oil and fractional distillation of the raw bio-oil for possible petro-fuel production were also explored.

2. Experimental

Raw Materials (Potato Peels) and Chemical Reagents

Locally available potato peels wastes (PPWs) were used as biomass feed stocks, which were collected from Sristi Dining of Fazlul Haque Muslim Hall, University of Dhaka, Dhaka-1000. The collected PPWs were sun dried and then oven-dried in an electrical oven at 105 °C for 6 hr for moisture removal from the peels. Subsequently, the dried samples were stored in plastic bags (air-tighted)or desiccator until further analyses. Analytical grade chemicals and reagents were used in this study and were purchased from Sigma Aldrich and Merek (india).

3. Methodology

Pyrolysis of the Dried Potato Peel Waste (PPW)

The dried PPWs was pyrolyzed in a horizontal pyrolyzer. In pyrolysis process, the PPWs was heated at 400-600 °C in the absence of oxygen/air to produce bio-oil. The horizontally fixed bed pyrolyzer was fabricated of stainless steel (304 grade; Length: 115 cm; Inner Dimeter: 6 cm) and there was a round distribution plate having 1.5 mm diameter. PPW samples (100 gm in each batch) were placed on the distribution plate set inside the pyrolyzer. To ensure the inert atmosphere inside the reactor, a nitrogen gas flow (50 mL/min; at 1.0 atmpressure) was maintained over the pyrolysis time. The pyrolyzer was heated (heating rate of 50 °C/min) until the reactor temperature reached to the set point. The temperatures of reaction and reactor were observed with two thermocouples (K-type, NTT Heating, SdnBhd, and Selangor, Malaysia). The reaction time for pyrolysis was kept in between 30 - 60 min after the reactor temperature reached to the set point.

The pyrolysis products i.e., fluid were condensed by passing the fluid through a series (4 sets) of condenser (consisting of bottles that placed in ice bath). The condensate (i.e., bio-oil and some dusts) remained in the bottles while uncondensed gaseous partt hat released from fourth condenser bottles vented to the atmosphere. The condensed bio-oil (that deposited in each of the four condenser bottles) was collected, filtered and processed for further analysis. The bio-char, obtained as residue in the pyrolyzer, was taken out from the pyrolyzer when cooled down. An overall material balance was then calculated. A schematic of the overall process starting from raw material to bio-oil production is shown in **Figure-1** and a photographic view of the overall process is illustrated in **Figure-2**.

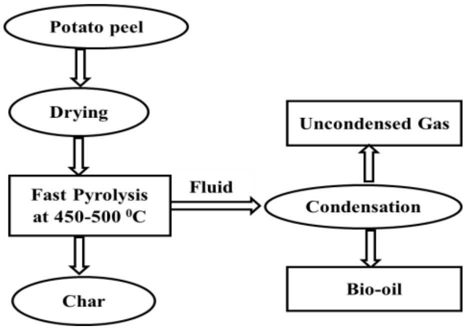


Fig. 1. A flow sheet for bio-oil, uncondensed gases and bio-char production from PPWs

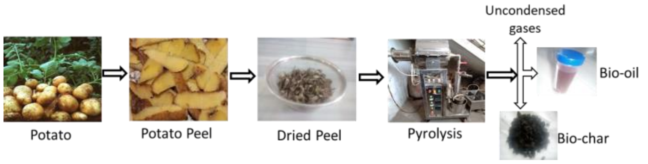


Fig. 2. A photographic presentation for the production of biofuel from PPW.

Fractionation of Raw Bio-oil

The raw liquid oil (bio-oil) produced via pyrolysis process was then fractionated using distillation apparatus based on boiling temperature range. Here, known volume of raw oil was taken into distillation flask and the flask was gradually heated using heating mantle. The obtained product was fractionated into three groups based on boiling temperature ranges: light distillate (room temperature to below 80 °C), medium distillate (80 - 100 °C) and heavy fraction (above 100 °C).The spectroscopic analysis of the distillates (using FTIR) were carried out to identify the functional groups presents in the distillates.

Characterization of the Produced Bio-oil

The produced bio-oil were characterized using analytical techniques and instruments. This study focuses on the characterization of liquid product. The properties of bio-oil e.g., pH, viscosity, density, water content, flash point, pour point etc. were carried out. Density of bio-oil was measured at 15 °C using the Picno-meter, were as the capillary stopper connected to a relative density bottle of 50 mL capacity. The kinematic viscosity of the sample were determined using Capillary U-Tube Viscometer where the time required for the gravity flow of 50 mL bio-oil sample was counted. The experiment was performed at 40 °C, and 100 °C. For the viscosity measurement, the ASTM D445-65 method was applied. The Flash point, a temperature at which a fuel will form vapor and ignites when exposed to flame, of bio-oil was determined by Eralytics Flash Point Apparatus following the ASTM-D 93-62 method. The pour point, the temperature (lowest) below which the oil lose its flow property, was measured following the ASTM-D 97-57 method. The Calorific Value (CV) of the produced bio-oil was determined by using a Bomb Calorimeter (Model-NW 21, Julius Peter, Berlin, Germany).

The Fourier-transform infrared spectroscopy (FTIR) of the raw bio-oil and distillates (organic phase) were carried out in FTIR (8400S Shimadzu) Spectrophotometer within the wavenumber of 4000-400 cm^{-1}. For FTIR study, 0.1 mL of bio-oil was taken on the KBr window of FTIR and around 0.20 mm round Teflon spacer was used in between the windows for allowing the path length.

4. Results and Discussions

Raw Materials Characteristics

The proximate analysis of dried PPWs showed that the sample contained 4-5 wt.% moisture, 71 wt.% volatile matters, 16-17 wt.% fixed carbon and 6 wt.% ash[21]. It is notable that the higher ash content may lead to formation of more char[24]. The higher heating value (HHV) of dried potato peel was found 17.3 MJ kg^{-1}.

Parametric Study of the Bio-oil Yield: Process Optimization

During pyrolysis of the dried PPWs, liquid oil, solid bio-char and gaseous product mixture were obtained. The liquid oil was found as a single phase and dark reddish brown to dark green in color. Various experiments were carried out to optimize the bio-oil production from dried potato peels. It is notable that the yields of the products vary with process conditions. **Table-1** shows the product yields at various pyrolysis temperature. The maximum yield of bio-oil was found at 450 °C for 45 min which was 32.14 wt.% of the dried PPW used in pyrolysis. With the decrease of the temperature below 450 °C, the percentages of oil and gas yield decreased whilst the char yield increased. It is notable that high temperature degradation of hemicellulose and lignin results in a significant loss products in the form of volatile materials, leaving carbon matrix i.e., bio-char. In contrast, with the increase of pyrolysis temperature, the oil yield did not varied but considerably increased the gaseous product yield along with the decrease of bio-char yield. Hence, 450 °C was considered as optimum pyrolysis temperature.

One of the reasons for the reduction of liquid yields at comparatively lower temperatures (less than 450 °C), may be that lower temperature was not sufficient for completion of pyrolysis. Furthermore, the high content of ash in the raw materials also accelerate the bio-char formation, which reduces the yield of bio-oil. In contrast, higher temperatures favors the gaseous yield, may be owing to secondary decomposition reactions of bio-oil constituents to lighter gaseous products[25].

Table 1: Effect of pyrolysis temperature on products yield. Pyrolysis time = 45 min.

Temperature (°C)	Oil yield(wt.%)	Char yield (wt.%)	Gas yield (wt.%)
400	15.2	70.21	14.59
425	22.7	51.45	25.85
450	**32.14**	**41.18**	**26.68**
475	32.28	38.56	29.16
500	**32.04**	**37.03**	**30.93**
525	31.3	34.44	34.26

The pyrolysis time has a considerable impact on the yield of liquid bio-oil. **Table-2** illustrates the effects of pyrolysis time on liquid yield at 450 °C. The bio-oil yield at 500 °C is also presented for comparison. It is observed that the yield of bio-oil surged with the increase of the reaction time, however, after 45 min of reaction time, the yield gradually decreased with the rise of reaction time.

Table 2: Effect of reaction time on bio-oil yield at pyrolysis of 450 °C and 500 °C

Pyrolysis time (min)	Bio-oil yield (Wt.% PPWs)	
	At 450 °C	**At 500 °C**
10	12.56	-
15	17.23	18.27
30	28.70	29.2
45	32.14	32.04
60	27.10	28.35

Physico-Chemical Characterization of Bio-oil

The common features of pyrolysis liquid products are acidic, contains certain amount of water and have moderate heating value as well as very low sulfur content [17]. **Table-3** represents the physical-characteristics of bio-oils derived from pyrolysis of dried PPWs at 450 °C for 45 min. The characteristics are also compared with the typical bio-oil. A low pH value of 3.6 of potato peel derived bio-oils indicates that the oil is corrosive. This acidic nature of the pyrolysis oils also indicates the presence of significant quantity of organic carboxylic acids in the bio-oil, mostly derived from lignocellulose part of the PPW. The sulphur in the raw bio oil was not detected indicates that the product is mostly sulfur free. The density and viscosity are found lower than those of typical bio-oils.

Table 3: Characteristics of bio-oil (Pyrolysis temperature: 450 °C and time: 45 min)

Properties		**Methods**	**Potato peel bio-oil**	**Typical bio-oil** [24]
Density@ 15 °C, g/cc		IP-131/57	1.03	1.12
Viscosity	At 40 °C, cSt	ASTM-D 445-65	1.78	5-20
	At 100 °C, cSt	”	1.18	-
pH value		pH meter	3.6	2-5
Water content, wt.%		ASTM-74/57	17	20-50
Heating value, MJ/Kg.		Bomb calorimeter	14.78	12-25
Flash point, °C		ASTM-D 93-62	89	85
Pour point, °C		ASTM-D 97-57	-9 to -11	-15
Ash content, wt.%		IP 4/58	0.02	0.10
Sulfur content, wt.%		ASTM-D 129-64	not detected	trace
Calorific Value, MJ/ kg		Bomb Calorimeter	20.23	32 - 37[23]

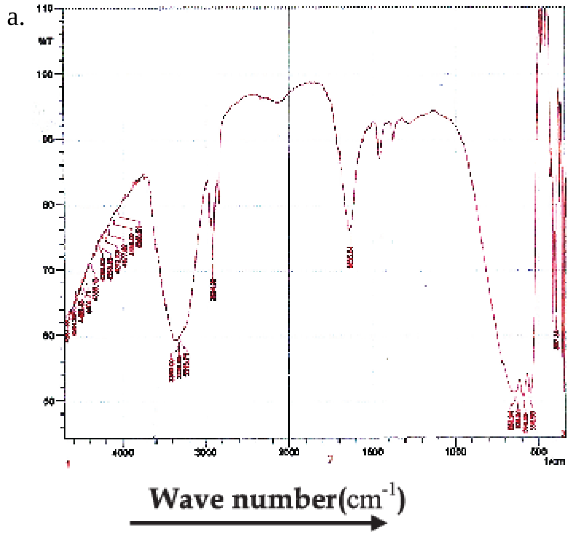
The viscosity (kinematic) of the produced bio-oil was lower than that of the traditional bio-oil. It is notable that the viscosity could be influenced by many factors, like the compositions of biomass, particle size of biomass feedstock, storage time, pyrolysis temperature, sweeping gas rate and usage of hot vapor filter. The flash point and pour point observed in this study were found similar to previously reported data from other authors [26]. The calorific value (CV) of the produced bio-oil from PPWs was found lowered to that of the reported value. The lower CV of the oil may be owing to the presence of carbonyl compounds [19].

Fractionation of Raw Bio-oil

The obtained bio-oil was fractionated **i**nto light distillate (room temperature to below 80 °C), medium distillate (80 - 100 °C) and heavy fraction (above 100 °C). The percentages of products distribution were found as follows: 21 wt.% light distillates, 68 wt.% medium distillates and 11 wt.% residue (heavy fraction).

FTIR Study of Bio-oil and Fractionated Medium Oil

The FTIR spectroscopic analysis of the samples were carried out to determine the functional groups present in the bio-oil. The major peaks was found in the region of 555.50 cm^{-1}, 594.08 cm^{-1}, 651.94 cm^{-1}, 1635.64 cm^{-1}, 2924 cm^{-1}, 3313.71 cm^{-1}, 3336.85 cm^{-1}, 3360 cm$^{-1.}$ The major functional groups of the produced bio-oil are halogeno compounds (C-X) e.g., C-Br, C-I that appears in 515 - 690 cm^{-1}. Cyclic alkene compound (C=C) that appears at 1635.64 cm^{-1}, alkane compound (C-H) that appears at 2924.1 cm^{-1}, secondary amine compound (N-H) appears at 3313.71 cm^{-1}, aliphatic primary amine (N-H) appears at 3360 cm^{-1}. The common bands appears both in the raw bio-oil and the medium distillates are illustrated in **Table-4** while the FTIR spectrums of the both products are shown in **Figure-3**. It is notable that the raw bio-oil showed an additional band at 2924.09 cm^{-1} may be due to C-H stretching vibration of medium alkanes whereas the medium distillates showed a band at 3275.13 cm^{-1} which probably due to C-H stretching vibration of strong, sharp alkyne.



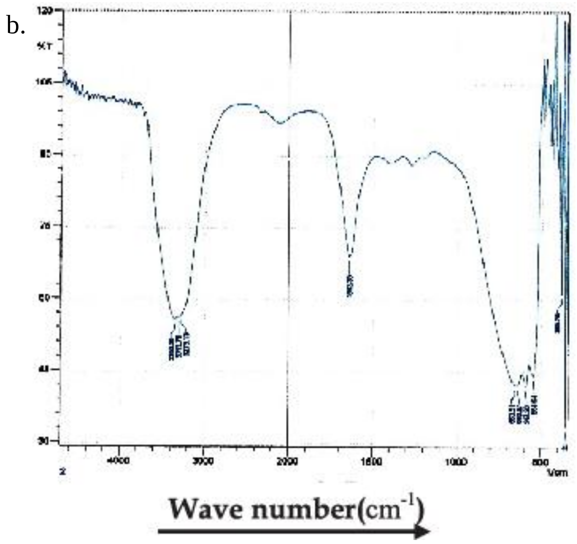


Fig. 3: FTIR Spectra of (a) Bio-oil after pyrolysis (Left)& (b) Medium oil (obtained at 80 – 100 °C temperature range during fractionation of bio-oil) (Right)

Table 4: The common peaks that observed in raw bio-oil and in medium distillates of fractionated bio-oil:

Wave number of band (cm^{-1})	Functional group
551.64 - 555.5	C-I stretching vibration of strong halo compound
594.08 - 97.93	C-I stretching vibration of strong halo compound
636.51 - 640.37	C-Br stretching vibration of strong halo compound
651.94 - 663.51	C-Br stretching vibration of strong halo compound
1635.64 -1643.35	C=C stretching vibration of medium cyclic alkene
2924.09	C-H stretching vibration of medium alkanes
3313.71	C-H stretching vibration of strong alkyne and sharp N-H stretching vibration of medium secondary amines
3352.28 -3360	N-H stretching medium aliphatic primary amines.

5. Conclusions

Potato (*Solanum tuberosum*) peel waste was pyrolyzed in a horizontal fixed bed reactor and the parametric effects of reaction time and temperature on product distribution during pyrolysis were studied. The characteristics of the produced bio-oil and fractionated distillates were investigated. During Pyrolysis at 450 °C and 45 min reaction time (Optimum condition), 32.15 wt.% bio-oil, 26.68 wt.% gaseous products and 41.18 wt.% bio-char were produced. The flash point, pour point, density, viscosity, other physical-chemical and fuel properties were compared with the reported data and found comparable. The fractionation of produced bio-oil provides mostly (68 wt.%) medium distillates (80-100 °C fraction). Direct use of bio-oil and its fractions as well as in blend with the commercial fuel will be an attractive and promising option to valorize and eco-friendly management of potato skin. The practical applications of the produced bio-oil and its fractions and comprehensive study on the produced bio-char and non-condensable gases will be explored in future to get a clear picture for further management of this kitchen waste.

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