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Production of Short Chain Aliphatic Hydrocarbon Fuel Gases – A new Renewable Energy Sources from Chrome Tanned Leather Wastes by Pyrolysis

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Abstract: *This paper focuses on production of short chain aliphatic hydrocarbon gases (C_xH_y) from proteinaceous chrome tanned leather solid waste (CLW) under pyrolysis process. The main objective of the present study was to develop a methodology for disposal of CLW without converting trivalent chromium (Cr^{3+}) into hexavalent chromium (Cr^{6+}). For this purpose the CLW was pyrolysed up to 800 °C in the batch type gasification reactor system. The composition of the yield obtained from CLW under pyrolysis process was renewable energy fuel gases, 33.03% out of which, maximum 6.20% short chain aliphatic hydrocarbon fuel gases generated at 700 °C; condensate liquid (CL), 33.32%; and residual ash, 33.65%. Gas samples were collected to determine the presence of short chain aliphatic hydrocarbon gases consisting of methane, ethane, propane, butane and pentane (C_1 to C_5) at 400 °C and at every 100 °C rise up to 800 °C. Gas chromatography-mass spectrometry (GC-MS) confirms the presence of (C_xH_y) in the fuel gases and the green energy renewable fuel gases comprising of C_xH_y and H_2 of about 16% could be generated from CLW. The X-ray photoelectron spectroscopy (XPS) analysis confirmed the solid residual ash contained no carcinogenic hexavalent chromium (Cr^{6+}).*

Keywords: *Pyrolysis, Leather wastes, Fuel Gases, Renewable Energy, Waste Management*

1. INTRODUCTION

Renewable fuels are important to the society due to an insatiable demand of conventional fossil fuels and its depleting nature over a period of time with respect to the massive uncontrolled inefficient usage of fossil fuels towards meeting the overall socioeconomic developmental activities which always widen the gap of energy demand and supply. If the finite amount of fossil fuels are depleted completely then all our routine activities will come to a screeching halt. To overcome this perennial problem, constant effort is made all over the world to generate energy from renewable sources including leather solid waste. Utilization of renewable energy sources and the application of environmentally sound energy efficient technologies are essential to sustainable development and to secure the quality of living and well-being of the future generations [1].

Leather solid waste generation from leather sector carries much significance because of their quantity and putrescible nature. It is a proteinaceous organic waste which can be treated as an alternative source of producing renewable green energy gaseous fuels. In tanning process, only 20 % of raw skin or hide is converted into leather [2] and remaining 80 % of raw materials are discharged as solid wastes. Approximately 8.5 million tons of leather solid waste is generated during the production of 11 million tons of rawhide processed in the world [3]. More than 90 % of global leather production is carried out through chrome-tanning process [4] which is also called wet-blue process. The pickled raw material absorbs 60 to 70% of the applied chromium in tanning process and the rest is discharged into the waste water and leather solid waste [5]. In tanning industry wet blue operation produces 290kg of chromium impregnated solid leather waste viz., wet blue trimmings, chrome splitting, chrome shaving, buffing dust and dyed trimming per ton of raw skins/hides [6]. CLW is impregnated with synthetic fat, oil, re-tanning agents and dye chemicals besides trivalent chromium [7]. The waste generated from chrome tanned leather is not biodegradable and toxic due to the chromium and nitrogen content [8]. Chromium containing leather waste material has been classified as one of the dangerous and hazardous waste if discharged into environment without any further treatment [9]. Increased risks for a number of cancers such as lung cancer, testicular cancer, soft tissue sarcoma, pancreatic cancer and bladder cancer have been reported [10].

Though chrome tanned leather solid wastes has been categorized under toxic material, it has high calorific value. The calorific value of the tanned leather solid waste is in the range from 17 to 20 MJ/kg [1, 11]. Gasification of this waste material can produce combustible gases with energy content in the range from 4.42 to 4.92 MJ/Nm^3 [12].

Regarding leather waste treatment, the techniques adopted presently to treat the primary leather solid wastes are: land filling, anaerobic digestion, composting, thermal incineration but these all are not viable technology to treat chrome tanned solid leather waste [2].

The available landfill sites rapidly reach their total capacity and the authorization of new sites becomes difficult [13]. The improper manual handling and transfer of leather waste in open vehicles create unhygienic conditions. Disposal of waste in low-lying areas without proper liners allow the leachate to mix with ground water which cause water contamination.

Thermal incineration is associated with serious air pollution problems due to emission of toxic hexavalent chromium (Cr^{6+}), halogenated organic compounds, poly-aromatic hydrocarbons etc. into environment. The major species formed from Cr^{3+} during thermal incineration of solid waste are $Cr_2(SO_4)_{3(s)}$, $CrOCl_{2(g)}$ and $Cr_2O_{3(s)}$ which later transformed into Cr^{6+} [14]. Hexavalent chromium (Cr^{6+}) is mobile can penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases [15]. At short-term exposure levels above the maximum contaminant level, Cr^{6+} causes skin and stomach irritation or ulceration. Long-term exposure at levels above the discharging limit causes dermatitis, damage to liver, kidney circulation, nerve tissue damage and death [16].

The main drawback of anaerobic digestion is the fact that proteins are incompletely broken down, producing amines that give rise to foul odors [17], it takes more detention period for complete digestion of the chrome tanned leather solid wastes. This technique is more suitable for generating biogas from chrome free leather waste and is less amenable for chrome impregnated leather waste. Investment cost on anaerobic digestion plant is very high and also it does not provide a solution for complete disposal i.e. zero waste disposals.

There are some reports on leather waste applications such as production of activated carbon from leather waste [18], production of ceramic materials, use of chromium tanned leather ash in ceramic bodies [19, 20] isolation and recovery of chromium from the organic matrix of leather waste [21, 22], conversion of dried sewage sludge into activated char and gas fuel [23], utilization of leather industry pre-fleshing in biodiesel production [24, 25] but no investigation on generation of short chain aliphatic hydrocarbon green energy gaseous fuel by pyrolysis without converting trivalent chromium into hexavalent chromium in the residual ash.

In recent years the interest in pyrolysis of wastes materials has increased as it provides an option for getting fuels with enhanced calorific value [26]. If leather solid wastes are pyrolysed, the leather industry will become more environmentally friendly due to less emission of global warming gases [27].

In pyrolysis, substances are not burnt but rather transform the waste into gaseous, liquid, char and tar at high temperature. The pollution caused from the leather industry wastes may be reduced and more valuable products can be obtained by converting them into green energy gaseous fuels through pyrolysis. Pyrolysis may be a useful way of waste management for energy and material recovery [28].

Hence, the focal theme of the present investigation was to generate green energy gaseous fuels through pyrolysis from proteinaceous chrome tanned leather solid wastes (CLW) without transforming the oxidation state of trivalent chromium (Cr^{3+}) to carcinogenic hexavalent chromium (Cr^{6+}).

2. MATERIALS AND METHODS

2.1. Description of Pyrolysis System

The reactor (SS 316 grade) used in the present investigation was fabricated in the laboratory with the following dimensions: inner diameter, 150mm; lid diameter, 200mm; and height, 300mm with wall thickness, 3mm. The main parts of the system as shown in Fig.1 are 1) induction furnace 2) air cooled condenser 3) water cooled condenser 4) gas filtration unit 5) suction pump 6) scrubber unit 7) dehydration unit 8) condensate collection container 9) energy recorder and 10) temperature controller. The desired functions of the above parts are that the induction furnace was used to supply the heat to the CLW for thermal decomposition under pyrolysis gasification process. In this gasification process the material (i.e. CLW) followed the sequential physical and chemical changes starting from removal of moisture to conversion into fuel gases, condensate liquid and residual ash. Air cooled condenser was used to bring down the temperature of raw fuel gases and separate the high fraction condensate. Water cooled condenser was used to further bring down the raw gas temperature nearer to the ambient and further condense the left over low fraction condensate.

Figure1.*Photo image of short chain aliphatic hydrocarbon fuel gases generating pyrolysis system*

A gas filtration unit was used to filter gas from non combustible volatile matters and ascertain the movement of gas. A suction pump was used to create an induced draft in the gas line and a scrubber unit was used to scrub the unwanted gas such as SOx and NOx. The dehydration unit was used to remove the moisture content of the wet gas. Condensate liquid (CL) was collected in the container and kept for further distillation. An energy recorder was used to measure the energy input to the reactor with respect to the temperature and mass of feeding. The residual ash collected from the bottom of the reactor was also subjected to hexavalent chromium analysis (Cr^{6+}). At the end of the experiment, the reactor was cooled to ambient condition using pre set temperature controller.

2.2. Characterization of CLW

The proteinaceous chrome tanned leather solid waste (CLW) was collected in air tight plastic containers (15 kg capacity) from a commercial tannery unit, processing raw skins/hides into chromium tanned finished leather in Chennai, India and stored at room temperature until for further use. CLW was characterised for moisture content, volatile matter, carbon, ash and calorific value in accordance with standard procedures IS : 1350 (Part 1) - 1984.

2.3. Analysis of Total Chromium and Hexavalent Chromium(Cr^{6+})

EPA Method 7196 A was used to determine the concentration of hexavalent chromium (Cr^{6+}) using UV-VIS-Spectrophotometer. The extract was transferred to a 100 mL volumetric flask. Diphenylcarbazide (DPC) solution 2mL was added followed by addition of H_2SO_4 to get pH of 2±0.5. Addition of DPC produced the red–violet product, and its absorbance was measured photometrically at 540 nm. The total chromium was determined by converting all the state of chromium in the sample to the hexavalent state by digesting the sample with sulfuric acid then oxidized with potassium permanganate (KMnO4) before reacting with DPC, measured the absorbent at 540 nm and the concentration was calculated using the standard calibration curve prepared using $K_2Cr_2O_7$.

2.4. Scanning electron microscopy and energy dispersive X-ray analysis

Scanning Electron Micrograph (SEM) analysis was carried out to determine the surface morphology of CLW and residual ash with high resolution using Hitachi, model S-3400N. Energy Dispersive X-ray analysis (EDX) was carried out to determine the elemental composition of the samples.

2.5. X-ray photoelectron spectroscopy analysis

The XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA) was used to analyse the composition and oxidation state of chromium elements in the near surface region of the samples kept under ultra high vacuum (10^{-8} mbar) conditions. The XPS spectra were acquired using a SPECS make XPS system with Al-Kα X-ray source at 1486.6 eV energy with 100 W power. The survey scan was obtained with 70 eV pass energy. Cr (2p), O(1s), N (1s) and C (1s) core level spectra were obtained with 25 eV pass energy. A commercially available CrO_3 compound was used as reference sample for hexavalent Cr. The Cr- 2p core level was fitted Gaussian-Lorentzian peaks to find the different oxidation states of Cr. The Cr $(2p)^{3/2}$ binding energy in different oxidation states are as follows: Cr^O at 574.2eV, Cr_2O_3 at 576.6 ±0.2eV; CrOOH at 577.3 ±0.2eV; CrO_3 at 579.2± 0.2eV.

2.6. Determination of short chain aliphatic hydrocarbon gases

The overall gas composition was analysed using LAND make Lancom III flue gas analyser. To determine methane, ethane, propane, butane and pentane (C_1 to C_5), gas samples were collected at 400 °C and at every 100 °C rise up to 800 °C using 5 mm hose, 1500 mm length S-type Pitot tube (Fig.2) connected to 3 L capacity tedlar bag.

The formation of short chain aliphatic hydrocarbon gases such as methane (C_1), ethane (C_2), propane (C_3), n-butane (C_4), iso-butane (C_4) and pentane (C_5) were identified using gas

chromatography GC-Methanizer, Model- Nucon 5765 (DASTA-720) and the test was carried out as per IS: 5182 (Part17). This was determined by injecting the respective authentic compounds of concentration 12ppm with a dilution factor of 5.

Figure 2. *Measurement of gas generated from CLW*

The retention time (min) of eluted aliphatic hydrocarbon compounds were 0.37-0.44 for C_1, 1.55-1.58 for C_2, 6.27-6.39 for C_3, 10.55-10.62 for n-C_4, 12.11-12.25 for iso-C_4 and 19.45-19.56min for $C_{5.}$ The short chain aliphatic hydrocarbon gases (C_1 to C_5) were quantified by dividing the sample area by standard area corresponding to the retention time of individual gases and then multiplied by the factors of standard concentration and its dilution factor.

3. RESULTS AND DISCUSSION

3.1. Characteristics of CLW

The CLW was characterised by pH, 5.64, moisture, 10.25 % and protein, 61.45 %. The composition of CLW as per ultimate analysis was Carbon, 44.20%; Hydrogen, 7.59%; Nitrogen, 9.55 %; Sulphur, 1.44 %; Oxygen, 26.64 % and Cr_{total}, 1.25 %. The proximate analysis showed the volatile matter, 55.55 %; ash, 7.58 % and fixed carbon, 26.62 %.

The density of CLW was 320 kg/m^3 and Gross Calorific Value was 17.78 MJ/kg (Table 1). The ultimate analysis of CLW, suggested that the present of carbon was high followed by nitrogen, hydrogen, chloride. The percentage of Chromium ($Cr._{total}$) was calculated as 1.25%.

The results revealed that chromium containing proteinaceous leather solid waste discharged from tanneries has high calorific value and there is a potential to generate alternative green fuels through pyrolysis treatment.

Table 1. *Characteristics of chrome tanned leather solid waste (CLW)*

Parameters	**Value**
Moisture %	10.25
Proximate Analysis (wt %)	
Fixed Carbon^a	26.62
Volatile Matter	55.55
Ash	7.58
Ultimate Analysis (wt %)	
Carbon	44.20
Hydrogen	7.59
Nitrogen	9.55
Sulphur	1.44
Chromium $Cr._{total}$	1.25
Chlorine	4.57
Silicon	2.94
Iron	1.69
Oxygen^b	26.77
Other Analysis	
Fat (dry wt %)	7.46
Protein content	61.45
pH of soluble matter	5.64
Density (g/cm^3)	0.320
GCV (MJ/kg)	17.78

3.2. Products of pyrolysis process of CLW

The composition of the yield obtained from CLW under pyrolysis process was gaseous fuel, 33.03%; condensate liquid, 33.32%; and residual ash, 33.65%. The condensate liquid on distillation left with combustible non aqueous diesel like fuel 2.73% and the rest with nitrogen, ammonia enriched aqueous distillate.

3.3. SEM and EDX Analyses of CLW and Residual Ash

The SEM image of CLW (Fig. 3a) shows the isolated collagen fibres. This is due to the presence of fat-liquors used in the manufacturing of leather that surrounded the fibres causing their separation. SEM image of residual ash obtained under pyrolysis process is presented in Fig.3b. It shows that the pyrolysed state of carbon slabs of collagen with inorganic chromium spreading as white granules over it.

The EDX spectrum of the CLW, (Fig. 4a) may be attributed to the presence of trivalent chromium (Cr^{3+}). Besides, Cr, CLW contains the evidence for the presence of other metal ions such as Mg, Al, Si, S, Ca and they may be due to the addition of chemicals during leather manufacturing p

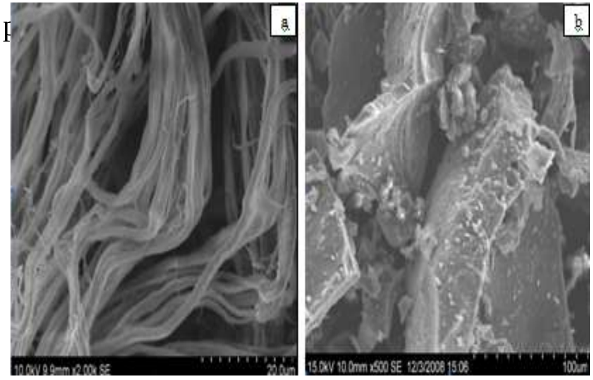


Figure3. *SEM image of a) CLW b) residual ash generated from pyrolysis*

EDX spectrum of the residual ash formed under pyrolysis process (Fig. 4b) shows the peak at 5.5 KeV, confirmed the presence of chromium in the residual ash in triavalent (Cr^{3+}) form and not in hexavalent (Cr^{6+}) form. The reduction atmosphere that was prevailing during pyrolysis process prevented the oxidation of trivalent chromium in to further oxidation states to Cr^{6+}.

3.4. Analysis of hexavalent chromium under colorimetric method

The colorimetric results shows that the solid biofuel resulted under pyrolysis process contained Cr^{6+} at BDL (Table 2). The reduced atmosphere maintained under pyrolysis process was preventing the conversion of Cr^{3+} to Cr^{6+}.

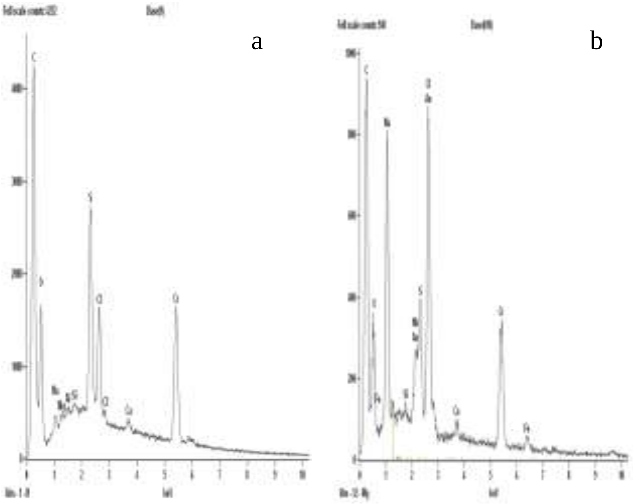


Figure 4. *EDX image of a) CLW b) residual ash generated from pyrolysis*

Table2. *Elemental composition of raw CLW and residual ash obtained under pyrolysis*

Element (%)	CLW	Residual Ash
C	44.20 ± 0.45	61.34 ± 0.42
H	7.59 ± 0.76	1.72 ± 0.68
N	9.55 ± 0.38	4.98 ± 0.41
S	1.442 ± 0.41	0.86 ± 0.50
Cr^{6+}, mg/kg	[a]B.D.L	[a]B.D.L
$Cr._{total,}$ mg/kg	12506 ± 2.50	11780 ± 2.50
GCV, kcal/kg	4246 ± 1.05	5420 ± 1.23

[a] *B.D.L.= Below detectable limit*

3.5 X-Ray Photoelectron Spectroscopy (XPS) Analysis of CLW and Residual Ash

The XPS survey scan presented in Fig. 5a shows the presence of Fe, O, N, C, Mo, Cl, S, Si along with very low concentration of chromium in CLW. Fig. 5b presented for XPS – Cr (2p) spectrum fitted with component peaks indicate that 70.09 % of chromium content in the CLW was in the form of Cr_2O_3 with binding energy

575.96 eV and 29.91 % was in the form of CrOOH with binding energy 577.78 eV. The Cr $(2p)^{3/2}$ component was fitted with two peaks to find the different oxidation states of chromium present in CLW.

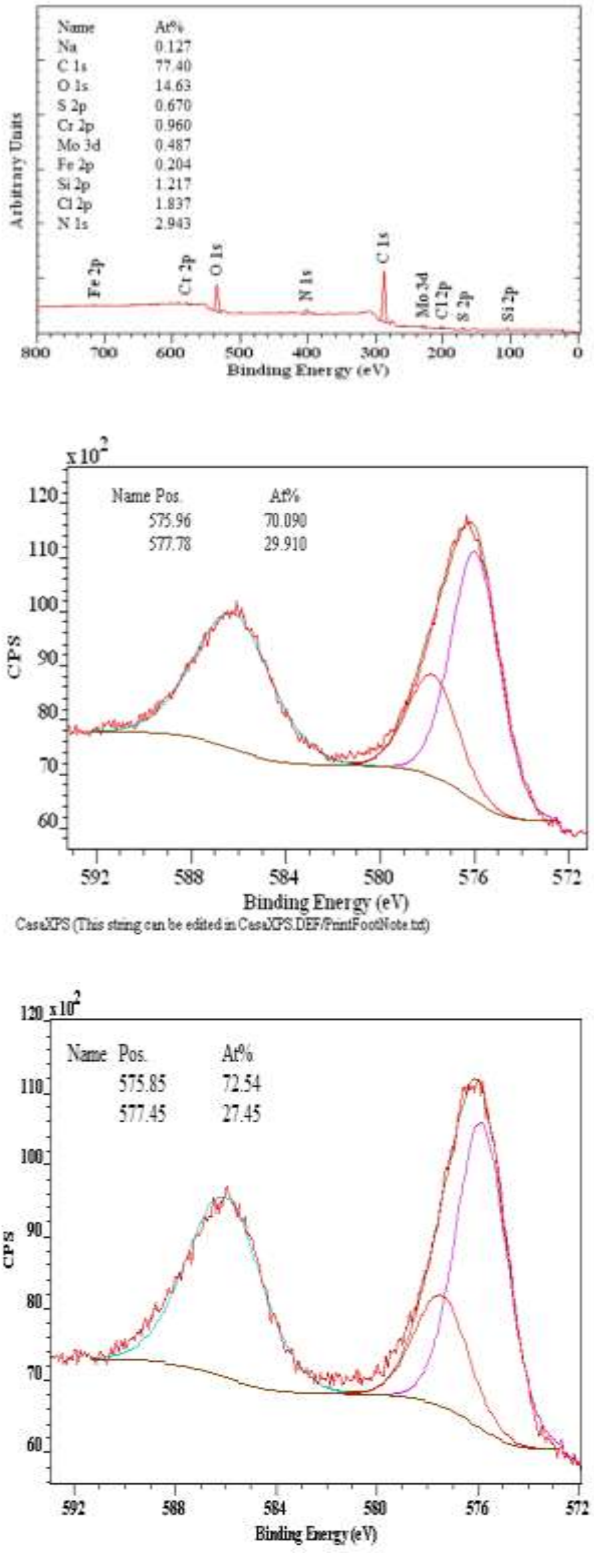


Figure 5 *a) XPS Spectrum* **-** *Survey scan of CLW, b) XPS – Cr (2p) spectrum of CLW fitted with component peaks and c) XPS – Cr (2p) spectrum of residual ash obtained under pyrolysis fitted with component peaks*

The absence of peak at 579.2 eV (Fig. 5b) indicates the non existence of Cr^{6+} *in CLW. Inorder to identify the chromium content and its oxidation state in the residual ash obtained from pyrolysis process, the residual ash sample was also analysed for XPS analysis. Fig. 5c presented for XPS – Cr (2p) spectrum fitted with component peaks. The component at 575.85 eV corresponds to* Cr_2O_3 *and the other at 577.45 eV is attributed to CrOOH which is 27.45 % of total Cr present.* Cr^{6+} *was not detected in the residual ash since there was no peak at 579.2 eV.*

3.6 Formation of Short Chain Aliphatic Hydrocarbon Gases

Standard GC spectra for short chain aliphatic hydrocarbon gases are shown in Fig. 6 represent the GC spectra of gas the samples recorded in varied temperature at 400ºC, 500ºC, 600ºC, 700ºC and 800 ºC respectively. The major peaks appeared in Fig. 6 were with retention time less than 10min and they coincided with the RT values of authentic aliphatic hydrocarbon gases. This indicates that CLW generated short chain aliphatic hydrocarbon gases such as methane, ethane, propane and trace quantities of C_4 and C_5 (i.e. < 2 ppm) gaseous compounds under pyrolysis process. The short chain aliphatic hydrocarbon gases (C_1 to C_5) were quantified. The composition of short chain aliphatic hydrocarbon gaseous samples generated at different temperatures is presented in Table 3.

Table3. *Composition of short chain aliphatic hydrocarbon gases generated at varied temperatures*

Compounds	Mol. Wt.	Unit	Temperature (°C)				
			400	500	600	700	800
CH_4	16.04	ppm	2962	11171	14213	21351	17784
		mg/	19	732	932	140	11

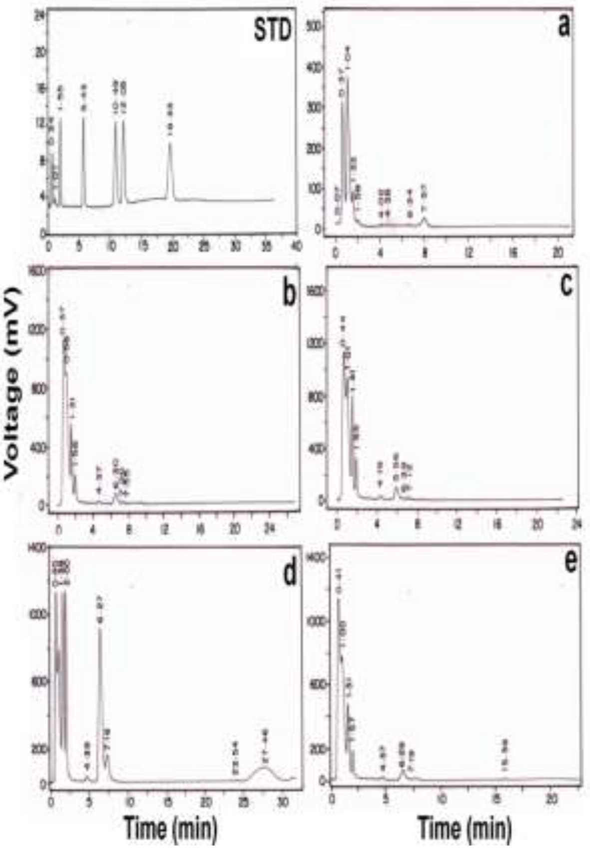
		m^3	43	9	4	07	667
C_2H_6	44.1	ppm	71	2099	5026	8772	552
		mg/m^3	87	2581	9066	15822	996
C_3H_8	30.07	ppm	25	689	5845	8994	1430
		mg/m^3	45	1243	7189	11061	1759
C_4H_{10}	58.12	ppm	< 2	< 2	< 2	< 2	< 2
		mg/m^3	< 5	< 5	< 5	< 5	< 5
C_5H_{12}	72.15	ppm	< 2	< 2	< 2	< 2	< 2
		mg/m^3	< 6	< 6	< 6	< 6	< 6

CH_4- Methane, C_2H_6-Ethane, C_3H_8-Propane, C_4H_{10}- Butane, C_5H_{12}-Pentane

Table 3 revealed that the generation of methane (C_1) was increased from 1944 mg/m^3 (0.29%) to 14008 mg/m^3 (2.13 %) with rise in temperature up to 700 °C and further increase in temperature to 800 °C, decreased its concentration to 11667 mg/m^3 (1.17 %). The increase in C_1 formation may be due to fusion of hydrogen with carbon atoms of CLW increased with rise in temperature which is less unlikely to take place at low temperature. The reduction in concentration of C_1 hydrocarbon beyond 700 °C may be due to synthesis of long chain molecule and the reaction is catalysed by chromium impregnated activated carbon. The profile shows that trace concentration of C_4-C_5 hydrocarbons were formed i.e. < 2 ppm irrespective of the reactor temperature. It was observed that the concentration of both C_2 and C_3 gases were also increased up to 700 °C and decreased thereafter due to breakage of C-H bond in C_2 and C_3 at high temperature. It was observed that the formation of C_2 was more than the formation of C_3, this may be due to elution of low molecular weight aliphatic hydrocarbon compounds first than the higher molecular weight compounds.

3.7 Analysis of overall gas composition

The fuel gases released during pyrolysis was characterised. The data presented in the Table 4 showed that Carbon Monoxide (CO) content increased from 2.74 % at 400 °C to 9.58 % at 550 °C and it was maintained almost at 16.50 % in the temperature range from 600 °C to 800 °C.The hydrogen (H_2) was 9.75 % at 400 °C, it was increased to 11.92 at 600 °C and it was reduced to 10 % at 800 °C. The hydrocarbon (C_xH_y) at 400 °C was nil and starts generated from 500 °C onwards. The maximum value of C_xH_y obtained was 6.2 % at 700 °C and further increase in temperature reduced the value. The increase in C_xH_y formation may be due to combination of hydrogen with carbon atom of the solid waste at higher temperature which is less likely taking place at low temperature. After attaining the maximum concentration of C_xH_y, the concentration decreased due to reduction of H_2 content at higher temperature. If the mass of feed was maintained constant inside the reactor at any point of time, reached maximum value of C_xH_y could be maintained.



The combustible gases (CG) comprising of CO, H_2 and C_xH_y was high i.e. 33.03 % at 700 °C and after this is decreased to 30.56 % at 800 °C which may be due to destruction of C_xH_y. The percentage of CG at 400 °C was 12.49 % and NCG was 87.51 %. There was a steep increase in CG upto 600 °C and after that there was a marginal increase upto 700 °C. The maximum GCV obtained was 4.85 MJ/Nm^3 at 700 °C could be due to increased formation of CG at 700 °C

Table 4. *Gas composition with respect to temperature*

Gas				
	400	500	600	700
CO	2.74	6.65	16.52	16.56
SO_2	14.78	388	2811	1939
O_2	3.42	2.43	2.30	1.0
NO_2	0	9.52	20.2	68.65
NO	12.46	46.0	122.7	350
C_xH_y	0	0.46	2.45	6.20
H_2	9.75	11.25	11.92	10.27
H_2S	0	68.54	146.0	300
CO_2	9.09	10.21	23.33	30
NO_x	12.48	56.43	143.65	418.60
CG*	12.49	18.36	30.89	33.03
NCG$^{\#}$	87.51	81.64	69.11	66.97
GCV of CG	1.83	2.70	4.53	4.85

Gas unit: CO, O_2, C_xH_y, H_2, CG, NCG are in %, SO_2, NO_2, NO, H_2S, NOx are in ppm and GCV in MJ/Nm^3

The combustible gases (CG) comprising of CO, H_2 and C_xH_y was high i.e. 33.03 % at 700 °C and after this is decreased to 30.56 % at 800 °C which may be due to destruction of C_xH_y. The percentage of CG at 400 °C was 12.49 % and NCG was 87.51 %. There was a steep increase in CG upto 600 °C and after that there was a marginal increase upto 700 °C. The maximum GCV obtained was 4.85 MJ/Nm^3 at 700 °C could be due to increased formation of CG at 700 °C.

4. CONCLUSION

Generation of short chain aliphatic hydrocarbon gases (C_xH_y) from proteinaceous chrome tanned leather solid waste (CLW) under pyrolysis process was examined in this study. The experimental studies showed that the adopted pyrolysis process yielded the renewable green energy fuel gases, 33.03% out of which 6.20% are of short chain aliphatic hydrocarbon; condensate liquid (CL), 33.32%; and residual ash, 34.67%. GC-MS confirms the presence of short chain aliphatic hydrocarbon fuel gases that could be generated from CLW under pyrolysis process. The fuel gases generated from the present investigation under pyrolysis process can be used for direct thermal applications or for generating electricity using in gas engine and it can be considered as one of the alternative renewable green energy bio-energy sources as the generation of waste from leather industries is not finite. The X-ray photoelectron spectroscopy (XPS) analysis confirmed the solid residual ash contained no carcinogenic hexavalent chromium (Cr^{6+}).

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