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Pyrolysis coupled pulse oxygen incineration for disposal of hazardous chromium impregnated fine particulate solid waste generated from leather industry

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ABSTRACT

This paper focuses on characterization and pyrolysis coupled pulse oxygen incineration (PyPOI) of hazardous chromium (Cr^{3+}) impregnated microfined solid particulate matter (MSPM) generated from leather industry. The PyPOI process yielded gaseous products, 47.46%; condensate oil, 34.20%; and remnant ash 18.34%. The energy profile of MSPM under PyPOI process was studied and compared with pyrolysis process. The energy released under varied mass loading of MSPM through PyPOI process was 4140 kJ, 9468 kJ, 12,816 kJ and 13,968 kJ for 0.5 kg, 1.0 kg, 1.5 kg and 2.0 kg respectively. The constituents of pyrolytic gases were CO, CO_2, C_xH_y, O_2, SO_2, NO_x and H_2. The MSPM, remnant ash and distillate were characterized using TGA, FT-IR and SEM/EDX. The TGA of remnant ash of MSPM confirmed that about 80% of the material was thermally stable up to 800 °C. Maximum weight loss of MSPM was achieved under PyPOI process using pulse oxygen supplied at the rate of 1.75 g/min inside the reactor vessel in the temperature range from 600 °C to 800 °C. The SEM images proved that unburnt carbon slabs were obtained under pyrolysis while crumbled carbon flakes were obtained under PyPOI process. FT-IR of condensate oil confirmed the presence of aromatic nitrogen compounds. The hexavalent chromium (Cr^{6+}) content of remnant ash under PyPOI process was 0.028 ± 0.006 mg/kg which was well within the limit of disposal (4 mg/kg).

Introduction

A wide spectrum of chemicals (about 0.4 ton/ton of raw skin or hide) is used to convert putrescible collagen fibers into non-putrescible leather matrix. Only 20% of raw skin or hide is converted into leather [1] and remaining 80% of raw materials are discharged as solid wastes. More than 90% of global leather production is carried out through chrome-tanning process [2]. Basic chromium sulfate (BCS) is the most widely used mineral tanning agent in leather processing. The pickled raw material absorbs 60–70% of the applied chromium in tanning process and the rest is discharged into waste water [3]. In the subsequent processes, leather manufacturing industry generates trivalent chromium (Cr^{3+}) impregnated micro-fined solid particulate matters (MSPM) in the order of 10 kg per ton of raw skins/hides processed. MSPM is proteinous impregnated with synthetic fatty substances, oil, tanning agents and dye chemicals besides trivalent chromium [4].

The production of chromium-containing solid waste in a tannery has been recognized as a problem for many years. The chromium in these solid wastes exists in the non-toxic trivalent chromium (Cr^{3+}) state, but there is growing concern that chromium could possibly be converted to a toxic carcinogenic hexavalent (Cr^{6+}) state [5]. Chromium containing leather solid waste has been regarded as one of the hazardous wastes if discharged into environment without any pre treatment [6]. Increased risks for malignancies such as lung cancer, testicular cancer, soft tissue sarcoma, pancreatic and bladder cancer have been reported among the tannery workers [7].

Tannery solid wastes contain organic substances and thus their energy value is higher than hard coal by 50% (nominally 20 MJ/kg as dry material). There are several ways of handling nontanned leather solid waste, but no satisfactory technology has been developed to treat chrome tanned leather solid waste [1] and to recover energy from the leather waste material. In the absence of any economically viable technology, leather solid wastes are being managed through land co-disposal [8] thermal incineration and anaerobic digestion methods. All the above methods have inherent limitations for field level executions. In recent years the interest in pyrolysis of wastes materials has increased as it provides an option for getting fuels with enhanced calorific value [9]. If leather solid wastes are pyrolyzed, the leather industry will become more environmentally friendly due to less emission of global warming gases [10].

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Though pyrolysis is an effective, reliable and environmentally safe solid waste treatment technique, it requires external energy to thermally decompose the leather solid waste and produces about 35–40% of unburnt remnant ash with major elemental carbon in its constitution. However, implementation of satisfactory pyrolysis technique for the management of solid waste in leather processing industry has not been developed yet [1].

The pyrolysis process involves heating of the carbonaceous material in an inert atmosphere, i.e. in pyrolysis, substances are not oxidized but rather transformed the waste into gas, oil and carbonaceous residue at high temperature [11]. Hence, there is a need for supplying controlled pulse air/oxygen into the reactor to decrease the unburnt residual carbonaceous mass and simultaneously to prevent the oxidation of trivalent chromium into hexavalent chromium.

However, there is no single report on thermal energy profile studied on MSPM under pyrolysis and PyPOI processes and disposal of chrome containing leather solid waste through thermal treatment supplying controlled pulse oxygen at high temperature without converting Cr^{3+} to Cr^{6+} and with generation of minimum quantity of remnant ash. Hence, the focal theme of the present investigation was to explore the methodology to dispose the MSPM through thermal treatment supplying pulse oxygen at high temperature in the range from 600 °C to 800 °C without converting the trivalent chromium into hexavalent chromium. The present investigation was also focused on to investigate the energy profile of MSPM under PyPOI process and was compared with pyrolysis process.

Materials and methods

Characterization of chromium containing solid waste

The MSPM was collected from a commercial tannery in Chennai, India processing raw skins/hides into finished leather. MSPM was characterized for moisture content, volatile matter, carbon, ash, chromium (total), fat, protein and calorific value using standard procedures.

Detail on pyrolysis and PyPOI processes

The reactor used in the present investigation under pyrolysis and PyPOI processes was fabricated in the laboratory. The main parts of the system as shown in Fig. 1 are: (i) MSPM hopper, (ii) an induction furnace containing pyrolysis and PyPOI reactor, (iii) gate valve, (iv) oxygen cylinder, (v) oxygen flow controller, (vi) residual spiral conveyer, (vii) temperature programmer, (viii) energy recorder, (ix) condenser, (x) oil collection tank, (xi) wet scrubber,

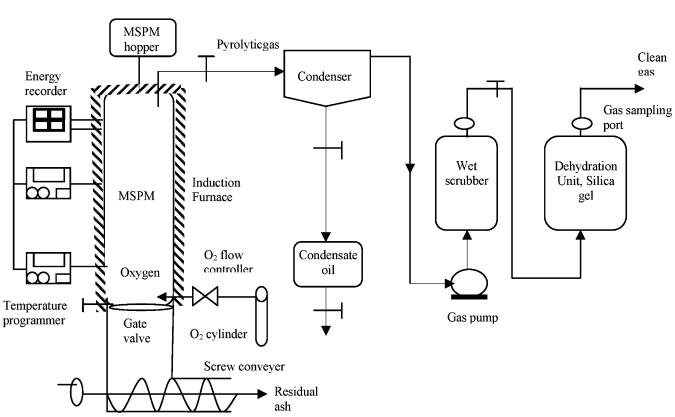

Fig. 1. Schematic diagram of pyrolysis coupled pulse oxygen incineration process for MSPM.

and (xii) dehydration unit packed with silica gel. The external surface of the chamber was fabricated using mild steel with necessary reinforcement for mechanical rigidity. The outer dimensions of the furnace were length, 650 mm; breadth, 650 mm and height, 750 mm. The energy input to the reactor was recorded through a digital single phase energy meter. The material of construction of the reactor was SS316 to prevent dry corrosion. The reactor was fabricated with dimensions inner diameter, 150 mm; outer diameter, 200 mm; and height, 300 mm with wall thickness, 5 mm. The reactor was fabricated with the provision to supply pulse oxygen in a controlled manner under PyPOI process to decrease the unburnt carbon content in the remnant ash.

Instrumental analysis

The elemental composition such as Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) of MSPM, remnant ash derived from pyrolysis and PyPOI processes were determined using Elementar-vario micro cube. Thermo-Gravimetric Analysis (TGA) was carried out to assess the weight loss as a function of temperature using Universal TGA Q50 V20.6 Build 31. Weight loss of the remnant ash with temperature was carried out under oxygen atmosphere using TGA Q500 V20.10 Build 36. Fourier transform infrared (FT-IR) spectroscopy analysis was carried out to determine the functional groups present in the samples. Scanning Electron Microscopy (SEM) analysis was carried out to determine the surface morphology of the samples with high resolution. Energy dispersive X-ray analysis (EDX) was carried out on raw MSPM, remnant ash and distillate to determine the elemental composition. The spectroscopic determination of hexavalent chromium (Cr^{6+}) in the remnant ash and in distillate was carried out using NaOH, Na_2CO_3, $MnSO_4$ in the presence of phosphate buffer (K_2HPO_4 and KH_2PO_4) as prescribed in the method 3060A: alkaline digestion for hexavalent chromium. The Cr_{total} content was determined by acid digestion using strong oxidizing agent and followed by reaction with diphenylcarbazide.

Process variables studied

The variables considered in the present investigation were; mass of MSPM (0.5, 1.0, 1.5, 2.0 kg) and temperature (400, 500, 600, 700 and 800 °C). The reactor vessel was heated to the maximum set temperature 800 °C without MSPM to determine the energy absorbed by constructional material of the reactor.

Conditions of the experiment

The measured quantity of MSPM kept in the hopper was fed to the reactor then the gas outlet line was housed to the condenser through metal coupling. The temperature of pyrolysis/PyPOI reactor was raised to the desired level using the microprocessor based temperature controller unit (programmer). The temperature sensor made up of chrome/alumel ("K" type) was kept inside the furnace to measure the temperature of the reactor vessel. The gas pump, the condenser, wet scrubber and dehydration unit were connected to the pyrolysis/PyPOI reactor. The pulse supply of oxygen required for the incineration of carbon was sourced from oxygen cylinder at a set pressure and the mass flow of oxygen was controlled using GFC mass flow transducers at 4–20 mA signal output.

Details of the experiment

The gas pump for the flow of gas from the reactor to condenser was operated manually when the process temperature was