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Thermal cracking of potato-peel powder-polypropylene biocomposite and characterization of products—Pyrolysed oils and bio-char

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ABSTRACT

Waste plastic disposal is a major environmental issue worldwide. Pyrolysis is an effective tool to convert plastic to liquid fuel. Pyrolysis of biomass yields liquid oil with high oxygen content and thereby low heating value. However copyrolysis of plastic with biomass yield oil of low oxygen content, better stability due to synergy between them. In our research work we have carried out thermal cracking process in which the liquid oil has better stability and with very low oxygen content has been adopted for pyrolysis of potato-peel powder/polypropylene (POPP40) biocomposite and neat PP individually under identical conditions. The liquid products generated have been compared for physico-chemical properties. Analytical techniques like gel permeation chromatography, fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, gas chromatography mass spectrometry and scanning electron microscopy has been utilized for detailed characterization of pyrolysed oils and bio-char. A potential use of these pyrolysed oils has been explored where the 10% pyrolysed oil blends in diesel exhibited excellent fuel properties with improvement in cetane index, density and viscosity.

1. Introduction

Usage of polymeric materials world-wide has increased in the recent times due to its low cost, good mechanical properties and light weight of polyolefin polymers. This increase in consumption has eventually lead to environmental pollution and depletion in landfill areas [1,2]. Bio-based polymer composites obtained from renewable resources also maintain carbon dioxide neutrality and help to establish ecological balance [3,4]. However accumulation of plastic and biocomposite waste after their use are very difficult to degrade in natural environment and their disposal poses a huge challenge. Conventional methods of plastic disposal include recycling, incineration and soil burial. Incinerations lead to emission of nitrogen and sulfur-oxides, dioxins and other toxic gases into the atmosphere whereas soil burial leads to seepage of toxic chemicals in plastic and thus pollute the environment [5]. Recently, a better alternate strategy for degradation of polymers and biocomposite is pyrolysis process, where thermal degradation of long chain polymer molecules into smaller molecules takes place through heat and pressure in the absence of oxygen and product selectivity can be achieved with use of catalysts [6,7]. The reason for the success of pyrolysis process is that the major products formed are oil, gas, and char which are considered as energy products with high calorific value and find their use as fuel to industries and refineries [8–10]. Among the polyolefin polymers, 93.1 and 84.7 wt% of liquid oil from low density polyethylene (LDPE) and high density polyethylene (HDPE) respectively were obtained in batch reactor at 550 °C and 82.1 wt% oil was obtained from polypropylene (PP) during pyrolysis at 500 °C [11]. Other advantages of pyrolysis process are that reaction parameters can be controlled to obtain the desired product type. On the other hand, pyrolysis of waste biomass resources has been widely explored as they yield value-added products like bio-oil and gases which are considered as energy materials and second generation biofuels [12,13].

Co-pyrolysis process for decomposition of plastic and biomass are also considered to be economical and generates valuable pyrolysed oils and gases [14–17]. This co-process has a distinct advantage over other pyrolysis process in generation of hydrogen atoms from polymeric material to remove oxygen generated from oxygenated hydrocarbons in biomass thereby causing a synergic effect producing pyrolysed oil with improved stability and other physical properties. In this process composition and nature of biomass and synthetic polymer as well as pyrolysis conditions have significant influence on the yield, chemical and physical properties of the products [18]. Disclosure of a pyrolysis

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process for co-processing of biomass with thermoplastic and non-thermoplastic materials using catalyst for conversion into liquid hydrocarbons has been patented [19]. Among the numerous biomasses available, potato-peel is one such biomass generated in abundance from food industries and has been explored for preparing composites with polymers [20,21]. A publication on preparation and characterization of bio-oil and bio-char from pyrolysis of potato peel waste has been reported [22]. An experimental study to investigate the synergistic effect of high density polyethylene (HDPE) addition to potato skin during co-pyrolysis has been carried out. High carbon and hydrogen contents, lower oxygen contents and higher heating value than neat HDPE during pyrolysis has been reported with improvement in the liquid yield due to addition of potato skin [23].

Bio-char is another potential renewable carbon resource obtained during the pyrolysis process of biomass or coprocessing of biomass with polymer. Bio-char is considered an efficient tool for carbon sequestration and soil fertility [24,25]. Application of bio-char as absorbent for removal of heavy metals and organic pollutants from water and waste water has been reported [26]. A study has been conducted on production of biocomposites using chars obtained from co-pyrolysis of olive pomace with plastic wastes [27].

In our earlier work, the authors have reported on preparation and characterization of potato-peel polypropylene biocomposites which may find application in automobile, food and package industry [28]. Disposal of these biocomposites after its use still poses a challenge, although some percentage of biodegradability occurs due to the presence of biomass. Therefore, an alternate method of disposal is related to pyrolysis of potato-peel powder/polypropylene biocomposites. However, to the best of our knowledge, there has been no study on the pyrolysis of potato-peel powder/polypropylene biocomposites and characterization of pyrolysed products.

The aim of the present study is therefore to carry out thermal cracking which is considered a simple and fast and environment friendly pyrolysis process for lab scale degradation of extruded neat PP and biocomposite prepared with 40% weight of potato-peel powder in polypropylene matrix (POPP40). Further, it is aimed to characterize the pyrolysed products for physical properties like viscosity, density and cetane index and elemental analysis using standard ASTM method and chemical properties by using various analytical techniques—elementar analyzer, gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FTIR), nuclear resonance magnetic resonance spectroscopy (NMR) and gas chromatography-mass spectrometry (GCMS). To understand thermal behavior of pyrolysed oils and bio-char, thermogravimetric analysis will be carried out. The morphological studies of bio-char obtained from biocomposite could be characterized using SEM technique. In an attempt to give value addition to the pyrolysed oils obtained, 10% blend of both the pyrolysed oils from neat PP and PP/POPL40 were blended with diesel fuel to study the effect on important properties of diesel such as density, viscosity and cetane index.

2. Materials and methods

2.1. Feedstock and thermal cracking procedure

Commercial homo polymer polypropylene PROPEL PP 1110MG designated as PP was obtained from M/s Indian Oil Corporation Ltd, India. Potato-peel powder polypropylene biocomposite (POPP40) was prepared by thorough mixing of 40 wt% dried potato-peel powder (particle size ≤ 300 μm) with polypropylene in a Batch blender. Neat polypropylene and the premixed POPP40 composition were compounded in a Twin-screw extruder (Labtech, Thailand) under nitrogen blanket and pelletized. The temperature profile in the extruder was maintained from 170 to 230 °C. Pyrolysis by thermal cracking was carried out on the extruded batches of neat PP and PP/POPL40.

700 gm of extruded neat polypropylene and PP/POPL40 biocomposite were pyrolysed by thermal cracking in bench top pyrolysis machine with processing ability of 0.7 to1.0 kg material one time depending upon the volume of the material used. The lower probe was 450 °C and the upper probe temperature was 430 °C, while for filter temperature was kept at 170 °C. The gases generated in the process were vented out. The liquid obtained was kept for 48 h at room temperature in order to check any sedimentation and found to be stable. The residual char obtained from the pyrolysis vessel was removed separately and dried. The pyrolysed oil from neat PP and POPP40 biocomposite were designated as PyO-PP and PyO-POPP40 respectively. Distillate boiling point upto 200 °C obtained from distillation of PyO-POPP40 as per ASTM-86 distillation method using TANAKA automated D-86 was designated as PyO-POPP40-A. The bio-char obtained as residue from pyrolysis of PyO-POPP40 was designated as BC-POPP40. Fig. 1 represents the images of pyrolysed oils, PyO-PP and PyO-POPP40 and bio-char BC-POPP40.

Fig. 1. Images of pyrolysed oils, PyO-PP and PyO-POPP40 and bio-char BC-POPP40.

2.2. Physico-chemical evaluation methods

The distillation of various pyrolysed oils were carried out as per ASTM-86 distillation method using TANAKA automated D-86 tester, Tokyo, Japan to generate simulated distillation data. Kinematic viscosity of pyrolysed oil samples were measured using Cannon − Fenske viscometer, USA as per ASTM D445-12 method. The density of pyrolysed oil samples were measured by RUDOLPH automated densitometer, USA as per ASTM 4052 method. The cetane index is calculated using four variables as per ASTM D4737-10 method. One of the variables, i.e., density at 15 g/ml was determined by ASTM D4052, and other three variables, 10% recovery temperature, 50% recovery temperature, 90% recovery temperature were determined by ASTM D86 test method and corrected to standard barometric pressure. Elemental analysis of the feedstock and products for carbon, hydrogen, nitrogen and sulfur (CHNS) content were carried out using Flash 2000 CHNS/O analyzer, Thermo Scientific instrument, Germany as per ASTM D 5291 method.

2.3. Characterization of pyrolysed products

2.3.1. Thermogravimetic analysis

Thermal analysis of pyrolysed oil from neat PP and POPP-40 and bio-char from POPP-40 were performed by using thermogravimetric analyzer (TGA) from TA instruments, model TGA-Q500, USA under nitrogen atmosphere. 10–15 mg of samples was taken in sealed aluminum pan for analysis. The oven heating was programmed from room temperature to 800 °C at a rate of 10 °C/min.

2.3.2. Gel permeation chromatography (GPC)

Viscotek Gel permeation chromatograph equipment fitted with