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Thermo-chemical conversion of waste rubber seed shell to produce fuel and value-added chemicals

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A B S T R A C T

Rubber seed shell (RSS), comprises of 96.67 wt% organic content and 38.6% crystallinity index, was used for the production of biofuel and value-added chemicals through semi-batch pyrolysis. Thermogravimetric analysis (TGA) of RSS at heating rate of 20 °C/min showed R50 value as 12.72%/min at 376.5 °C. The gaseous product evolved during the decomposition of RSS were analyzed through inline Fourier transform infrared (FT-IR) coupled with TGA instrument. The effects of pyrolysis temperatures (350°C-600 °C) and heating rates (10°C/min–40 °C/min) on the product distribution (liquid, gas and bio-char) were investigated. The maximum yield of liquid product (46.14 wt%) and the carbon-rich bio-char (31.92 wt%) were obtained at 550 °C temperature for heating rate of 30 °C/min. The fuel characteristics of produced bio-char such as higher calorific value (34.5 MJ/kg), higher fixed carbon (79.74 wt%), lower ash (1.87 wt%) and lower moisture content (2.11 wt%) suggested its potential to be used as solid fuel. Value-added organic compounds such as acetic acid, phenolic compounds, creosol, pilocarpine, benzene and levoglucosan were identified in the liquid product using gas chromatography. The pH values of liquid products (2.55–3.0) support the presence of organic acids and phenolic fraction. The presence of various functional groups was also identified using FT-IR spectroscopy. In depth analysis of physico-chemical-thermal properties of RSS and obtained products (liquid and bio-char) suggested that RSS can be considered as a suitable feedstock for the production of value added chemicals including fuel.

1. Introduction

Biofuels are gaining remarkable attention and interest due to the abundant availability of feedstocks [1]. Various raw materials such as oil seed (vegetable oil), rice husk, saw dust, wheat stalk, sugarcane bagasse, algae, de-oil cake, shell of oil seeds, etc. can be exploited for this purpose [2]. Agricultural waste such as non-edible oil seeds have been investigated to produce biodiesel [3–7]. Beside the production of biodiesel, non-edible oil seed can also be a suitable feedstock to produce value added products and fuels through biochemical and thermochemical conversion means [8,9]. Thermochemical methods include the processes such as incineration, gasification, combustion, carbonization, pyrolysis, etc. [8–14]. Pyrolysis process offers certain advantages; low temperature, oxygen absent condition, higher yield and quality of liquid products, better control to produce value added chemicals, safe storage and transportation, etc. [10,15,16]. In the pyrolysis process, the solid (biomass) converts to liquid, gas and char products at moderate temperature range, 300–700 °C in the absence of oxygen [17]. About 25–70% liquid product yield can be obtained from oil containing seeds [18].

Rubber seed is one of the promising non-edible source which contains 52–60 wt% of the kernel and, the oil extracted from the kernel can be used for biodiesel production [19,20]. Rubber seed is a solid by-product obtained from *hevea brasiliensis* (rubber tree) which mainly grows in the tropical region and cultivated wildly for use of its latex as source of natural rubber. India is one among the top five countries in the world producing rubber seeds (754,330 ton) next to China (928,450 ton), Malaysia (1,735,522 ton), Thailand (3,172,394 ton) and Indonesia (5,367,980 ton) [21]. In our previous work [19], rubber seed kernel has been used for biodiesel synthesis and, the obtained biodiesel was tested in IC engine. Meanwhile, utilization of the shell part of the rubber seed (RSS) as biomass feedstock can offer more benefits and

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potency to reduce current environmental challenges, energy crisis as well as sustainability of biodiesel industries. Rubber seed comprises of 40–48 wt% shell [20]. The shell contains very less extractable oil compared to kernel thus performing direct pyrolysis is beneficial. Utilization of oil seeds and seed shell through pyrolysis for synthesis of value-added products has been reported [22–26]. Sun and Jiang [27] studied the synthesis of activated carbon from rubber seed shell by physical activation with steam. The study demonstrated that rubber seed shell is a good precursor source of raw material for the production of high capacity activated carbon by physical activation with steam. Abnisa et al. [22] found the maximum liquid product yield (46.4 wt%) from palm seed shell at 500 °C pyrolysis temperature in a fixed bed reactor. Pyrolysis of pomegranate seeds has been investigated by Ucar and Karagoz [28] and, liquid yield (~54 wt%, maximum) was reported at two pyrolysis temperatures, 500 °C and 600 °C. The solid residue obtained has been reported to be a carbon rich fuel with high calorific value and low sulfur content.

The present study focuses on the characterization and utilization of RSS (40–48 wt% of seed) for the production of value-added products and solid fuel. Based on the reported literature on TG analysis and pyrolysis of various biomass [9,10,14,22,28], rubber seed shell (RSS) was pyrolyzed at six isothermal temperatures, 350, 400, 450, 500, 550 and 600 °C. The effects of pyrolysis temperatures and heating rates on the product distribution and calorific values of produced bio-char were discussed in detail. Further, compositional analyses of the liquid and solid products were also investigated. For this purpose, Fourier transform infrared (FT-IR), gas chromatography with mass spectroscopy (GC-MS), thermogravimetric analysis (TGA), field emission scanning electron microscope (FESEM) with energy dispersive X-ray (EDX), elemental analysis (CHNSO), proximate analysis, X-ray powder diffraction (XRD) analyses were considered.

2. Material and methods

Rubber seeds were collected from Assam, India. The kernel were separated manually and used for oil extraction to produce methyl esters (biodiesel) [19]. Shell part of the seed (RSS) was sun dried for 2 days, then grinded and sieved to a particle size of less than 2 mm. Chemicals, such as methanol (99.8% HPLC-Gradient grade), ethanol (99.9%, analytical reagent), hexane (98.5% purity) were procured from Marck India, Ltd.

2.1. *Thermal pyrolysis*

Thermal degradation profile of rubber seed shell (RSS) was evaluated with TG analyzer (Netzch STA449F300) from 30 °C to 800 °C at a heating rate of 20 °C/min under nitrogen (60 ml/min) atmosphere (99.9% purity). RSS sample (~10 mg) was exposed to programed TG condition and the evolved gaseous products were continuously monitored and measured using coupled FT-IR system. Gas transfer tube and gas cell were heated to 250 °C to prevent condensation of the evolved products.

Lab scale pyrolysis experiments of RSS were performed in a semi-batch pyrolyser with a continuous flow of nitrogen at 400 ml/min (Fig. 1). For each experiment 50 g of RSS was placed inside a stainless steel (SS316) reactor. The reactor was heated externally by an electric furnace with PID controller to achieve pyrolysis temperature of 350, 400, 450, 500, 550 and 600 °C, at heating rates ranged between 10 and 40 °C/min and kept isothermal for 1 h. Two condensers in series connected with flasks (at average temperature of −2 °C) were assembled to collect condensable vapor in the flasks. The amounts of solid (bio-char) remained after the pyrolysis process was also measured. The yield of

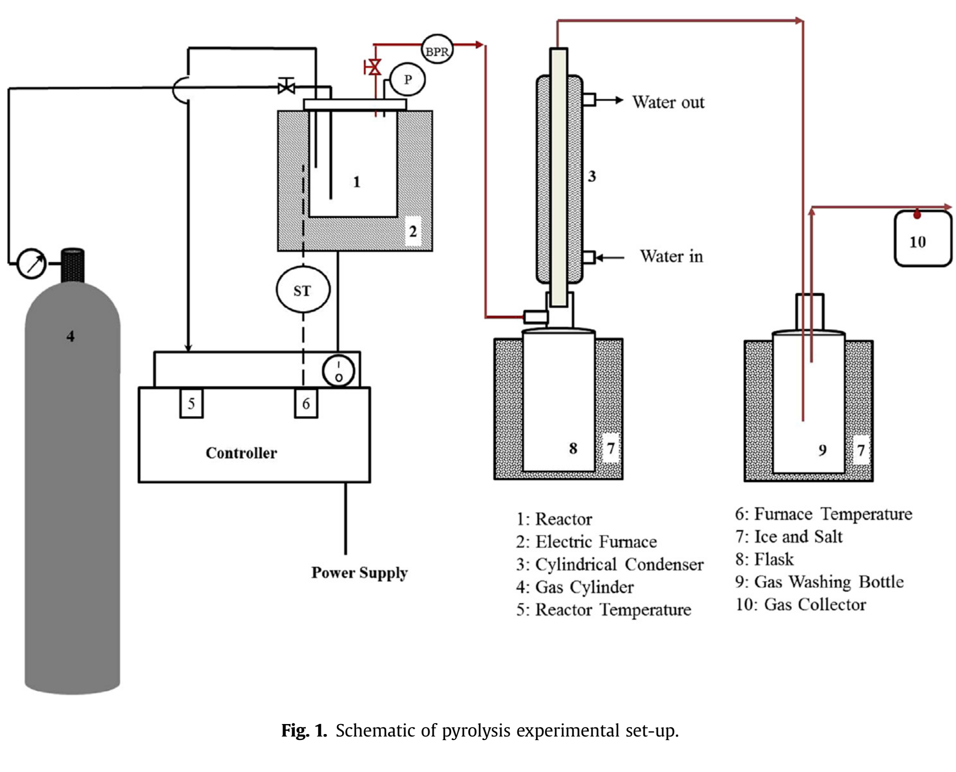

Fig. 1. Schematic of pyrolysis experimental set-up.