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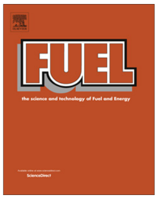


Guayule (*Parthenium argentatum*) pyrolysis biorefining: Fuels and chemicals contributed from guayule leaves via tail gas reactive pyrolysis ☆

Akwasi A. Boateng *, Yaseen Elkasabi, Charles A. Mullen

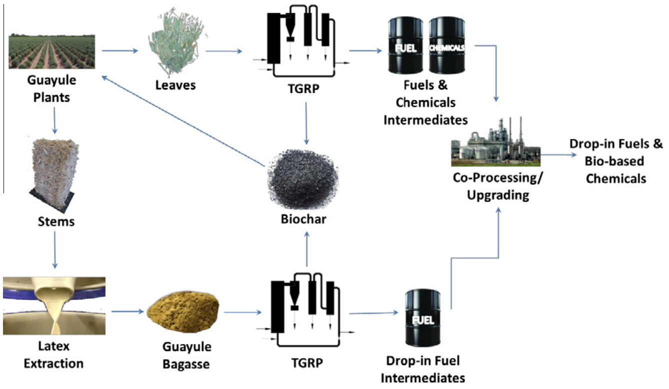
USDA-ARS, Eastern Regional Research Center, 600 E. Mermaid Lane, Wyndmoor, PA 19038, USA

HIGHLIGHTS

- Guayule plant leaves were converted into deoxygenated bio-oil using tail-gas reactive pyrolysis.
- The bio-oil possessed low oxygen (19 wt%) and high H/C and C/O molar ratios (1.27 and 4.82, respectively).
- Distillation and catalytic upgrading produced high yields of fuel hydrocarbons and paraffin compounds.
- Ammonium bicarbonate and paraffin compounds are easily isolated.

GRAPHICAL ABSTRACT

Guayule leaves biomass was converted into a stable deoxygenated bio-oil using tail-gas reactive pyrolysis, then upgraded into fuels and chemicals.



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ABSTRACT

Guayule (*Parthenium argentatum*), a woody desert shrub cultivated in the southwestern United States, is a source of natural rubber and organic resins that promises to revolutionize the tire and rubber industry. Some 20,000 kg ha^{-1} yr^{-1} is reported to be harvested worldwide and expected to grow due to renewed interest in guayule to replace imported *Hevea* rubber. We have recently reported the use of guayule bagasse, the residual biomass after latex extraction, as feedstock in a pyrolysis process that employs a reactive gas environment to formulate a special intermediate bio-oil product that is easily distillable and readily synthesized to hydrocarbon (drop-in) fuels (Boateng et al., 2015). This submission reports on the use of the same pyrolysis process for the leaves of the guayule plant and the array of fuels and chemicals that the leaves can contribute to a co-located guayule biorefinery at a latex plant that could utilize the entire biomass residue value chain. The composition of the guayule leaves is different from the bagasse, with the main differences being lower resin content along with higher ash (>16 wt%) and higher nitrogen (2.6 wt%, dry ash free, daf) contents resulting from the higher concentration of the plant proteins (16.4 wt% (daf)). Since the former two components have exhibited a drastic influence on

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* Corresponding author. Tel.: +1 (215) 233 6493; fax: +1 (215) 233 6406.

E-mail address: akwasi.boateng@ars.usda.gov (A.A. Boateng).

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pyrolysis product distribution in the past, it was incumbent upon us to explore whether the resin content would provide additional synergistic effects and influence product selectivity pathways to bio-based chemicals. We found that the combined effect of the tail gas reactive pyrolysis process, the proteinaceous nature of the guayule leaf and resin combine to create a complex mechanism that results in an interesting bio-oil intermediate product from which a slew of fuel and commodity chemical compounds can be synthesized upon mild upgrading.

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1. Introduction

Guayule is a hardwood desert shrub that is cultivated in the southwestern United States and northern Mexico that biosynthesizes high quality natural rubber [2]. Some 20,000 kg ha^{-1} yr^{-1} is reported to be harvested worldwide, and this amount is expected to grow due to renewed interest in guayule by the tire and rubber industry giants [3]. Of this, only about 10% of the plant is used for the latex. To extract the latex, the leaves from the shrub are stripped off, and the stems are used as feedstock in either an organic solvent (the Bridgestone process) or water-based (the Yulex process) extraction process to remove the rubber, leaving a residual solid behind called bagasse which has a residual rubber and/or resin [4]. Guayule bagasse has been a source of energy to local guayule farmers and/or to the latex plants for some time due to its high energy content, 24 MJ/kg on a dry-ash-free (DAF) basis [5] contributed in part by the resins in the residue. Unlike the bagasse, the leaf has not found much application although it also contains resin and is also proteinaceous, leading to high nitrogen content compared with the stems from which guayule bagasse is derived. Like most plant leaves, the ash content of guayule leaves is higher than that of its stems, with the ash potentially capable of having a catalyzing effect during its pyrolysis. Potassium in the ash of guayule shrub can be as high as 19 wt% of the ash [5], and potassium has been found to correlate negatively with the production of certain oxygenates during pyrolysis and aromatic hydrocarbons during catalytic pyrolysis [6–9]. In order for guayule biorefinery to be more economically viable the impetus should be to expand on the utilization of the whole guayule shrub and improve the economic potential of the crop. This can only be realized through production of rubber, energy, fuels, and chemicals from both the bagasse and the leaves. We have recently reported the use of guayule bagasse as a feedstock in the USDA-ARS' tail gas reactive pyrolysis (TGRP) process to successfully formulate a liquid fuel intermediate product (TGRP bio-oil) which, due to its thermal stability, could support a co-located biorefinery concept at existing guayule latex extraction plant that allows use of a simple distillation followed by a one-step hydrotreating process with conventional noble metal catalysts to synthesize hydrocarbon (drop-in) fuels [1] (Fig. 1). For such a pyrolysis biorefinery to be economically viable, full utilization of the entire guayule plant matter (leaves and bagasse) would be beneficial to the economics of the latex extraction value chain. Prior to this we had also previously demonstrated that the presence of protein can cause a substantial deoxygenation effect during pyrolysis [10–12] which suggests the guayule leaves could be a viable feedstock for pyrolysis biorefining. Herein, we explore whether the resin and high ash content in the guayule leaves combined with the TGRP process would provide an overall synergistic effect that would influence product selectivity pathways toward fuels and/or bio-based chemicals of any economic yields to contribute to the guayule pyrolysis biorefinery value chain.

2. Experimental

2.1. Materials

Guayule leaves, were generously provided by Yulex Corporation (Phoenix, AZ). Prior to the pyrolysis experiments the leaves were ground and sieved to 2 mm using a Wiley mill and oven dried overnight to a moisture content of approximately 5–6 wt%.

2.2. Tail gas reactive pyrolysis (TGRP)

The ARS pyrolysis system used here has been previously described by Mullen et al. [13]. The TGRP arrangement modified from this setup has also been described by Mullen et al. [13]. Two upgrading protocols are possible due to the thermal stability of the bio-oil produced by TGRP; the bio-oil can be centrifuged, distilled followed by mild hydrodeoxygenation or can be subjected to HDO first then distilled to desired cut products. The former affords the opportunity to explore whether desirable bio-based chemicals are extractable in high yields other than fuel.

2.3. Pyrolysis oil characterization

The elemental analysis of the feedstock and product streams (C, H, N, S) was carried out using a Thermo EA1112 CHNS analyzer. Water content was measured using Karl-Fischer titration in methanol with Hydranal Karl-Fischer Composite 5 (Fluka) used as titrant. Oxygen was then determined by difference. Total acid number (TAN) was measured using a Mettler T70 automatic titirator using 0.1 M KOH in isopropanol as titrant and wet ethanol as the titration solvent. GC/MS analysis was done using a Shimadzu QP2010. Calibration curves for each quantified compound were made from authentic samples purchased from Sigma–Aldrich and used as received. The GC column used was a DB-1701 60 m × 0.25 mm, 0.25 μm film thickness. The oven was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C and hold there for 20 min. The injector temperature was 250 °C, and the injector split ratio set to 30:1. The flow rate was 1 mL/min of the He carrier gas. The bio-oil samples were prepared as ~3% solutions in acetone which were filtered through a 0.45 μm PTFE filter prior to injection.

Concentration of ammonium bicarbonate in the pyrolysis oil aqueous phase was determined by adding acetone to a 10 g sample of the aqueous phase, filtering and weighting the resulting precipitate. The white solid was identified as ammonium bicarbonate by ^{13}C NMR in D_2O.

2.4. Distillation

For catalytic upgrading of distillates, short-path distillation of bio-oils was conducted prior to catalytic upgrading, according to previous methods [14]. Briefly, 150–200 g of bio-oil was placed in a 1000 mL round-bottom flask and clamped to a distillation head with adapter. Using a heating mantle, the temperature of the