
Hydrothermal liquefaction of agricultural and forest biomass residue: Comparative study

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Abstract

Biomass is a promising feedstock for the chemical industry due to the presence of wide range of functionalities available with the lignocellulosic biomass (the natural polymer). Hydrothermal liquefaction is an attractive approach for the conversion of lignocellulosic biomass feedstocks because it obviates energy intensive drying steps. The objective of this study is to investigate the distribution of products, i.e. liquid, gas and solid from forest (pine wood, deodar) and agricultural (wheat straw, sugarcane bagasse) biomass, produced by hydrothermal treatment (280 °C for 15 min) under non-catalytic and catalytic (KOH, K₂CO₃) conditions and analysis of bioresidue obtained as well as liquid hydrocarbons (oils) for the differences in the bio-oil composition with respect to feed material. Agricultural biomass showed higher conversion rates under thermal and catalytic conditions compared to forest biomass. Sugarcane bagasse showed the highest conversion (95 %) among the four samples investigated. Pine wood and deodar has similar conversions. The compositions of bio-oils from agricultural and forest biomass residue contained both phenolic compounds and furans. FTIR and Powder XRD analysis of lignocellulosic biomass as well as bioresidue samples showed that the peaks due to cellulose, hemicellulose and lignin became weak in bio residue samples.

Keywords: Lignocellulosic biomass, hydrothermal liquefaction, subcritical water, thermochemical conversion, bio-oil

1. Introduction

Biomass is an abundant and carbon-neutral renewable energy resource for the production of biofuels and valuable chemicals. Energy production from biomass has the advantage of forming smaller amounts of greenhouse gases compared to the conversion of fossil fuels, as the carbon dioxide generated during the energy conversion is consumed during subsequent biomass regrowth [1]. Abundant and inexpensive lignocellulosic biomass does not compete with the production of food crops. Cellulose is a polydisperse linear homopolymer consisting of regio- and stereo-selectively β -1, 4-glycosidic linked D-glucopyranose units [2]. Hemicellulose (copolymer of any of the monomers glucose, galactose, mannose, xylose, arabinose, and glucuronic acid), the second most abundant component of lignocellulose, are plant cell wall polysaccharides that are not solubilized by water but are solubilized by aqueous alkali. Lignin is a three dimensional amorphous polymer consisting of methoxylated phenyl propane structures. The three primary monolignols p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol are the building blocks of lignin.

There are several methods of biomass conversion which can be either biochemical or thermo-chemical routes. Biochemical routes involve several steps such as pretreatment, fermentation and separation of products by various unit processes. Thermochemical routes also require feedstock pretreatment steps such as moisture reduction, size reduction. Superior to pyrolysis technology, hydrothermal process (high-pressure direct

liquefaction technology) has the potential to produce liquid oils that is not miscible in water, with much higher calorific values and a range of chemicals including vanillin, phenols, aldehydes, and organic acids, etc [3-5].

The process is especially best suited for wet materials as the drying of feedstock is not necessary and water is used as one of the reactants. Hydrothermal liquefaction involves the reaction of biomass in water at high temperature and pressure with or without the presence of a catalyst. The products include a bio-crude, an aqueous fraction and a gaseous fraction. Hydrothermal technologies are broadly defined as chemical and physical transformations in high-temperature (200–600 °C), high-pressure (5–40 MPa) liquid.

The objective of this study is to investigate the distribution of products, i.e. liquid, gas and solid from forest (pine wood, deodar) and agricultural (wheat straw, sugarcane bagasse) biomass, produced by hydrothermal treatment (280 °C for 15 min) under non-catalytic and catalytic (KOH, K₂CO₃) conditions and analysis of liquid hydrocarbons (oils) for the differences in the hydrocarbon composition as well as bioresidue obtained with respect to feed material.

2. Materials and Methods

Hydrothermal liquefaction experiments were conducted in a 500 ml high pressure autoclave (Autoclave Engineers) at 280 °C for 15 min using solutions of KOH and K₂CO₃. The reaction conditions were selected based on our earlier investigations [6-8] In a typical hydrothermal liquefaction experiment, the reactor was

loaded with lignocellulosic biomass and H₂O/alkaline solutions (1:6 by weight). Then the reactor was purged five times with nitrogen to remove the inside air. The temperature was then raised up to 280 °C at heating rate of 5 °C min⁻¹ and kept for 15 min at 280 °C. After reaction, the reactor was left to cool down to the room temperature. The gaseous products were vented. The liquid portion was then extracted with equal quantity of diethyl ether. The ethereal solution thus obtained was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was weighed and designated as bio-oil1. After extraction, the remaining water phase contained the water-soluble hydrocarbons. Solid products were extracted with acetone in a Soxhlet extraction apparatus until the solvent in the thimble became colorless. After removal of the acetone under reduced pressure in a rotary evaporator, this fraction was weighed and designated as bio-oil2. Acetone insoluble fraction was dried at 80 °C then weighed, called as bioresidue (solid residue).

3. Results and Discussion

Thermal and catalytic hydrothermal treatment of lignocellulosic biomass was carried out at 280 °C for 15 min in the presence of various alkaline catalysts (KOH and K₂CO₃). Fig 1 shows the conversion of various agricultural and forest biomass residue under thermal and catalytic conditions.

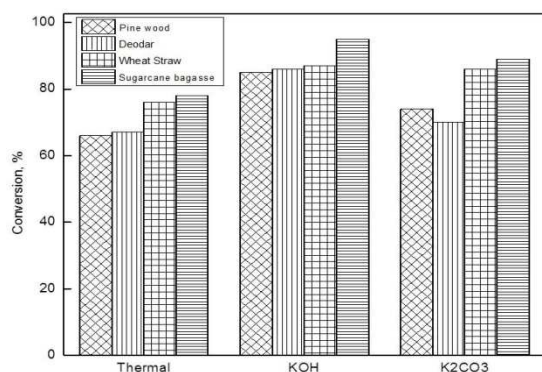


Fig 1: Effect of feedstock type on Conversion rates under thermal and catalytic conditions.

Agricultural biomass (wheat straw and sugarcane bagasse) showed higher conversion rates under thermal and catalytic conditions compared to forest biomass (pine wood and deodar). In case of liquefaction of wheat straw using distilled water bio-oil yield was 29 % without catalyst. The bio residue yield was 24 % and the conversion was 76 %. Using 0.5N KOH and K₂CO₃ solutions the bio-oil yield and conversion was increased. The maximum bio-oil (35 %) yield was observed with 1N KOH for wheat straw. In case of liquefaction of sugarcane bagasse with distilled water the bio-oil yield was 25 %. The bio residue yield was 22 % and conversion was 78 %. Greater than 90 % conversion was observed with the alkaline catalyst in case of liquefaction of sugarcane bagasse. The product distribution from pine

wood and deodar was almost same. 0.5 N K₂CO₃ solution showed greater conversion and bio-oil yields in case of pine wood compared to deodar. In case of both pine wood and deodar 0.5N KOH showed great conversion rates(86 %) and bio-oil yields (34%). Both bio-oil yield as well as conversion rates were higher with 0.5N K₂CO₃ for agricultural (wheat straw and sugarcane bagasse) biomass compared to forest (pine wood and deodar) biomass. From all the four tested feedstocks sugarcane bagasse showed highest conversion (95 %) and bio-oil yields (36 %). The yield of gaseous products were very less in all cases. The compositions of bio-oils from agricultural and forest biomass residue contained both phenolic compounds and furans. Use of different types of biomass (agricultural and forest) have an important effect on the formation of various compounds in oil fraction. The ratio of biomass components differs in agricultural and forest biomass. Thus, the composition of the functional hydrocarbons in bio-oil was different in all the samples. FTIR and Powder XRD (X-ray diffraction) analysis of lignocellulosic biomass as well as bioresidue samples show that the peaks due to cellulose, hemicellulose and lignin became weak in bio residue samples which suggest that these components have undergone hydrolytic cleavage/decomposition.

4. Conclusions

Agricultural biomass (wheat straw and sugarcane bagasse) showed higher conversion rates under thermal and catalytic conditions compared to forest biomass (pine wood and deodar). Alkaline catalysts (KOH and K₂CO₃) have found an important effect on the decomposition of both agricultural and forest biomass residue in terms of both bio-oil yield and conversion. Product distribution of Pine wood and deodar was almost same. 0.5N K₂CO₃ showed higher catalytic activity in terms of both bio-oil yield as well as conversion rates for agricultural (wheat straw and sugarcane bagasse) biomass compared to forest (pine wood and deodar) biomass. The compositions of bio-oils from agricultural and forest biomass residue contained both phenolic compounds and furans.

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