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Production of bio-oil via hydrothermal liquefaction of birch sawdust

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ABSTRACT

The effect of weight ratio of plywood manufacturing by-product birch sawdust (BS) to water (1/2–1/8), reaction temperature (200–340 °C), initial H_2 pressure (0–10 MPa), residence time (5–90 min), catalysts amount (0.25–7.0 wt.%) and type ($FeSO_4$, $ZnSO_4$, $NiSO_4$, Raney-nickel, Ni65%/SiO_2—Al_2O_3, Na_2CO_3 and NaOH) on hydrothermal liquefaction of BS was investigated. High yield of bio-oil (54.1%) with calorific value (CV) 24.9 MJ/kg under developed optimal experimental conditions in the presence of NaOH (5 wt.%) utilizing weight ratio of BS to water 1/4, residence time 5 min, mixing speed 250 rpm at 300 °C without pressurized particular inert gas or H_2 atmosphere was achieved. Compounds in bio-oil analyzed by gas chromatography-mass spectrometry (GC-MS) have suitable chemical structures for conversion into renewable hydrocarbons. Marketable solid residue (SR) with yield 7.1%, high CV (29.8 MJ/kg) and perspective characteristics for industrial application was obtained. Produced gas in process analyzed by gas chromatography-thermal conductivity detector (GC–TCD) contains 60.1 vol.% of CO_2.

1. Introduction

Since the industrial revolution, demand and consumption of fossil sources dramatically increased and caused environmental pollution [1]. Biomass is one of the most widespread renewable energy sources. Bioethanol, biodiesel and hydrotreated vegetable oil already has been produced in large amounts worldwide mainly from food crops for partial substitution of fossil transportation fuels and CO_2 emissions reduction [2,3]. Lignocellulosic agriculture and wood industry wastes are available, low cost feedstock for energy production. Furthermore, lignocellulosic biomass has high potential for synthesis of alternative fuels and/or its precursors (synthesis gas and bio-oil) by widely investigated thermo-chemical conversion processes – gasification, pyrolysis and liquefaction. Lignocellulosic biomass generally contains cellulose, hemicellulose, lignin and extractives. The components in lignocellulosic materials vary according to biomass feedstock type, growth stage and growing conditions of the plant. Extractives are fatty acids, sugars, proteins, fats, phenols, resins, resin acids, terpenes, etc., soluble in organic polar or non-polar solvents. Polysaccharides cellulose and hemicellulose consists from various pentose, hexose and uronic acid monomers, but macromolecule of lignin contains different phenol derivative units [4]. The monomers and polymers in lignocellulosic material are linked by ether, ester, hydrogen and C—C bonds. At high temperature the chemical bonds of macromolecules and other substances in lignocellulosic material can be broken down to fragments with a wide range of molecular weight distribution [5]. Catalytic hydrothermal liquefaction is one of the most promising thermo-chemical conversion paths of biomass into bio-oil with high calorific value (CV) and chemical structure suitable for liquid renewable aliphatic and/or aromatic hydrocarbon production [6]. The process is similar to geological formation of fossil sources, except bio-oil synthesis from biomass in autoclave-reactor can be performed at low exposure time expressed in hours or even minutes [1]. The hydrothermal experiments typically are carried out at high temperature (up to 400 °C) and pressure (up to 40 MPa) in the aqueous medium [7]. The bio-oil formation by hydrothermal liquefaction is complex process and degradation mechanisms comprise the following three general steps – depolymerization of the biomass, decomposition of monomers and recombination of reactive fragments. Under hydrothermal conditions at high temperature and pressure the water acts as a solvent and participates as a reactant in hydrolysis reactions of lignocellulosic material [1,8]. Further hydrothermal degradation of fragmented compounds produced by rapid hydrolysis of polysaccharides leads to formation of wide range of different organic compounds, such as, furan derivatives, diols, carboxylic acids, alcohols etc. [9,10]. Depolymerization of lignin by hydrolysis reactions of ether-bonds producing different phenol derivatives is similar to cleavage of carbohydrates [7]. Then depolymerizated fragments of lignocellulosic material are exposed to dehydration, dehydrogenation, decarboxylation and deoxygenation reactions forming compounds with low molecular weight. The benzene ring has a high thermal and chemical stability allowing only further

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degradation, elimination and rearrangement of substituent groups at hydrothermal conditions. Reactive fragment rearrangement, condensation, isomerization, cyclization, polymerization, recombination and other chemical transformation leads to new compounds [5]. Hydrothermal liquefaction experiments of biomass in scientific literature usually are performed in inert He [11] and N_2 [9,12,13] atmosphere. There are also some reports about bio-oil production without utilization of certain initial gas pressure [14] and abundant number of investigations performed in compressed H_2 atmosphere [11,15]. The influence of reducing H_2 atmosphere on biomass conversion are extensively investigated in presence of different supported transition (Ni, Mo, Co) and platinum group metal catalysts. Commercial heterogeneous metal catalysts with similar characterizations are widely used in chemical and petroleum refining industry. High pressure reducing atmosphere may provide chemical accession of H_2 to fragmented compounds of lignocellulosic material under hydrothermal conditions [7]. An H_2 involvement in biomass conversion processes improves the chemical structure of compounds in bio-oil and increases its CV. There are some reports in literature about effect of various water miscible metal Fe(II) Zn(II), Ni(II), Co(II), Mg(II), Cr(III), and Sn(II) sulfates on bio-oil production by hydrothermal conversion of biomass [16,17]. Furthermore, bio-oil with high yield (up to 61.8%) and CV (up to 35.9 MJ/kg) was obtained in presence of strong alkaline catalysts (NaOH, KOH Na_2CO_3, K_2CO_3) [14,18–20]. Water soluble alkaline compounds have strong effect on hydrolysis related reactions of lignocellulosic materials producing smaller molecules exposed to thermal decomposition. The alkaline earth metal oxides CaO and MgO also successfully catalyze bio-oil production from biomass [20,21]. However, CaO and MgO usually delivers lower yield of bio-oil in comparison to strong alkali metal hydroxides, due to lower solubility and basicity of $Ca(OH)_2$, $Mg(OH)_2$ formed by hydration of oxides in aqueous medium.

Thermo-chemical biomass conversion processes are connected with liquid, gaseous and solid product formation. Yield and characteristics of each separate product depends on many factors – chemical composition of biomass feedstock, experimental conditions, including reaction atmosphere, reaction mixture medium and catalyst type.

Present study demonstrates the catalysts screening for the bio-oil production from plywood manufacturing by-product birch sawdust (BS) by hydrothermal liquefaction. Gaseous products (GP), marketable solid residue (SR) and high yield of bio-oil were obtained under developed optimal hydrothermal conditions in presence of best catalyst. Gas chromatography-mass spectrometry (GC-MS), gas chromatography-thermal conductivity detector (GC–TCD), thermogravimetric (TG) and C,H,N,S elemental analysis were utilized for product characterization.

2. Materials and methods

2.1. Materials

BS (without bark fraction) was supplied from the local plywood producer Latvijas finieris AS (Latvia) with water content 5.8 wt.%. 6.0 kg of BS was grinded and sieved until particle size ≤120 mesh. Afterwards the BS was dried at 110 °C for 6 h. The main characteristics of dried and sieved BS sample are given in Table 1.

$FeSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}7H_2O$, Na_2CO_3, NaOH, tetrahydrofuran (THF) with purity of ≥98 wt.%, concentrated mineral acids HCl (35.7 wt.%), H_2SO_4 (96.3 wt.%), Raney-nickel (activated nickel catalyst slurry in water, nickel content ≥89 wt.%), Ni65%/SiO_2—Al_2O_3 (specific surface area ~175 m^2/g) and activated carbon (mesh 20–40), CH_4 (assay ≥99.999 wt.%) and CO (assay ≥99.0 wt.%) were purchased from Sigma–Aldrich Chemie GmbH. The concentrations of mineral acids were determined using volumetric acid-base titration. Acetone (assay ≥99.7 wt.%) was supplied from Latvijas kimija SIA and H_2, CO_2 (assay ≥99.999 wt.%) from Elme messer L SIA.

2.2. Hydrothermal liquefaction of birch sawdust (BS)

The effect of various catalysts ($FeSO_4$, $ZnSO_4$, $NiSO_4$, Raney-nickel, Ni65%/SiO_2—Al_2O_3, Na_2CO_3, NaOH), reaction temperature (200, 250, 300, 340 °C), catalyst amount (0.5, 2.5, 5.0, 7.0, wt.% calculated from anhydrous compound of the dried BS amount), weight ratio of BS to water (1/2, 1/4, 1/6, 1/8), initial H_2 pressure (2.0, 5.0, 8.0, 10.0 MPa) and residence time (5, 20, 40, 60, 90 min) on hydrothermal liquefaction of BS were investigated. Each experiment was conducted using accurately mixed 40 g of dried BS, catalyst and distilled water in a batch type stainless steel autoclave-reactor (Parker Autoclave Engineers Inc.) designed to maximum pressure 37.9 MPa at 343 °C, volume 500 ml, equipped with magnetically coupled mechanical mixer (6 blade agitator impeller) and Sentinel Series Controller.

After the filling and sealing the autoclave-reactor was purged with H_2 (flow rate 10 ml/s) for 3 min to fully eliminate air atmosphere from the system, when H_2 atmosphere was utilized in experiments. Then initial H_2 pressure was increased to necessary value. Heating rate was chosen from 3 to 6 °C/min to reach predetermined temperature. From this point of reference the residence time of the hydrothermal liquefaction process of BS was measured. The experiments without initial H_2 pressure also were performed to compare the results. Mixing speed of 250 rpm in all the experiments was utilized. After hydrothermal liquefaction process the autoclave-reactor was cooled down to ~25 °C with air fan

Table 1
The main characteristics of birch sawdust (BS).

Proximate analysis, wt.% (d.b.[a])			Ultimate analysis, wt.% (d.a.f[d])					Calorific value (d.b.[a]), MJ/kg
VM[b]	FC[b,c]	Ash	C	H	N	S	O[f]	
85.6	14.1	0.3	48.5	6.3	≤0.3[e]		45.2	19.4

Composition analysis, wt.% (d.b.[a])			
Cellulose	Hemicellulose[g]	Lignin	Extractives
45.3	24.2	22.9	7.6

[a] On a dry basis.
[b] VM - volatile matter, FC - fixed carbon.
[c] By difference (FC% = 100% − VM% − Ash%).
[d] On a dry and ash free basis.
[e] Method detection limit.
[f] By difference (O% = 100% − C% − H%).
[g] By difference (Hemicellulose% = 100% − Cellulose% − Lignin% − Extractives% − Ash%).