

Study Of The Degradation Of Biomass (News Paper Waste, Cassava Cork And A-Selulosa) In Sub- And Supercritical Water Hydrothermal Liquefaction

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ABSTRACT: Hydrothermal liquefaction (HTL) of news paper waste, cassava cork and α -cellulose were investigated. Experiments were carried out in an autoclave at different reaction temperature and the fixed of solid water ratio of 1 gram in 50 ml water. The temperature reactions are 300, 370, 400, and 450 °C were investigated. The α -cellulose gave a lower conversion rate, and the cassava cork gave a higher conversion rate in each temperature reaction. Cassava cork has higher soluble liquid and gaseous products. The bio-oil component was dominated by organic acids, the second component was alcohol/ketones and the least component was alkanes/alkenes.

Keywords: HTL, temperature, composition, solid, soluble liquid

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I. INTRODUCTION

Biomass is a renewable and abundantly available feedstock for the production of biofuels and chemicals. The general sources of biomass are agricultural (food grain, straw, seed hulls, corn stalk, cattle manure, and poultry waste), forest (wood waste, bark or wood, trees, mill scrap, and sawdust), municipal (paper waste, sewage sludge, and food waste), energy (switch grass, willow, poplars, corn, canola, soybean, and other plant oils), and biological (animal waste, biological waste, and aquatic species) (Jindal, 2016).

The basic reaction mechanisms of biomass liquefaction can be described: (i) depolymerization of the biomass; (ii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iii) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds (Huang, 2011). In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols (Wettstein, 2012)

The degradation of biomass cannot be described by detailed chemical reaction pathways with well-defined single reaction steps. The reason is that biomass is a combination of cellulose, hemicelluloses, and lignin, and these components interact each other, leading to very complex chemistry (Kruse and Gawlik, 2003). The analysis of complex reactions which occur in the liquefaction of biomass, is important to the description of the reactions behavior and to the optimization of the operating conditions.

Sasaki et al (2000) reported that the hydrolysis of cellulose was faster in supercritical or near-supercritical region in which cellulose mainly converted into aqueous oligomers (cellubiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose) and monomers (glucose, fructose). Decomposition and deoxygenation are major reactions, which produce final products containing acids, aldehydes, and aromatic compounds. Further fragmentations and dehydrations lead to the formation of a variety of low molecular weight compounds such as formic acid, acetic acid, lactic acid, acrylic acid, 2-furaldehyde, and also aromatic compounds such as 1,2,4-benzenetriol (Toor, 2011).

Kabyemela (1998) discussed the mechanism of degradation of cellobiose in sub- and supercritical water. Cellobiose was decomposed and hydrolyzed simultaneously resulted glucose fructose as the major intermediates hydrolysis. Glucose and fructose intermediates were further decomposed into pyruvaldehyde, erythrose, 1,6-anhydroglucose and acids, and also oligomers (Yu, 2008). Yin (2011) analyzed that hydrolysis of cellulose in strong alkaline mainly resulted carboxylic acids. For weak alkaline the main product is 5-HMF, In medium alkaline both products of carboxylic acid and 5-HMF occurs.

Esterification is effective for the transformation of the carboxylic acids in bio-oil into neutral esters via the acid treatment of bio-oil in alcohol. Esterification of bio-oil was generally performed at the temperature

under 250 °C. At the higher reaction temperature (i.e. 400 °C) cracking of the components in bio-oil became dominant (Wang, 2013).

The main purposes of biomass liquefaction processes is to decrease oxygen contents of the biomass. Dehydration and decarboxylation are two major reactions that can remove oxygen heteroatom in the form of H₂O and CO₂ respectively. High operating conditions cause dehydration of the biomass components. Decarboxylation is the thermal cracking of long chain carboxylic acids, which releases CO₂ and reduces the chain size (Zhengang, 2008).

Bio-oils is contains significant amounts of carboxylic acids, creating difficulties in handling and application of bio-oil. Bio-oil is a mixture of hundreds of chemicals (Sharma, 1991). It has some deleterious such as a high viscosity, a high water content, a high instability and a high corrosiveness (Adjaye, 1992). These undesirable properties make the direct use of bio-oil as the fuel for transfortation difficult. Bio-oils are primarily composed of various oxygenated hydrocarbons including phenols, aldehydes, ketones, acids, esters, and benzene derivatives. The compositions of bio-oils depends not only on the types of biomass but also on the hydrothermal process conditions (Tekin, 2013).

Bio-oil has to be stabilized and be upgraded to improve its properties for the use as the fuel for vechiles (Wang, 2009). The carboxylic acid in bio-oil reacted with the produced alcohols to form neutral esters (Tang, 2008). Hydrogenation/ esterification of furfural or other aldehydes with acetic acid were also invertigated (Yu, 2011).

II. EXPERIMENTAL

II.1. Materials and Chemicals

The news paper waste was cutting raftly in cm in long and widht. The cassava cork was slices in 1 mm along the depth, α -cellulose and all chemical are analytical reagent grade provided by Sigma, the solvent was distilled water.

II.2 Experimental procedures

Liquefaction experiments were carried out in a reactor of 60 ml stainless steel cylindrical, temperature of 300, 370, 400 and 450 °C and pressure follow the temperature. The raw biomass of (news paper waste, cassava cork and α -cellulose) were contained to the reactor, added of 50 ml water solvent. After that the reactor was sealed properly and make sure that there is no leakage. The reactor was mounted into the furnace that the temperature can be set in certain point as the reacting temperature desired. The reactor leave there for several hours as the reaction time. After reaction time was reached the reactor was pull out and poured with tap water to chill and stop the reaction. In ambient temperature the reactor valve was open to leave the gas out, the reactor was opened properly to pull out all the reaction products. The solid and liquid products are separated by filtering. The solid was rinsed with same solvent and dried at 105 °C until the weight remained unchanged as solid product or carbon-rich material. The soluble liquid was evaporated in vacuum evaporator to measure the soluble liquid products precentage, and then the sample was analysis by GC-MS to evaluate the degradation fragments.

II.3 Separation procedure

After the reaction time was reached the reactor pulled out from the furnace, and then poured with tap water until to the ambient temperature. The liquid and solid was filtered, the solid was washed with the same solvent, until the liquid was cleared. The solid was dried at 105°C overnight, and then quantified until the weight is unchanged (carbon fraction). The soluble liquids were evaporated under vacuum evaporator overnight until the weight is unchanged (soluble liquid/biooil fraction).

$$\text{Yield of bio-oil} = \text{Mass of bio-oil} / \text{mass of biomass} \times 100\% \quad (1)$$

$$\text{Yield of carbon} = \text{Mass of carbon} / \text{mass of biomass} \times 100\% \quad (2)$$

$$\text{Conversion rate} = 100 \text{ wt\%} - \text{yield of carbon wt (\%)} \quad (3)$$

II.4 Products analysis

The biomass was degraded hydrothermally at temperatures 300, 370, 400 and 450 °C in a certain of reaction time of 7 hours, and no catalyst used. The gas produced was leaf out not to be analyzed. The soluble liquid products were analyzed using GC-MS, Agilent technologies 7890B, with DB5 Column (30 m x 0.32 mm x 0.25 μ m, detector MSD 5977A, Helium (He) was used for mobile phase or carrier gas with flow rate 1 ml/min. Injector temperature was 250 °C. The temperature of ion source and MS Quadruple were 230 °C and

150 °C, respectively. The soluble liquids are also evaporated under vacuum evaporator overnight until the weight is unchanged (soluble liquid).

III. RESULTS AND DISCUSSIONS

III.1. Biomass decomposition

Temperature seems to be the process parameter that has the biggest influence on the products characteristics. High temperatures lead to higher reaction rates, and have a decisive influence on the number of biomass compounds that can be hydrolyzed (Funke et al., 2010). The effect of temperature on the Liquefaction of biomass of (news paper waste, cassava cork and α -cellulose) were investigated. HTL process of biomass were degraded into three phases, gaseous, soluble liquid and solid phases. Solid phase resulted carbon-rich materials. Liquid phase resulted of bio-oil, gaseous products were the different between raw material minus solid and soluble liquid products, as shown in Tabel 1.

Tabel 1. The solid carbon, soluble liquid and gaseous products from hydrothermal liquefaction.

T (°C)	News paper waste			Cassava cork			α -cellulose		
	Solid Carbon (%)	Soluble liquid (%)	Gas (%)	Solid Carbon (%)	Soluble liquid (%)	Gas (%)	Solid carbon (%)	Soluble liquid (%)	Gas (%)
300	76.04	2.69	10.66	54.18	16.61	29.21	86.57	1.23	12.2
370	71.28	11.58	17.14	32.69	23.24	44.07	83.36	5.06	11.58
400	68.2	16.1	15.70	36.2	21.83	41.97	80.78	5.31	13.91
450	54.6	19.2	26.28	10.52	24.48	65.0	44.55	18.15	37.3

Each biomass has endurance it self to the temperature exposed, α -cellulose was more endurance compared to the other biomass. It's shown that it has higher carbon product or lower conversion rate compared to the other biomass such as news paper waste and cassava cork. The higher crystallinity index of α -cellulose may have the major influence on the decomposition (Lu, 2000). The higher crystallinity index gave a lower liquefaction products (Moller, 2013). Cassava cork was less endurance to the temperature exposed, it has higher biomass conversion to soluble liquid and gaseous. News paper waste has conversion rate in the middle between α -cellulose and cassava cork.

Increase the temperature process increase the conversion of the biomass into liquid and gaseous or the solid products were decreased. In sub-critical water, the biomass conversion was also lower compared in the supercritical water. The soluble liquid products were also increased by increasing the temperature processes. The gaseous products were also increased by increasing the temperature processes. It's meant that in supercritical water, the further degradation of fragments are also increase resulted more gaseous products

(Tabel 1).

Cassava cork has higher conversion rate in all degree of temperature compared to others biomass (news paper waste and α -cellulose). In temperature of 300 oC the carbon product was about 54.18 %, soluble liquid was about 16.61% and gaseous product was about 29.21%. At temperature of 450 oC the carbon product was about 10.52 %, soluble liquid was about 24.48% and gaseous product was about 65.0 %. It's meant that cassava cork was more degradable compared to newspaper waste and α -cellulose.

III.2. Bio-oil composition

Conversion of biomass during HTL is a combination of an initial heterogeneous degradation of the biomass particles. Lignocellulosic biomass is converted into its monomers; glucose (from cellulose), xylose, arrabinose, and mannose (from hemicellulose). The amorphous lignin is typically decomposed into small phenylpropane entities soluble in supercritical water. The secondary reactions depend on the process conditions and included dehydration, dehydrogenation, rearrangements, retro-aldol condensation, Canizarro reaction, cyclization, and polymerization (Arturi, 2016). The reactive molecules like organic acid and aldehydes are converted by the reactions with alcohols to esters and acetals (Mahfud, 2007).

The decomposition of cellobiose in sub-and supercritical water in short residence times (0.04 – 2 s) resulted glucose, erythrose, and glycolaldehyde, glucosyl-erythrose (GE), dan Glucosyl-glycolaldehyde (GG) (Kabyemela, 1998). In continuous process, in long-time runs or it can be seen that is very steady, the main components of water-soluble products were acids, oligomers, glucose, levulose, pyruvic aldehyde, 5-HMF, and furfural (Lu, 2000). Prolong the residence time, phenolic products were lower quantity due to the further decomposition (Wang, 2014).

Esterification is effective for the transformation of the carboxylic acids into neutral esters via the acid treatment of bio-oil in alcohols. Esterification of bio-oil was generally performed at the temperature under 250 °C. Increase the reaction temperature to 400 °C cracking of the components of bio-oil is became dominant (Wang, 2013). Alcohol is believed that alcohols could also stabilize other reactive components in bio-oil.

The bio-oils collected after the liquefaction of biomass contained a complex mixture of hydrocarbons and have been analyzed by GC/MS. The identification of the main compounds was performed using a NIST mass spectral database. Tabel 2 gives a comparison of the identified compounds in the bio-oils from the liquefaction of biomass processed at 370 °C without any catalysts.

Tabel 2. The major composition of bio-oil

Retention time	Compound name	Area (%)		
		Substrate		
		News paper waste	Cassava cork	α -cellulose
6.331	-2,6,6-Trimethylbicyclo [3.1.1] hept-2-ene	-	-	11.59
6.557	Glycolic acid	47.16	-	-
6.570	Morpholine	-	3.43	-
6.709	2-butanone	1.44	-	-
6.784	Arsenous acid	2.22	-	-
6.898	Trimethylsilyl 3-oxobutanoate	5.65	-	1.63
7.036	Ethylene glycol	2.13	-	-
7.528	3- Carene	-	-	1.4
7.818	Tetrasiloxane	1.02	-	-
7.931	Diacetone alcohol	6.5	-	1.52
8.209	Lactic acid	1.76	9.14	13.22
8.473	Glycolic acid	-	2.19	7.78
9.255	2-Hydroxybutyric acid	-	3.16	6.2
9.318	Furfuryl alcohol	-	-	1.12
9.406	Levulinic acid	-	8.28	3.01
9.544	Hydracrylic acid	-	1.93	2.09
9.645	2-methyl-1-pentanol	-	1.05	-
9.809	Pentanoic acid	-	1.16	-
10.137	Propanoic acid	-	1.18	-
10.364	Naphthalene	-	-	1.05
10.414	5-Hydroxy-2-methylpyridine	-	1.08	-
10.452	p-Vinylbenzamide	-	-	1.60
10.477	1-Butanol	-	3.56	-
10.717	Dihydroxyacetone	-	-	1.83
10.969	5-Oxohexanoic acid	-	1.34	-
11.41	Glycerol	1.01	1.52	-
12.027	Butanedioic acid	-	9.41	6.91
12.178	Methylsuccinic acid	-	3.58	-
12.519	2-Butenedioic acid	-	1.06	-
12.998	1,3-Oxathiane, 2-(1,1-dimethylethyl)-2-methyl	-	-	1.2
13.212	Syringol	-	1.58	-
13.262	Pentanedioic acid	-	1.94	-
14.46	Propylene glycol	-	12.89	11.5
14.951	Vanillin	-	1.0	-
15.128	Cinnamic acid	3.60	-	-
16.325	Dodecanoic acid	3.60	-	-
16.804	D-Erythro-pentonic acid	-	2.13	-
16.879	Syringaldehyde	-	2.19	-
17.61	D-Arabino-Hexonic acid	-	9.59	-
17.825	D-Ribo-Hexonic acid	-	4.46	-
20.343	Palmitic caid	2.52	-	5.92
22.009	9-Octodecenoic acid	1.65	-	-
22.236	Stearic acid	-	-	11.11
24.655	Phthalic acid	12.43	-	-
	Total	92.69	88.85	90.68

The peak area (%) for each compound identified was defined by percentage of the compound's chromatographic area out of the total area. Only those compounds with peak area (%) higher than 1 % were presented in tabel 2. The percentage values indicate the proportions of individual compounds in the bio-oil but not present the actual concentration.

Tabel 3. The major compound of the bio-oil from different substrate

Compound group	Substrate		
	News paper waste	Cassava cork	α -cellulose
Alkanes/ alkenes (%)	8.11	7.70	18.47

Organic acids (%)	74.94	60.55	56.24
Alcohol/ ketones (%)	9.64	20.60	15.97
Total	92.69	88.85	90.68

It is clearly seen that acids compounds are the major components identified in the bio-oil obtained from the liquefaction of all substrates. Followed by alcohols/ketones are the second major compounds. The alkanes/alkenes are the least compounds that come from from all the substrates.

The substrate of news paper waste gave acids compounds as the higher major compounds of 74.94 %, followed by the substrate of cassava cork of 60.55%, and then α -cellulose of 56.24%. The alcohols/ketones compounds, from the substrate of cassava cork gave the higher compared to the others substrate, is about 20.6 %, followed by the α -cellulose gave of 15.97 %, and then news paper waste gave 9.64 %.

IV. CONCLUSION

The decomposition of biomass in hydrothermal liquefaction has been performed successfully using batch reactor in the different temperature operation and type of biomasses. Increase the temperature increased the conversion rate of the biomass into carbon like materials, solubles liquid and gaseous. The higher conversion rate came from the substrate of cassava cork, news paper waste and then α -cellulose, respectively.

The major component resulted from the degradation of biomass can be classified into alkanes/alkenes, acids, and alcohol/ketones. The major components of acids come from the substrate of news paper waste, cassava cork and then α -cellulose, respectively. The major components of alcohol/ketones come from the substrate of cassava cork, α -cellulose and then news paper waste, respectively. The major components of alkanes/alkenes come from the substrate of α -cellulose, newspaper waste and then cassava cork, respectively. The major components is the marked of the degradation pathways that can be explained for the route of the degradation reaction.

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