

Optimization of Aqueous Condensate Recovery from Fast Pyrolysis of Biomass (Theoretically & Modeling)

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Abstract - In fast pyrolysis, ligno-cellulosic biomass is converted to a large fraction of liquid bio oil along some char/ash and non-condensable gases. When ash content is high in the biomass, it results in higher water content and a possible phase separation. For desired water content and bio oil composition, it is necessary to adjust the condensation temperature. Residence time is also of high immense value during pyrolysis of biomass. The results are used to for the development of a proper surrogate mixture. The experimental data is presented with a key focus on the activity of water and how to optimize it. The data extracted shows a non-ideal behaviour of water in the bio oil. Several methods to control the water content of pyrolysis oil from fast pyrolysis of biomass is evaluated experimentally. Parameters varied are the operating temperature of the condenser, the gas load of the condenser, and the moisture content of the feedstock. However, decreasing the water content by these measures always results in a loss of organic vapours, leading to a lower oil yield in the condenser. In the fast pyrolysis of woody biomass, at 550°C, the aqueous condensate amount obtained is highest with a weight percentage of 10.62%. At this temperature, the aqueous condensate free bio oil yield resulted to be 56.41%, bio char yield is 16.23%, and pyrolytic gases weight percentage came to be 16.74%. This value is analysed and finally compared with the modelling value done using UNIFAC.

Key Words: Aqueous Condensate, Woody Biomass, Bio-oil, Fast pyrolysis, Pyrolysis.

1. INTRODUCTION

Everything in today's world is about energy. Energy is one of the fundamental particle for the existence and development of life on the Earth. It is important for both internal and external security of the country. Energy is the core of social, environmental as well as economical development of nations worldwide [1]. Energy supplied all over the world mainly comprises of fossil fuels which contributes to about 80% of the total energy used [2]. The consumption and demand of energy is increasing globally due to which the amount of fossil fuels are depleting at a very fast rate. Mainly, the hunger for development, to become powerful and to raise the standard of living of people in the country is putting much pressure on energy demand. The search for energy alternatives is still the largest concern of people, nations,

scientists as well as business people worldwide. This search has brought us to renewable sources of energy as one of the biggest alternative of depleting fossil fuels. The renewable sources of energy have a large number of advantages over fossil fuels. First of all, it is one of the best replenishment of fossil fuels to get energy. Alongwith this, it is available in abundance worldwide. If once harnessed properly, it can provide energy for years. Not only this, renewable energy sources have zero emissions which has no polluted impact on air, water or land. As per the report of MNRE (Ministry of Renewable Energy), the renewable energy installed capacity got increased by 226% in the last 5 years. It brought India to the 5th position at the world level for the total installed capacity of renewable energy. Renewable energy contributes upto 23.29% of the total installed generation capacity in the country i.e-368.98 GW (upto 29th February 2020). Biomass is an important energy source for the country. It is renewable, available in abundance, acts as a carbon-neutraliser and has the potential to eradicate poverty and unemployment problems in the rural areas. Biomass can also assist in providing firm energy. As per the MNRE (Ministry of Natural Resources Energy), about 32% of the total primary energy used in the country is still derived from biomass and more than 70% of the country's population depends upon it for its energy needs. Ministry of New and Renewable Energy has realised the potential and role of biomass energy in the Indian context and hence has initiated a number of programmes for promotion of efficient technologies for its use in various sectors of the economy to ensure derivation of maximum benefits. For efficient utilization of biomass, bagasse based cogeneration in sugar mills and biomass power generation have been taken up under biomass power. The current availability of biomass in India is estimated at about 500 million metric tonnes per year [3]. Studies sponsored by the Ministry has estimated surplus biomass availability at about 120-150 million metric tonnes per annum covering agricultural and forestry residues corresponding to a potential of about 18,000 MW. This apart, about 7000 MW additional power could be generated through bagasse based cogeneration in the country's 550 Sugar mills, if these sugar mills were to adopt technically and economically optimal levels of cogeneration for extracting power from the bagasse produced by them. Biomass has been classified as woody biomass, herbaceous biomass, fruits biomass, blend & mixtures, virgin biomass and waste biomass. Woody biomass is defined as the by-product of management, restoration, and hazardous fuel reduction treatments, as well as the product of natural disasters, including trees and woody plants (limbs, tops,

needles, leaves, and other woody parts, grown in a forest, woodland, or rangeland environment) [4]. Trees, shrubs and bushes mainly comes under woody biomasses. Woody biomass is sustainably available in ample amount in various regions of the world. Scandinavia, New Zealand, Canada and South America are the largest producers of woody biomass [5]. About 370 million woody, i.e. about 30% of total biomass is available for fuel production. For more growth of woody biomass, they suggested short rotation intensive culture is adopted.

Woody biomass are formed mainly when sunlight falls on living plants in the presence of water with the help of chlorophyll and water. This process is known as photosynthesis. For every mole of CO₂ absorbed into carbohydrate or glucose in biomass, 1 mol of oxygen is released. The chlorophyll promotes the absorption of carbon dioxide from the atmosphere, adding to the growth of the plant. Important ingredients for the growth of woody biomass are living plant, visible spectrum of solar radiation, carbondioxide, chlorophyll and water. The chemical composition of woody biomass can be characterized by five primary components which are cellulose, hemicellulose, lignin, extractives/volatiles and ash. In fast pyrolysis process the feed stock is rapidly heated in absence of oxygen at high temperature. During the decomposition, vapours and char are formed. After condensation of the vapours, a dark brown liquid is obtained. Fast pyrolysis is an advanced process which can be controlled to produce higher yields of liquid products. Fast pyrolysis process produces 60-75% liquid bio-oil, 15-25% char and 10-20% non-condensable gases [6]. The bio-oil and char can be used as source of fuel and the non-condensable gases can be recycled back in the process.

A.V.Bridgwater, D.Meier, D.Radlein [7] in their paper stated that woody biomass can be utilised in a number ways to provide energy. Some of them are by direct combustion (It provides heat in application of heating, steam generation and electricity generation.), gasification (The final products can be used as a fuel for providing heat, or running a turbine or an engine.) and fast pyrolysis (The fuel obtained can be used as a substitute fuel oil in static heating, electricity generation applications, and major application is in the production of chemicals.) The final product came out to be a miscible mixture of polar organics about 75-80wt% and aqueous condensate about 20-25wt%. The yield is upto 80wt% in total (wet basis) on dry feed. Westerhof et al. [8] in his paper tested upon a two staged condensation system to control the water content. In their work, they also proved the essential assumption that equilibrium is reached in the condenser by quenching a mixture consisting of nitrogen, steam and ethanol. Such a two-staged condensation system becomes increasingly important if feedstocks with high ash content are used due to the increased formation of water during pyrolysis. A two staged condensation system was important for feedstocks with high ash content. Biomass with high ash content gives out high amount of water on condensation during pyrolysis. Pollard et al. [9] in his paper investigated a five stage condensation system with indirect cooling using red oak as biomass. The interesting thing about this setup is the use of two electrostatic precipitators, which collect the aerosols separately from the

condensates. With aerosol formation as a key challenge in the modelling of condensation systems, this set up is especially well suited to investigate aerosol formation mechanisms. Experiment was done in an 8kg/h process development unit consisting of a fluidized bed pyrolyzer, hot cyclones and a series of condensers and ESP's that recover five stage fractions. The first two stages collected water soluble sugars and water insoluble "pyrolytic lignin". aqueous condensate was driven out in the last stage.

2. Materials and Method

The focus of doing experiments on biomass is to use waste biomass resources and converting them into valuable by-products. We selected woody biomass as our material to be used in the experiment. The advantages of using woody biomass was that it is available in abundance, is too cheap, has reduced impact on the environment. These advantages makes woody biomass as one of the best biomass to do the experiment. The woody biomasses used in our experiment consisted mainly in the form of wooden chips, barks of the trees, their braches and leaves. The woody biomass used in the experiment were collected from furniture shops (The wooden chips samples were collected from furniture shops. These chips were irregular in shape and were about 4-6 cm in length and 3-5 cm in thickness), carpentry shops of college workshop (More amount of wooden chips were collected from the carpentry shops of ITI colleges workshops), barks of trees, branches and green leaves (The dried barks of trees were collected from the forests around Central University of Jharkhand). The wooden chips were grinded and the size particle was brought to about 2mm size in diameter uniformly using wood grinder machine. The grinded woody biomass was allowed to dry naturally at atmospheric temperature and pressure for several days under the sunlight. After being dried, this biomass was weighed. 9 samples each of 30 gram were made.



Fig.1. Collected wooden chips (left) and converted to 2mm uniform particle size (right).

Experimental setup and procedures

The principal components of the pyrolysis reactor set-up are a furnace, a reactor, a temperature controller and a vapor condensing unit. Within an electrically heated furnace, the reactor that holds the feed is mounted vertically. At each cycle, the feed was pyrolyzed and the vapors produced by the reactor were condensed into a condenser cooled with aqueous condensate. The condensed liquid was stored in a flask for calculation. Within the reactor the residue (char) is known as the pyrolytic char. Usually the residue char was collected after updating the reactor. The SS tube is heated externally by an electric furnace, with the temperature being measured by a thermocouple fixed inside the reactor and temperature is controlled by external PID controller. PID controller was used to control the temperature of the furnace. The accuracy of this PID controller is $\pm 0.3\%$ FS (FS = 1200°C). So the temperature can be measured with $\pm 3.6^\circ\text{C}$. Water is circulated through the outer jacket of condenser by a pump for cooling the vapors coming out from the reactor due to pyrolysis reaction of woody biomass and hence condensed pyrolytic oil is collected at the other end of the condenser in a collecting jar. Some amount of non-condensable gases also evolves which is let go into the atmosphere. The liquid product is the mixture of aqueous condensate and bio-oil. The temperature of the furnace is maintained by a highly sensitive PID controller. The heart of the setup is the electrically heated furnace. In this furnace, one can attain as high as temperatures of 700°C.

Biomass samples (chips, barks, leaves, braches) were blended in uniform ratios and used in the experiment. These blends can be directly used in tubular reactor for thermal pyrolysis. Different samples with different temperatures will be used in tubular reactor for pyrolysis. Moisture content, ash content, volatile matter content and fixed carbon content of the sample will be carried out using ASTM D3172-07a method. Ultimate analysis will be performed to determine the elemental composition of the material using a CHNSO elemental analyser which provides carbon, hydrogen, nitrogen and sulphur percentage. Calorific value of a material will be determined using a bomb calorimeter.

In this work the temperature range was set between 400°C-600°C. The sample pyrolysis runs were done with 30 grams of the grinded woody biomass. Mainly 9 pyrolysis runs were performed with an interval of 25°C to determine the temperature at which maximum yield of aqueous condensate is obtained. For each experiment, 30 gm of grinded woody biomass was taken into the reactor. The temperature in the reactor was increased set at 400°C and after each run, 25°C of temperature was increased. At the point when temperature of the heating furnace achieved the desired value, the reactor was set in the furnace system. The experiments were carried out 9 times to ensure the total conversion of sample and mixture of aqueous condensate and bio-oil were collected in measuring cylinder and weighted for yield. The mixture was put in a separating funnel and aqueous condensate and bio-oil was allowed to separate. After separating, aqueous condensate

and bio-oil both were stored in separate measuring cylinders and were weighed. After pyrolysis, the solid residue left in the reactor was measured and the gaseous product yield was calculated by material balance. During sample runs various data like reaction time, yield of char, and yield of liquid product were noted down.

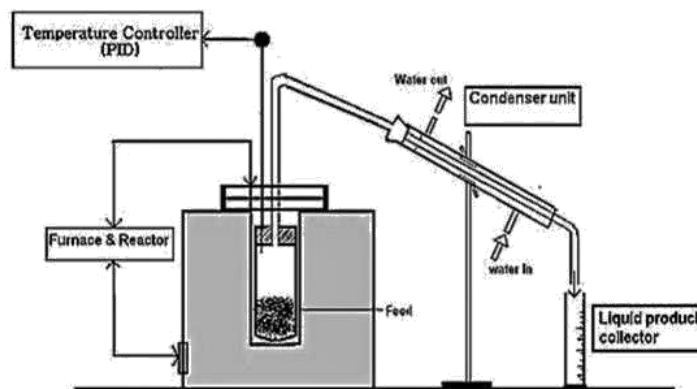


Fig -2: Tubular batch reactor: An Experimental setup for fast pyrolysis of woody biomass.

3. Characterizations

Characterization of raw material

The proximate analysis evaluates a solid biomass fuel's behavior when heated on the basis of four specific elements: humidity, fixed carbon, volatile matter and ash content. It was carried out using ASTM D3172 - 07a method. High volatile matter favored the aqueous condensate production while high ash content decreased the amount of aqueous condensate, consequently increased the gaseous yield and char formation.

While an ultimate analysis analyses the %wt of C, H, O & S present in woody biomass. It determines the elemental composition of the solid fuel substance. This involves the detection of sulphur which is one of the proved source of pollution. Sulphur falls in the form of minerals of sulfide, minerals of sulfate, or organically bound sulfur. It was conducted using a CHNSO elemental analyzer which provides a percentage of carbon, hydrogen, nitrogen, and sulphur. When the sum of these compositions is subtracted from 100, the percentage composition of oxygen is given.

Calorific value is defined as the amount of heat liberated by the complete combustion of a unit mass of fuel. Calorific value was determined for the woody biomass using a bomb calorimeter.

Characterization of aqueous condensate

The density of the aqueous condensate was kept in thermal bath at 26 °C as per ASTM D 4052. A small volume (approximately 6 ml) of aqueous condensate samples was introduced into an oscillation U-shaped tube and the change in oscillating frequency caused by the change in the mass of the tube was used in conjunction with calibration data to

determine the density of the sample. The calorific value of the aqueous condensate was determined using Parr 6100 Calorimeter. The calorific value is a direct measure of the chemical energy stored in the fuel. The energy released in the form of heat when a substance undergoes complete combustion in the presence of oxygen under standard conditions releasing carbon dioxide and water. The concept of calorific value requires the condition that the combustion products are cooled to 298 K which means the reactive heat and latent condensation heat of the water generated during combustion is included in the released heat. Hence the fuel's calorific value is referred to as 'Gross Calorific Value (GCV)' or 'High Heating Values (HHV)'. The gross calorific value of a solid biomass fuel is generally measured. The viscosity of the aqueous condensate was determined using a dynamic shear rheometer RHEOPLU/32v2.66 Cone (dia 39.018 mm and length 60 mm) and cup (internal diameter 41.97) type geometry was used to determine the viscosity, where the temperature was controlled accurately ± 0.05 °C by TC 30 temperature controller. Flash point of a fuel is the temperature to which the fuel must be heated to produce an ignitable vapour mixture above the liquid fuel, when exposed to an open flame. Generally, flash point is used in industry specification for fuel oil. Fire point of the fuel is the temperature when an oil in an open container gives off vapour at a sufficient rate to continue to burn after a flame is applied. Pour point is defined as the lowest temperature at which the oil will just flow under standard test conditions. The flash point, fire point and pour point of all the aqueous condensate were determined by using the ASTM D 92 for flash point, ASTM D 92 for fire point and ASTM D 97 for pour point, respectively.

Modeling

For the calculation of activity coefficients, UNIFAC is applied [10]. As a group contribution, GS-MC analysis directly calculates the components of the mixture. A proper thermodynamic model is required in order to predict the properties of the final products. These types of mixtures are highly non ideal. A GCA-EoS model has already proven to have excellent predictive capacity to represent the phase behaviour of mixtures. However, for the modelling of phase equilibria, GC-MS can be used. Following the GC-MS user guide, the model is created by identifying major stages of the process and select model blocks to represent each stage. Creating a flow diagram for process identification and linking streams. Setting up thermodynamic and chemical properties and feed rates of each stream. Setting the properties of each block. Defining sensitivity calculations. Running simulation and verify the results. Making corrections as required and repeat the previous setup .

Proposed Surrogate Mixture

In the present work, the FPBO is separated in three groups. The first fraction consists of solids, i.e. methanol insoluble fraction at room temperature. The second fraction comprises the acetone-soluble compounds as acetone is used as a solvent in the GC-MS measurements

and therefore this fraction can be analyzed by GC-MS (named GC-MS fraction in the following). Last, the third fraction is the remaining of the sample, representing mostly higher molecular weight components. It is calculated by the difference from total mass of the two first fractions. In analogy to the evaluation of the measurement results (see previous section), the solid fraction is disregarded since it is not relevant. The GC-MS fraction containing lighter and more volatile fraction is analyzed in detail and comprises of hundreds of components (a detailed GC-MS is provided in the supplementary data). To allow for modelling by reducing the number of components, similar molecules are grouped in a single representative substance. As FPBOs contain many different functional groups which lead to a strong non ideal behavior, components of the surrogate mixture have been chosen so that the fractions of functional groups over the whole boiling range are represented correctly. As a result, a model mixture is proposed comprising the substances shown in Table 1.

Component	wt%
<i>Aqueous condensate</i>	9.846
<i>Acetone</i>	6.217
<i>Ethanol</i>	6.204
<i>Benzene</i>	1.016
<i>Diethyl ether</i>	1.337
<i>Furfural</i>	1.604
<i>Phenol</i>	1.658
<i>Ethylenglycol</i>	1.450
<i>Guaiacol</i>	2.762
<i>Syringol</i>	2.494
<i>Levogluconan</i>	3.785

Table 1: Proposed surrogate mixture on GC-MS analysis for optimized aqueous condensate content.

Results and discussion

The proximate analysis of aqueous condensate was done using ASTM D3172.07a method. The proximate analysis of woody biomass resulted of about 18.65% of fixed carbon, 76.90% of volatile matter, 0.58% of ash content and 3.87% of moisture as on as received basis. Based on dry basis, fixed carbon, volatile matter and ash content yielded

19.40%,80% and 0.60% respectively. On the basis of dry ash,19.52% of fixed carbon and 80.48% of volatile matter was analyzed (Table 2).

Properties	Unit	As received	Dry basis	Dry Ash free
Fixed Carbon	w t %	18.65	19.40	19.52
Volatile Matter	w t %	76.90	80	80.48
Ash content	w t %	0.58	0.60	-
Moisture	w t %	3.87	-	-

Table 2: Proximate analysis of woody biomass.

The ultimate analysis yielding the weight % of CHNSO in the woody biomass. On doing ultimate analysis 49.80% of carbon, 5.87% of hydrogen, 39.60% of oxygen, 0.29% of nitrogen and 0.01% of Sulphur was seen .On the daf basis, 52.11% of carbon, 6.14% of hydrogen, 41.44% of oxygen, 0.30% of nitrogen and 0.01% of Sulphur was obtained (Table 3).

Elements	As received	Dry ash	Dry ash free
Carbon	49.80	51.80	52.11
Hydrogen	5.86	6.10	6.14
Oxygen	39.60	41.19	41.44
Nitrogen	0.29	0.30	0.30
Sulphur	0.01	0.01	0.01

Table 3: Ultimate analysis of woody biomass.

Heating value or calorific value of woody biomass is of great significant in the experiment and modelling of aqueous condensate . The calorific value was divided mainly into net calorific value was divided mainly into net calorific value and gross calorific value. The heating value of aqueous condensate was analysed using bomb calorimeter. In this analysis 18.72, 19.56 and 19.68MJ/Kg of NCV was seen on ar, da, daf basis respectively. The GCV was 20.89, 20.89 and 21.02 MJ was seen as on ar, da and daf basis (Table 4).

The experiment on the woody biomass was performed under a tubular batch reactor. This fast pyrolysis yielded four products bio-char, bio-oil, aqueous condensate and pyrolytic gas. The temperature range considered was in between 400°C-600°C with

an interval of 25°C every time so, a total of 9 samples undergone the fast pyrolysis. Initially, at 400°C, the reaction time was maximum with highest percentage of bio-char. While at 600°C, the reaction time decreased with highest percentage of pyrolytic gases. As our work is confined only to aqueous condensate , so the Table 5 shows the percentage of aqueous condensate and aqueous condensate free bio oil products.

Element	Unit	As received	Dry ash	Dry ash free
Net calorific Value	Mj/kg	18.71	19.56	19.68
Gross calorific value	Mj/kg	20.89	20.89	21.02

Table 4: Heating value of woody biomass.

Temperature	Aqueous Condensate	Bio oil	Bio Char	Gas
400	6.3	54.82	32.29	6.59
425	8.48	56.26	31.36	3.9
450	9.26	59.23	28.98	2.53
475	9.48	62.41	25.33	2.70
500	9.76	63.73	22.69	3.82
525	9.91	61.39	18.11	10.59
550	10.62	56.41	16.23	16.74
575	10.46	50.23	15.47	23.84
600	10.21	47.42	14.35	28.02

Table 5: Percentage of aqueous condensate in total by product after separation using separating funnel.

Graph of percentage aqueous condensate in total by product after separation using separating funnel shows the production of aqueous condensate is almost linear but due to its less percentage, the graph is slightly curved. However, at 550°C, the weight of aqueous condensate is maximum. The weight percentage of bio-oil was maximum at 500°C.

On the basis of the experimental results, proposed surrogate mixture and assumptions, a model for optimised value of aqueous condensate was carried out at different temperatures between 400°C-600°C. The graph shows the weight percentage of aqueous condensate experimentally as well as on modelling basis at proper intervals of temperature. The optimised value of aqueous condensate both experiment and modelling came out to be 550°C but due to the proposed

surrogate mixture, it's amount got different from experimental one. Thus we can see that the value of aqueous condensate experimentally was 10.63% but in modelling it came out to be 9.83% only.

Conclusion

The results made as per experimental study on optimisation of aqueous condensate recovery of woody biomass on fast pyrolysis was that woody biomass seems to have a high potential to extract bio oil and finally aqueous condensate in high yield weight percentage compared to any other biomass.

The highest yield weight percentage of the mixture was found to be 73.49% at a temperature of 500°C. On further separating the bio oil and aqueous condensate from the mixture of bio oil and aqueous condensate, the yield weight % of aqueous condensate was found highest to be 10.62% at a temperature of 550°C. However, the ratio of aqueous condensate to bio oil was found to be maximum at 550°C as per our experiment with a ratio of about 1:5. The ratio of aqueous condensate to bio oil keeps on increasing with temperature but the amount of bio-oil decreased. So, the objectives with which we started our experiment are successfully achieved with a view that the optimised result for the aqueous condensate is at 550°C keeping in mind that the production of bio-oil is not much effected. In comparison to the experimental values, the model slightly differs. A better value can be approached with more complex surrogate mixture. Because of the lack of a proper surrogate mixture, a proper thermodynamic model is still not designed. The lack in finding a suitable surrogate mixture is because of several factors like changing chemical composition of the mixture on reducing temperature, aging and dependency on activity coefficient. The assumptions & model were good for predicting water content in equilibrium state. But the behaviour of other components of bio-oil was not predicted and experimental data such as vapour liquid equilibrium, liquid-liquid equilibrium can be used to do so.

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BIOGRAPHIES



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