

# Effect of Pre-Biotreatment on the Liquefaction Process of Sawdust (SD)

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**Abstract:** *The conversion of biomass to useful liquids needs sever conditions of temperature and pressure. The present study aims to reduce pyrolysis temperature and pressure to lower limits, so as to reduce cost of the process. To achieve this goal, bio treatment step of biomass before pyrolysis was adopted. Special types of fungi were used that are well known of its activity on producing cellulase enzyme. The biomass, was treated with fungus, and incubated for various durations. Then the bio treated samples were pyrolyzed in order to get liquid products. The study show that bio treatment was successful to provide higher liquids yield compared with untreated raw materials.*

**Keywords:** Biomass wastes, Bio pretreatments, Liquefaction, Analysis

## 1. Introduction

Demand for energy and its resources are increasing with the rapid outgrowth of population and industries <sup>(1)</sup>. The combustion of fossil fuel causes pollution to environment with carbon dioxide which has its adverse effect on the global climate <sup>(2)</sup>. Rising in burning fossil fuel make concern for unstable and uncertain petroleum Sources <sup>(3)</sup>. The use of biomass for energy supplies is very useful to environmental assets and reduces global pollution climax with carbon dioxide <sup>(4)</sup>. Bio mass is renewable energy source found in a large varieties and different kinds <sup>(5-6)</sup>. Wood is aligno hemicelluloses, cellulose and lignin. <sup>(7-8)</sup> Currently the world utilized and interested with bio mass resources <sup>(9-11)</sup>. Thermo chemical conversion of bio mass is one of the ways to utilize bio mass sources and pyrolysis can be used to convert bio mass to useful types of liquid & gaseous fuels, on the other hand, liquid & gaseous fuel can be obtained as a result of biodegradation of biomass by different types of bacteria & fungi <sup>(12-15)</sup>. Bacteria have the capability to biodegrade the organic material producing methane & ethanol <sup>(12-15)</sup>. Fungi (isolated from different soils) are capable of reducing the large cellulose molecule to a variety of smaller molecules <sup>(16)</sup>. cellulose degradation took place by cellulase enzyme produced by special kinds of fungus <sup>(17)</sup>. In this study, we aim that the subjection of biomass to the bio action of one of these fungi would result in a lower molecular weight feed. Lower molecular weight feed may pyrolyze at lower thermo limits <sup>(17)</sup>. This would be reflected positively on the quantity of the resulting liquids, the process conditions and finally the economy of the process <sup>(17)</sup>.

## 2. Procedure Methods

### 2.1 Feed Stock & Chemicals

Biomass sources include wide and different kinds of materials. Sawdust (SD) was chosen as a feedstock for the purposes of this study. This material was used to testify & confirm the effect of bio treatment (if any) on pyrolysis conditions of biomass. Sample of SD was collected, washed from impurities, then dried in shadow at room temperature for four weeks and then in oven up to 90°C for 48 hours,

after that crushed and ground to get fine granules. By using multi sieves we obtained several sizes of granules from less than 0.5mm to  $\leq 4$ mm by several experiments were carried out to define what size gives the best results. Then this definite size was used for the rest of work in this study.

All chemical used in this study were obtained from well recognized chemical producing companies.

### 2.2 Biotreatment

#### 2.2.1 Activation of fungus

The fungus is activated by incubating it in special media that consists of potato, glucose and agar (PGA), this media was prepared by mixing 20 gm of glucose, 20 gm of agar and 20 gm of potato with 1 liter of water on hot plate until they dissolved, then disinfected with steam (autoclaved). Antibiotic was added to protect it from any bacterial growth.

#### 2.2.2 Samples incubation

5 gms of dry sawdust was accurately weighted in a 2 liter disinfected conical flask, then 100 ml of growth solution and loop wipe from the culture media of the fungus was added, after that the flask covered with piece of cotton and left in incubator at 27°C. The sample was watched & shacked every day, more over samples from this flask (incubator sample) were taken after (10, 25, 40, 60, 75) days from incubation to follow up changes in the composition of samples.

### 2.3 Thermal degradation (Pyrolysis)

#### 2.3.1 Charging the reactor with samples

Before charging the reactor it was cleaned & pressure tested to make sure it will keep liberating gases and will not leak. The sample charged to the reactor was SD (biotreated or not) and the charging goes as follows; about 2-4gm of the sample (accurately weighted) was charged to the vessel together with 80ml of tetralin (used as hydrogen donating solvent). Then the reactor was closed, evacuated from air, sealed & subjected to heating to the required temperature & time (rate of heating is 5 degree per min.). At the end of the experiment the reactor was allowed to cool down to room temperature, then gases were discharged (if any). Then the cover was removed & the contents were discharged. The contents were filtered using filter paper no1, washed with

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many solvents (n-hexane, methanol, petroleum ether (80-100), carbon tetrachloride, dichloroethylen, acetone). The solvents were recovered & the remaining liquids were collected altogether and weighted.

### 2.3.2 Analysis

The samples were subjected to analysis using different technique such as (FTIR, XRD, TGA).

### 2.3.3 Calculation of liquefaction

The main purpose of this work is to minimized thermal degradation limits of lignocelluloses materials. Liquid products are the most important products of cellulose pyrolysis. Liquefaction of cellulose was calculated as follows :

- 1) Quantity of carbon in sample = weight of sample\* percentage of carbon in samples.
- 2) Quantity of carbon in liquid product = weight of liquid product\*percentage of carbon in liquid product.
- 3) Liquefaction =  $\frac{\text{Quantity of carbon in liquid product}}{\text{Quantity of carbon in the sample}} * 100 \dots 1$

## 3. Results & Discussion

Cellulosic based materials are considered as a potential energy source. One of the most important routes to utilize these materials is through pyrolysis processes. Pyrolysis of cellulose usually commences around 350°C. However, most pyrolysis processes operate at higher temperature levels for different periods of time to produce the required fuel products (either gases or liquids). Lowering pyrolysis commencing temperature of cellulosic materials could have its positive impact on the economic feasibility of the whole pyrolysis process. Pyrolysis commencing temperature is a chemical property that relates to the chemical structure of the feed. Accordingly, changes in the chemical structure & the molecular weight of the cellulosic feed may have its effect on this temperature. Changing the chemical structure of the cellulosic feed can be achieved only either through chemical treatments which supposed to be costly & unfavoured from the economic point of view, or can be achieved through a biological degradation treatment which presumed to be much cheaper than the chemical treatment. From this point of view, this study has been developed.

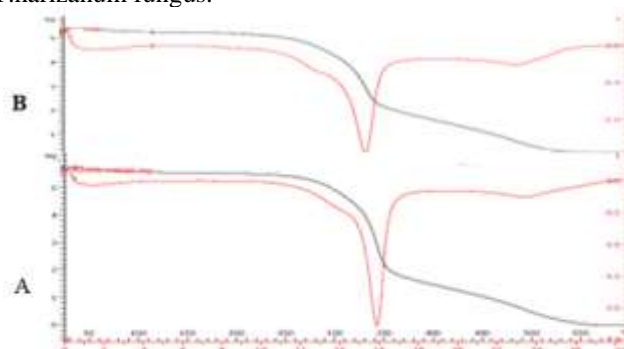
Accordingly, cellulosic based materials were subjected to bio pre-treatment (partial biodegradation) and the effect of this treatment on the physical & chemical properties of the feed was assessed. Results were obtained through comparable experiments between bio treated cellulosic feed & untreated natural cellulosic feed. The induced structures of the feestock by the biotreatment were detected by TGA, FTIR & X-ray diffraction techniques.

### 3.1 Thermal analysis (TGA)

Pyrolysis is one of the main important routes to produce organic liquid products from lingo-cellulose feedstock (biomass). Although the quantity of liquid products can vary quit widely according to the prevailing conditions of pyrolysis, however pyrolysis cannot be a achieved unless a definite temperature limit was attained. However lingo-cellulose feedstock composed mainly of three major

components, namely, hemicellulose, cellulose & lignin. Hemicellulose is the least thermally stable component of lingo-cellulose, because they lack a crystalline structure. Accordingly, they pyrolysed at a temperature level that is lower than that of cellulose & lignin. Cellulose is a more stable compound in lingo-cellulose samples due to its crystalline structure. Thermal analysis (TGA), was used to determine the pyrolysis temperature of our lingo-cellulose samples. Thermal analysis of lignocelluloses samples gives a peak at 275-350°C indicating the hemicellulose & cellulose decomposition temperature, while lignin decomposition peak (the third compound) appears in a distinct position over 400°C.

Figure1 (A&B) depict thermal analysis spectrum of SD before and after the bio treatment. We can notice the effect of fungus on feedstock through the appreciable reduction in the pyrolysis temperature of cellulose and hemicellulose from 345°C in untreated SD to 333°C for treated SD with T.harizanam fungus.

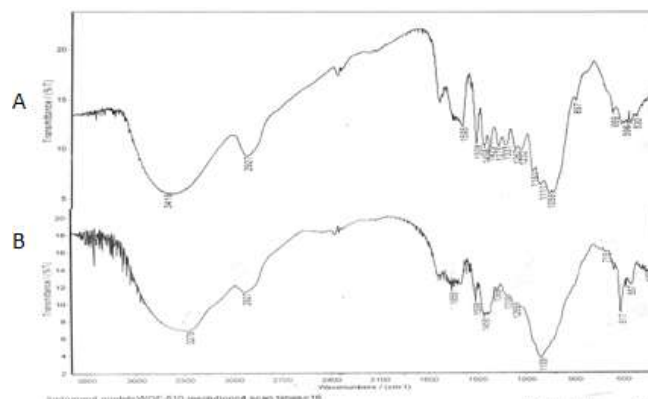


**Figure 1:** (A&B) untreated (SD) and treated with T.harizanam respectively

### 3.2 FTIR analysis

Figure 2: (A & B) depicts the FTIR spectra of untreated sawdust and that treated with T.harizanam fungus

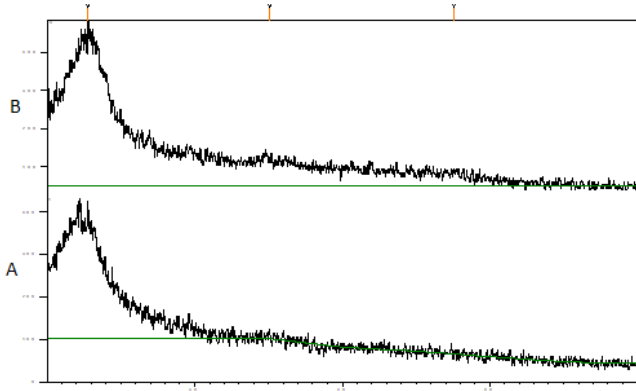
The FTIR spectra of SD treated with fungus revealed the presence of the same functional groups with a slight displacements. It can be seen from FTIR spectra of SD treated with T.harizanamfungus, that the area under the absorption peak for the treated SD was lower than those observed in the raw material, indicating that biological treatment was effective in inducing some changes to the structure of the raw material.



**Figure 2:** (A & B) FTIR of untreated (SD) and treated with T.harizanam respectively

### 3.3 X-Ray Diffraction (XRD)

The mechanical and structural properties of wood are based on a network of semi-crystalline cellulose chains embedded in an amorphous matrix of lignin and hemicellulose.<sup>(18)</sup> Cellulose is a high molecular weight linear polymer composed of D-glucopyranose units linked by  $\beta$ -1, 4-glycosidic bonds. Hydroxyl groups present in cellulose macromolecules are involved in a number of intra-and intermolecular hydrogen bonds, which result in various ordered crystalline arrangements.<sup>(18-20)</sup> The nature of bonds between the glucose molecules ( $\beta$ -1, 4 glucosidic) allows the polymer to be arranged in long straight chains. Figure 2 (A&B) shows the XRD of the untreated sawdust and that treated with T.harizantum respectively. It was found that bio-treatment resulted in formation of new peaks compared with untreated SD. This can be attributed to the new crystal structures that produced from the bio degradation of feedstock contents chains which could be detected in XRD. It is quite evident that the bio-treatment has fractionated the authentic feedstock into different fractions. Feedstock that was treated with T.harizantum resulted in three peaks compared to one peak for the untreated feedstock.



**Figure 3:** (A&B) XRD of untreated (SD) and treated with T.harizantum respectively.

**Table 1:** X-ray data for untreated S

Pos. [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
22.3419	56.74	3.97600	100.00

**Table 2:** X-ray data for SD treated with T.harizantum

Pos. [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
22.6946	79.36	3.91825	100.00
35.0497	13.91	2.56024	17.53
47.5219	6.62	1.91178	8.34

### 3.4 Liquefaction

The main purpose of this work is to reduce the pyrolysis conditions of biomass through a preliminary biological treatment with fungus.

Based on the results obtained from the present study, we found that the optimum conditions are as depicted in table (3).

**Table 3:** Optimum treatment conditions

Parameter	Conditions
Feedstock particle size	Up to 0.5 mm
Active fungus type	T.harizantum
Incubation period	60 days
Pyrolysis temperature (with tetralin)	300-330°C
Pyrolysis time	30 minutes

The main pyrolysis products of this process were liquids and solids while the amounts of gases were very low, this could be one of the main features of this process. The gases were neglected in all calculations related to liquid products.

**Table 4:** Weight percentages of pyrolysis liquid product in different temperatures

SD feedstock	Yield wt % of liquids product in 30 min.		
	250°C	300°C	330°C
Untreated	17.6	40.3	59.4
Treated with T.harizantum (60 days)	22	50.1	80

Table (4) presents the amounts of pyrolytic liquids from treated & untreated SD that were produced at different pyrolytic temperature.

These Tables represent the wt % of the organic & aqueous liquids that were produced from the reaction. However if we have to make an accurate notation about liquefaction this should be made in terms of the percentage of carbon in the feed that has been changed into organic liquids. This was achieved by calculating the amount of carbon in the feed & in the organic liquids that were generated from the reaction (equation 1). Table (5) depicts the elemental analysis of the feed & the organic liquids, while Table (6) presented the optimum percentage of liquefied carbon that was obtained according to our procedure. The percentage of liquefied carbon (76.5) at 330°C and atmospheric pressure and without using any catalyst seems to be quite acceptable, compared with many other pyrolysis processes

**Table 5:** Elemental analysis of the feed & the organic liquids

Solvent		Untreated						Treated with T.harizantum					
		Feed			Organic liquid			Feed			Organic liquid		
		C	H	O	C	H	O	C	H	O	C	H	O
Tetralin	SD	47.96	6.37	45.2	46.1	6.9	46.45	42.73	6.13	50.34	40.27	6.4	52.53

**Table 6:** Liquefaction percentages obtained at optimum reaction conditions.

Sample Type	wt % of liquefaction (with tetralin)
	SD
Untreated	56.87
Treated with T.harizanum	75.6

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