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Modified Fractionation Process via Organic Solvents for Wheat Straw and Ground Nut Shells

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Abstract

Modified organic solvent fractionation process involves the degradation of lignin, which is the main barrier of lignocelluloses biomass and the other two elements are cellulose and hemicelluloses. The treatment of organic solvent is given at a different concentration ratio, i.e. varies according to 10 ml mixture of ethyl alcohol and water, acetone and water is made for ground nut shells and wheat straw residues at elevated temperature and pressure conditions. Resulting in the decomposition of lignin and hemicelluloses hydrolysis and remaining solid residues mainly contains cellulose, which is further undergoing for enzymatic or microbial fermentation. The main aim of the study is to produce biodiesel in an efficient way by following the treatment of organic solvents. The present approach depends totally on the type of organic solvent and effect of process condition is highlighted that is useful for fractionation of lignocelluloses biomass. Statistical analysis is done to show the significant and non-significant values as well as standard deviation and standard errors are discussed here in this paper.

Keywords: Biomass pretreatment; Lignin; Lignocellulose biomass; Organic solvents

Introduction

The main objective of bio-refineries is to modify the fractionation process of biomass by utilizing the chemical functionalities process to coproduce bio-fuels as well as its byproducts [1].

Objective of Study

1. To develop a modified method fractionation process using organic solvent and water combination, i.e. is capable to break the main barrier Lignin of lignocelluloses biomass.

2. Determination of required optimization condition for organic solvent- water mixture.

3. Selection of better residue, i.e. Wheat Straw or Groundnut shell for biodiesel production.

Lignocellulose biomass consists of three polymers: cellulose, hemicelluloses and lignin. These polymers are associated with each other to form a hetero-matrix in different degrees and found in varied relative composition depending on the type of resources [2-4] and the relative abundance of cellulose, hemicelluloses and lignin are, inter alia, key factors in determining the optimum energy conversion route for each type of lignocellulosic biomass [5].

The main aim of pretreatment process is to break the fibrous structure and separate the main barrier, i.e. lignin via following the physically/chemically methods, therefore, it allows the easy accessibility of cellulose fraction for saccharification and hydrolysis of hemicelluloses [6].

Traditionally, pretreatment technologies are optimized for sugar production and produce a solid residue containing lignin, un-hydrolyzed sugar polymers, minerals, added process chemicals and fermentable inhibitors like organic acids but the hydrolyzed product obtained from sugar and lignin fraction only. In addition, novel pretreatment technologies overcome traditional conventional technology because its prime targets are to achieve full fractionation of biomass including lignin and remaining solid mass has been utilized for the generation of power and heat and biochemical products as well.

Currently, pretreatment technologies are utilizing the combination of organic solvents and water or combination of organic solvents and catalyst (synthetic or natural catalyst) [7] for degrading the lignocelluloses biomass.

The big advantage of pretreatment technology: combination of organic solvents and water or combination of organic solvents and synthetic or natural catalyst is that the full biomass conversion into bio-fuels occurs with an efficient rate. Organic solvent methodology depends upon on process parameters (Physical and chemical parameters), type of feedstock and type of organic solvent used. Another Similar technology has been developed recently, Using tetra-hydro-furan (THF) as a co-solvent to aid in the breakdown of raw biomass feed stocks to produce valuable primary and secondary fuel precursors at high yields at moderate temperatures. Those fuel precursors can then be converted into ethanol, chemicals or drop-in fuels. Drop-in fuels have similar properties to conventional gasoline, jet and diesel fuels and can be used without significant changes are made in vehicles [8].

Here, the organic solvent methodology is performed on residues: Wheat straw, Groundnut shells.

Methodology

This experiment is performed in a lab scale; organic solvent

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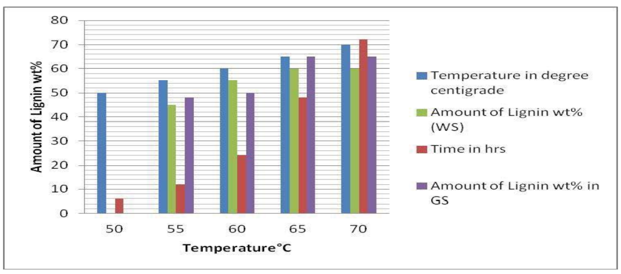
treatment is given to non edible biomass of Wheat straw and Ground nut shell. The procedure to perform the experiment is as follows: first of all the biomass is milled up to the approximate size of >0.7 mm. Subsequently, a mixture of organic solvent-biomass-water in a suspended form was made for 100 mg biomass approx. According to the requirement of 10 ml quantity of organic solvent and water (5% organic solvent and 5% water, 6% organic solvent and 4% water, 7% organic solvent and 3% water) of different concentration ratio were made (Figures 1 and 2).

A 10 ml mixture of organic solvent and water were made to treat the biomass under different conditions of temperature and pressure. Treated biomass undergo to the next step of biochemical analysis via (Spectro-photometric method is used for the analysis of extracts, Hemi cellulose content Cellulose content and Lignin content) [9] of both the filtrate and solid mass remain over the filter. The filtrate is heated at a temperature range of 150°C-210°C for 1 hour and then the suspension is settled in reaction time of around 60 mins and kept it for cooling.

Filtration of resulting slurry is performed and remaining solid residues were washed with an identical organic solvent-water mixture and then dried at 60°C. Both the Filtrate and washed suspension were undergoing for Spectro-photometric analysis. This analysis checks the level of oligomeric sugar and lignin content present after and before giving the treatment of organic solvent and water mixture.

Figure 1: Physical appearance of untreated biomass



The above graph (1) is plotted between the Temperature (°C) vs. Amount of Lignin (weight %) which shows the amount of Lignin present in Groundnut Shells (GS) and Wheat Straw sample at a temperature range of 55°C-70°C. No treatment of organic solvents. (Reference graph) is given.

Figure 2: Wheat Straw and Ground nut shell before the treatment of organic solvent and water (Standard data)

Results

Hemicelluloses hydrolysis

Hemicelluloses are branched, heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and acetylated sugars. The second most abundant polymer (20-50% of Lignocellulose Biomass) and it can be easily hydrolyzed thermo-chemically sensitive [10,11] due to presence of branches with short lateral chains [4,12]. In the present study, hydrolysis of hemicellulose take place via using organic solvent Ethyl alcohol and the Acetone and water combination. Hydrolysis of hemicelluloses occurs faster at lower concentration of organic solvent and water combination, i.e. 5:5 as compared to higher concentration of organic solvent and water combination i.e. 7:3. As depicted in Figures 3 and 4 Xylan hydrolysis was increasing. During the treatment of organic solvent, un-branched homo-polymers i.e. cellulose was hardly unaffected.

Lignin decomposition

The separation of lignin is a complex process known as delignification [13]. This process involves the degradation of lignin macromolecules into smaller fragments [14]. Almost all pretreatment methods can be used to fractionate the lignocelluloses biomass and the term "delignification" is associated with treatment that uses solvents. Here, organic solvents: Ethyl alcohol and water, Acetone and water combinations are used in a different concentration ratio of 5:5, 6:4 and 7:3. At these concentration all the sample were kept in Hot air oven at elevated temperature (55°C, 60°C and 65°C for 12 hrs, 24 hrs and 48 hrs) conditions required for the full fractionation of Lignocelluloses biomass i.e. lignin. (Figure 2 is easily compares with reference figure) This depicts that how much lignin remaining in the sample (GS) Groundnut shells and (WS) Wheat straw after the treatment with combination of organic solvents and water.

Alternative solvent used

Acetone, ethyl alcohol, acetyl chloride, hexane, dioxane or other organic solvents are used for the purpose of lignin decomposition. Lignin decomposition is indicated via mass loss and amount of lignin precipitated during the organosolvent experiment. Based upon the total mass loss, influence of solvent type on hemicelluloses hydrolysis is limited, but makes an easily accessible of other sugar, i.e. cellulose remaining in solid residues over the filter paper and the exposed sugar is utilized for further enzymatic sacchrification or microbial fermentation.

Discussion

Researchers are tried to develop the cost effective pretreatments technology using an organic solvent with water in combination. This technology is known as co-solvent technology. Recently another similar pretreatment technology develops by researchers of University of California, River side i.e. co-solvent-enhanced lignocellulosic fractionation (CELF) [15]. This technology definitely reduces the amount of enzymes required to breakdown the raw material which forms biofuels. This development could mean reducing enzyme costs from about $1 per gallon of ethanol to about 10 percents or less as well as more effective in terms of yield of ethanol twice as compared to dilute acid pretreatment technology.

Potential error

In the present study, co solvent technology is effective for bioconversion into bio-fuels but its real problem is that if organic solvents are not properly

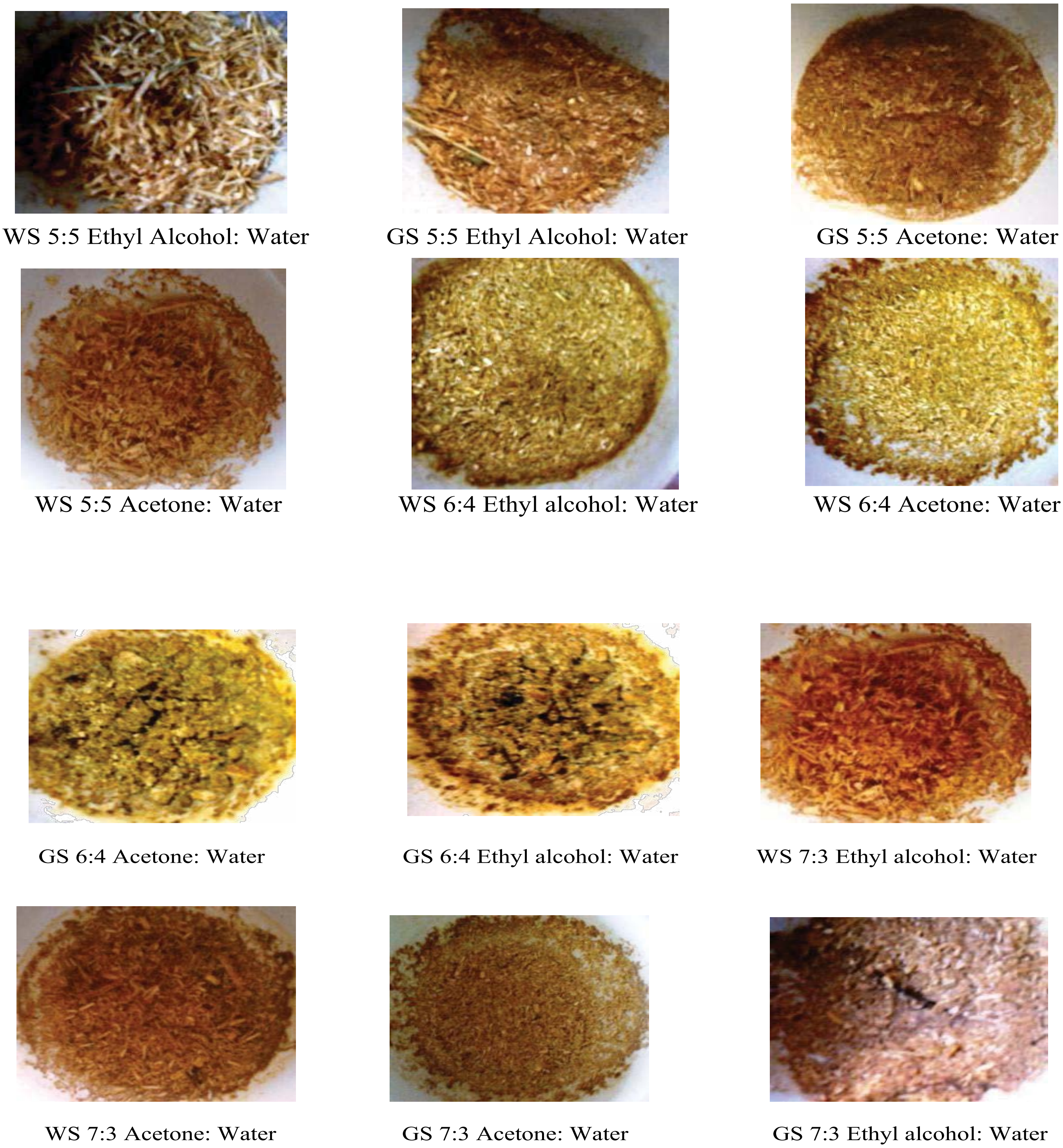
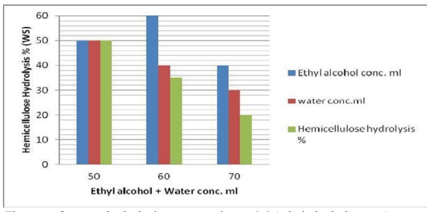
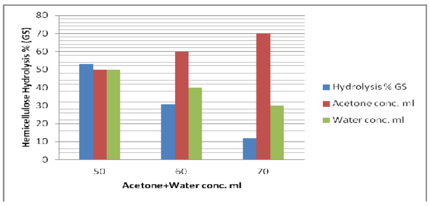


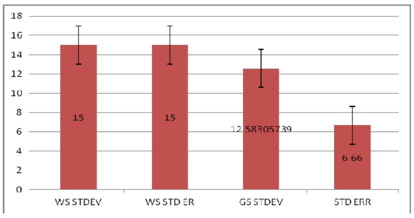
Figure 3: Physical appearance of Wheat straw (WS) and Groundnut shell (GS) residues after the treatment of organic solvent at different solvent concentration mixture.



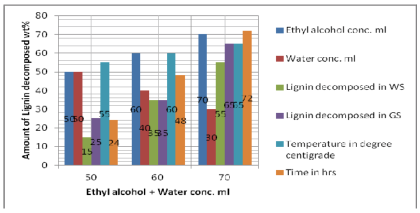
The most frequent hydrolysis are occurring at 5:5 (ethyl alcohol: water) as compared to higher concentration of 7:3 (ethyl alcohol: water).



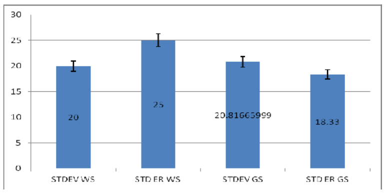
The most frequent hydrolysis were occurring at 5:5 (acetone: water) as compared to higher concentration of 7:3 (aectone: water).



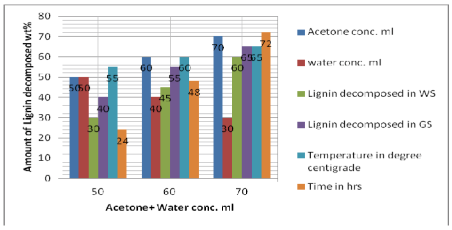
Graph shows standard deviation and standard error values according to the above graph plotted between the amount of lignin decomposed (wt%) vs Acetone +water conc.(ml) in wheat straw (WS) and Ground nut shells (GS).



Representation of decomposition of Lignin in Wheat Straw (WS) and Groundnut Shells (GS) expressed in wt% by giving the treatment of organic solvent (Ethyl alcohol) and (Water) concentration expressed in ml at different Temperature (°C) for 24 hrs, 48 and 72 hrs.



Standard Deviation and Standard Errors between the amount of lignin decomposed (wt%) vs. Ethyl alcohol + water conc.(ml) in wheat straw (WS) and Ground nut shells (GS).



Plot of decomposition of Lignin in Wheat Straw (WS) and Groundnut Shells (GS) expressed in wt% by giving the treatment of organic solvent (Acetone) and (Water) concentration expressed in ml at different Temperature (°C) for 24 hrs, 48 hrs and 72 hrs.

Figure 4: According to figure 2 graphs is plotted between % hydrolysis of Hemicellulose vs. different used organic solvent.

eliminated by evaporation, some unwanted reactions occurring such as inhibitors production during fermentation which inhibits the actual yield of bio-fuels. To avoid this problem, researchers are utilizing solvents such as Tetra hydro furan (THF) having more volatility.

Conclusion

Based on the result drawn so far, the following important points are drawn out:

- Modification of organo solvent and water combination is an interesting approach which is useful for enhancing the delignification of biomass and increased hemicelluloses hydrolysis. Another approach acid or base used as a catalyst to increase the more hydrolysis of hemicelluloses. This approach becomes the subject of further study.
- Selection of the best residues for an efficient production of Bio-energy: this is decided on the basis of amount of lining remaining and reduced moisture content after the treatment of organic solvent. In present study clearly indicates the ground nut shells sample is better than the wheat straw sample.
- Additions of catalyst or organic solvents are used in different a physical condition which inhibit the formation of inhibitors and decreases the processing cost.
- Here the required condition is defined, i.e. At a different concentration ratio is 5:5, 6:4 and 7:3 of Ethyl alcohol + water and acetone + water at different temperature 55°C, 60°C, 65°C and ≥70°C for 24 hrs, 48 hrs and 72 hrs. Out of obtaining data the required optimum condition for maximum delignification of biomass is occurring at 65°C for 72 hrs.
- Acetone is more effective than ethyl alcohol in terms of degree of delignification at same physical condition.

The reason behind this color change is that the re-condensation or decomposition of lignin occurs from the lignin - carbohydrate complex. In addition, above pictures clearly indicate that the structure of residues has been dramatically changed as well as it becomes very harder as compared to fresh sample. In addition, the present study clearly indicates that acetone is more effective organic solvent as compared to ethyl alcohol at a concentration of 7%: 3% (% of acetone or alcohol: water) at 65°C for 72 hrs i.e. required condition to dissolve the lining completely.

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Sample	Concentration (mg/ml) of	Color	Temperature (°C)	Time (hrs)
Wheat straw (WS) 100 mg	5% Ethyl alcohol: 5% water and 5% Acetone: 5% water per 100 mg of WS	No color changes occur	55°C	24 hrs
Groundnut shells (GS) 100 mg	5% Ethyl alcohol: 5% water and 5% Acetone: 5% water per 100 mg of GS	No color changes	55°C	24 hrs
Groundnut shells (GS) 100 mg	6% Ethyl alcohol: 4% water and 6% Acetone: 4%water per 100 mg of GS	Dark Brown & Hard residue	60°C	48 hrs
Wheat straw (WS) 100 mg	6% Ethyl alcohol: 4% water and 6% acetone: 4% water per 100 mg of WS	Darkish brown, thickness& Hardness increases	60°C	48 hrs
Wheat straw (WS) 100 mg	7% ethylalcohol:3% water and 7% acetone: 3% water per 100mg of WS	Darkish Yellowish Color & hardness Increases	65°C	72 hrs
Groundnut shells (GS) 100 mg	7% Ethyl alcohol: 3% water and 7% acetone: 3%water per 100 mg of GS	Light brown, Hardness& Thickness increases	65°C	72 hrs

Table 1: Shows the physical changes occur in Wheat straw and Ground nut shells sample under different physicochemical conditions. A biochemical change is observed after the treatment with organic solvents such as color of residue changes from light yellow to dark brown.Statistical analysis: All the experiment was conducted in a triplicate manner in a laboratory. Using the Annova software, statistical analysis can be carried out to find out the experimental significant values at $P<0.05$ level.
Statistical analysis: Organic solvent: Solvent Conc. ratio of (Acetone: Water)

Acetone: water conc.(ml)	Lignin reduction (wt%) in (WS*)	Temperature °C	Time interval (hrs)
5:5	30%	55°C	24 hrs
6:4	45%	60°C	48 hrs
7:3	60%	65°C	72 hrs

X^2 cal=10>X^2tab (5%) 5.991 (S) *WS stands: Wheat Straw sample This table clearly indicates the significant values (S) of lignin reduction in WS sample after the treatment with acetone: water at different temperature range of 55-65°C for 24-72 hrs.
Table 2: Lignin reductions (wt %) in WS after the treatment with acetone: water mixture.

Acetone: water conc. (ml)	Lignin reduction (wt%) in (GS*)	Temperature °C	Time interval (hrs)
5:5	40%	55°C	24 hrs
6:4	55%	60°C	48 hrs
7:3	65%	65°C	72 hrs

X^2 cal=5.932<X^2tab (5%) 5.991 (NS) *GS stands: Groundnut shells sample This table clearly indicates the non significant values (NS) of lignin reduction in GS sample after the treatment with acetone: water at different temperature range of 55-65°C for 24-72 hrs.
Table 3: Lignin reductions (wt%) in GS after the treatment with Acetone: water mixture.

Ethyl alcohol: water conc. (ml)	Lignin reduction (wt%) in (WS*)	Temperature °C	Time interval (hrs)
5:5	15%	55°C	24 hrs
6:4	35%	60°C	48 hrs
7:3	55%	65°C	72 hrs

X^2 cal=22.85>X^2tab (5%) 5.991 (S) *WS stands: Wheat straw sample This table clearly indicates the significant values (S) of lignin reduction in WS sample after the treatment with ethyl alcohol: water at different temperature range of 55-65°C for 24-72 hrs.
Table 4: Lignin reductions (wt%) in WS after the treatment with Ethyl alcohol: water mixture.

Ethyl alcohol: water conc. (ml)	Lignin reduction (wt%) in (GS*)	Temperature °C	Time interval (hrs)
5:5	25%	55°C	24 hrs
6:4	35%	60°C	48 hrs
7:3	65%	65°C	72 hrs

X^2 cal=20.79>X^2tab (5%) 5.991 (S) *GS stands: Groundnut shells sample This table clearly indicates the significant values (NS) of lignin reduction in GS sample after the treatment with ethyl alcohol: water at different temperature range of 55-65°C for 24-72 hrs.(S) = Significant values (NS) = Non significant values

Table 5: Lignin reductions (wt %) in WS after the treatment with Ethyl alcohol: water mixture

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