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(54) **Title:** PREPARATION OF HYDROLYSATE OF LIGNOCELLULOSIC MATERIALS

(57) **Abstract:** This invention relates to a process for the preparation of hydrolysate of lignocellulosic materials. An admixture of an organic acid and mineral acid is used for the pretreatment of lignocellulosic materials to get fermentable sugars like pentose and hexose sugars from the fibres present in said materials upon hydrolysis at a higher rate of conversion and yield.



TITLE: PREPARATION OF HYDROLYSATE OF LIGNOCELLULOSIC MATERIALS

FIELD OF INVENTION

The invention relates to a process for the preparation of hydrolysate of a lignocellulosic material and more particularly to a mixed acid heat treatment of lignocellulosic materials to obtain fermentable pentose and hexose sugars from hemicellulose and cellulose polymers present in said lignocellulosic materials.

BACKGROUND

Ethanol has a number of industrial and fuel applications. Of particular interest is the use of ethanol as an additive to gasoline to boost octane value, reduce pollution and partially replace gasoline in the mixture. This composition of gasoline and ethanol is well known commercially as "gasohol". Beside pure ethanol is also used as a motor fuel without any additives. Ethanol added fuels produce considerably less air pollution due to reduced emissions of carbon monoxide and hydrocarbons. Furthermore, ethanol is renewable chemical and can be prepared from a variety of natural vegetative materials like lignocellulosic biomass.

Presently a large portion of total global production of ethanol is achieved by using sugars obtained from food crops like sugarcane, sugar beet, maize, etc. The use of food crops for the production of ethanol has been controversial for some time now due to challenges associated with food requirements. However, over the past decades governments in several countries have been promoting non-food crops and biomass as feedstocks for production of ethanol for industrial applications.

Lignocellulosic materials [LCM] like wood, grasses, agricultural waste obtained from crops like corn, sugarcane, etc contains substantial amount of sugars in polymers of cellulose and hemicellulose, which are constituents of LCMs. However, LCMs are difficult to process compared with starchy materials due to hardy and complex nature. They require pretreatment to hydrolyse the hemicellulose and expose the cellulose for enzymatic hydrolysis to produce monomeric hexose for fermentation to ethanol.

Several methods of the pretreatment of LCMs have been described. However, yield from these methods have been limited or uneconomical and there exists a need for improving these methods for effective and economic utilization of LCMs for the preparation of ethanol. Presently, pre-treatment methods are based on thermal or chemical hydrolysis of the polymers of hemicellulose and to some extent cellulose to get free sugars. Thermal methods use steam at a high temperature and pressure to hydrolysis hemicellulose/ cellulose. The chemical methods utilize acids, alkali or other corrosive chemicals. These methods have advantages and disadvantages such as the overall conversion efficiencies achieved by these methods are quite low or economically not feasible in certain cases. They also produce many inhibitors of fermentation like phenolic residues besides effluent problems. The residual cellulose obtained by these processes is also difficult to digest enzymatically.

LCM is ubiquitous in all wood species and all agricultural and forestry waste. In addition, industrial waste that typically contains feedstocks like distillers wet grains, distillers dried grains and solubles, grasses, corn stover, corncob, sugarcane bagasse, sweet sorghum bagasse and agricultural residues are sources of LCMs. Currently, these industrial wastes are buried or burnt at considerable expenses.

LCM is a complex structure of cellulose fibres wrapped in a lignin and hemicellulose sheath. The composition of the main components varies depending on the type of biomass as listed in the table below:

| LCM | Cellulose [%] | Hemicellulose [%] | Lignin [%] |
|-------------------|----------------------|--------------------------|-------------------|
| Corn Stover | 22-29 | 13-18 | 12-17 |
| Corn Cob | 25-35 | 25-32 | 13-17 |
| Grasses | 25-34 | 12-16 | 18-22 |
| Soft woods | ~35 | 20-25 | 22-25 |
| Corn DWG | ~17 | 14-18 | 22-25 |
| Sugarcane bagasse | 38-45 | 18-25 | 22-25 |

The present processes have the drawback that if exposed to acid for too long a period, the glucose derived from cellulose degrades into hydroxymethylfurfural [HMF] that can be further degraded into levulinic acid and formic acid. Xylose, which is formed from hemicellulose, is degraded by acids into furfural and then results in tars and other degradation products. The sugar degradation not only reduces the ethanol yield, but the furfural and other by-products can inhibit the fermentation process. Thus, though the dilute acid process has the advantage of faster reaction, yet it has the drawback of low sugar yield.

Another drawback of using inorganic acid for hydrolysis is that even if the hydrolysis is carried out in two stages, with first stage being conducted under mild conditions to recover the 5-carbon sugars from hemicellulose and second stage being conducted under stronger conditions to recover

the 6-carbon sugars. On the other hand, if sufficiently gentle conditions are used so that only an insignificant degradation of sugars occurs, then in that case it does not result in complete hydrolysis of the substrate. Further drawback of using inorganic acids is that inorganic acids are corrosive and require special handling and expensive resistant equipments. Therefore there is a need for new methods of pretreatment of LCMs to achieve higher conversion and yield of fermentable sugars obtained from the biomass.

BRIEF DESCRIPTION OF THE INVENTION

An embodiment of the invention provides a process for the preparation of hydrolysate of a lignocellulosic biomass comprising: providing a lignocellulosic biomass having a hemi-cellulose, a cellulose and a lignin; transforming of said biomass into a particulate material; preparing a slurry of said particulate material in water; contacting said slurry with an admixture of an organic acid and a mineral acid creating a reaction mixture; continuously introducing said reaction mixture into a hydrolyser; maintaining a desired temperature and pressure in said hydrolyser for desired time to create a hydrolysate from said reaction mixture; continuously withdrawing said hydrolysate from said hydrolyser; and separating said hydrolysate into a liquid stream and a solid stream is provided.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for preparation of hydrolysate of lignocellulosic materials [LCM] like corn cob, corn stover, sugarcane bagasse and other similar materials to obtained fermentable sugars from the cellulose and hemicellulosic components of these LCMs. LCMs are mainly consists of three components: 1] hemicelluloses, 2] cellulose and 3]

lignin. The hemicelluloses are heterologous polymers of pentose sugars, mainly xylose and arabinose, along with a variety of pentose or hexose sugars derivative intermittently appearing in the polymer. Hemicellulose compositions vary depending on the source, though it constitute between about 10% to about 30% of the LCM. The celluloses are homologous polymers of mainly of glucose and are arranged in crystalline forms, constituting between about 15% to about 45% of the LCM. The third component, lignins are complex aromatic heterologous polymers varying nature having recalcitrant properties, and upon degradation lead to formation of phenolic and other undesirable organic molecules.

In one embodiment of the present invention, a dry LCM biomass is shredded [using mechanical means such as grinding, chopping, cutting or milling] into small particulate material with a mechanical means to obtain coarse powdery form of said biomass. In the next step, this material is soaked in water to achieve wetting and removal of soil matters from said particulate material. In the further step, slurry is prepared of said material at about 20% total solids by weight and introduced continuously through a plug screw type hydrolyser [also called digester, and it includes an autoclave] at a high temperature and pressure. In the hydrolyser said slurry is continuously mixed with an admixture of an organic acid [such as oxalic acid, formic acid or succinic acid] and a mineral acid [such as sulphuric acid, hydrochloric acid or nitric acid] more particularly with an admixture of oxalic acid and sulphuric acid at a specified amount of acids to that of total dry solids present in said slurry. Due to the unique combination of these acids, the hydrolysis is performed at relatively mild conditions leading to depolymerisation of hemicellulose and some extent cellulose polymers to monomeric sugars. Next, said hydrolysate is continuously removed and separated into two streams, a solid stream with most of undigested cellulose and lignin and a liquid stream with hydrolysed hemi-cellulosic material comprising xylose. Also formation of inhibitory compounds like phenolics and other organic substances that have negative effects on

fermentation of sugars by microorganisms remains to the minimum. In the next step, said hydrolyzed material is subjected to pH adjustment to about 5 with hydroxides of sodium, calcium or ammonia. Then to this stream cellulolytic enzymes are added for further hydrolysis of remaining cellulose polymers to glucose.

The advantages of the invention disclosed include: 1] higher efficiency of hemicellulose hydrolysis by said mixed acid treatment compared with known methods at a lower temperature and pressure; 2] due to reduced temperature and pressure requirements toxic/ inhibitory products are produced to lesser extent giving rising to good efficiencies in sugar fermentations; 3] the residual cellulose obtained after said pretreatment is also more amenable to enzymatic digestion by cellulases compared with other methods; and 4] the amount of inhibitors like phenolics, HMF, furfurals, etc in the hydrolyzed materials are at much less and tolerable levels compared with previous methods.

Examples provided below give wider utility of the invention without any limitations as to the variations that may be appreciated by a person skilled in the art. A non-limiting summary of various experimental results is given in the examples, which demonstrate the advantageous and novel aspects of the process of using an admixture of an organic acid and a mineral acid to prepare a hydrolysate of lignocellulosic materials optimally suitable for enzymatic hydrolysis treatment and fermentation of sugars so obtained.

EXAMPLE 1

A batch of about 118 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a feedstock. It was subjected to mechanical milling for size reduction to less

than 40 mm particles affording about 108 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 360 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 240 litres of the admixture of oxalic and sulphuric acids. This admixture of mixed acids contained about 1.08 Kg of oxalic acid and about 2.16 Kg of sulphuric acid on dry biomass weight basis [total 3% acid on dry biomass weight basis]. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 160 °C and pressure of about 6 bar[absolute] for a period of about 24 minutes at pH of about 1.3. At the end of this pretreatment the final slurry of about 603 Kg contained about 15.77% of total solids; and about 0.52% of glucose, about 4.77% of xylose, about 0.05% of furfural, about 0.04% of HMF and about 3800 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 31 Kg of pentose [xylose and arabinose] and about 3.2 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 86% and that of glucan to glucose conversion was about 8% in this embodiment. After mixed acid hydrolysis, said hydrolysate was subjected to pH adjustment to about 5 with hydroxides of sodium, calcium or by ammonia. This was followed by treatment of said hydrolysate with cellulolytic enzymes to further hydrolysis of remaining cellulosic polymers into monomeric sugars.

EXAMPLE 2

A batch of about 118 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a

feedstock. It was subjected to mechanical grinding for size reduction to less than 40 mm particles affording about 108 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 360 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 240 litres of the admixture of oxalic acid. This admixture contained about 5% of oxalic acid on dry biomass weight basis. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 160 °C and pressure of about 6 bar[absolute] for a period of about 45 minutes at pH of about 1.7. At the end of this pretreatment the final slurry of about 520 Kg contained about 14.20% of total solids; and about 0.45% of glucose, about 4.80% of xylose, about 0.02% of furfural, about 0.02% HMF and about 3500 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 26.6 Kg of pentose [xylose and arabinose] and about 2.3 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 80% and that of glucan to glucose conversion was about 6% in this embodiment.

EXAMPLE 3

A batch of about 59 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a feedstock. It was subjected to mechanical chopping for size reduction to less than 40 mm particles affording about 54 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 180 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug

screw reactor. Here the slurry was mixed with about 120 litres of the admixture of oxalic and sulphuric acids. This admixture of mixed acids contained about 0.54 Kg of oxalic acid and about 0.54 of sulphuric acid on dry biomass weight basis [total 2% acid on dry biomass weight basis]. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 160 °C and pressure of about 6 bar[absolute] for a period of about 24 minutes at pH of about 1.8. At the end of this pretreatment the final slurry of about 310 Kg contained about 14.20% of total solids; and about 0.52% of glucose, about 3.40% of xylose, about 0.02% of furfural, about 0.02% of HMF and about 3200 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 11.40 Kg of pentose [xylose and arabinose] and about 1 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 64% and that of glucan to glucose conversion was about 5% in this embodiment.

EXAMPLE 4

A batch of about 114 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a feedstock. It was subjected to mechanical milling for size reduction to less than 40 mm particles affording about 105 Kg of the particulate material. This particulate material was soaked in water for about 20 min. Then about 350 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 210 litres of the admixture of oxalic acid. This admixture contained about 3% of oxalic acid on dry biomass weight basis. The resultant reaction mixture was then

subjected to hydrolysis in said hydrolyser at a temperature of about 160 °C and pressure of about 8 bar[absolute] for a period of about 45 minutes at pH of about 2.1. At the end of this pretreatment the final slurry of about 601 Kg contained about 14.50% of total solids; and about 0.42% of glucose, about 3.56% of xylose, about 0.02% of furfural, about 0.02% HMF and about 3700 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 23 Kg of pentose [xylose and arabinose] and about 2.5 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 65% and that of glucan to glucose conversion was about 6.5% in this embodiment.

EXAMPLE 5

A batch of about 39 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a feedstock. It was subjected to mechanical shearing for size reduction to less than 40 mm particles affording about 36 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 120 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 80 litres of the admixture of oxalic acid. This admixture contained about 0.5% of oxalic acid on dry biomass weight basis. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 180 °C and pressure of about 10.5 bar[absolute] for a period of about 24 minutes at pH of about 3.1. At the end of this pretreatment the final slurry of about 205 Kg contained about 14.50% of total solids; and about 0.02% of glucose, about 0.73% of xylose, about 0.01% of furfural, about 0.01% HMF

and about 4500 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 8.3 Kg of pentose [xylose and arabinose] and about 0.04 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 85% [however this fraction mostly contained oligomers (about 5 times over monomers) of xylose] and that of glucan to glucose conversion was about 0.18% in this embodiment.

EXAMPLE 6

A batch of about 58 Kg of corncobs having total dry solids of about 92% by weight, cellulose of about 33.20% by weight, hemicelluloses of about 27.32% by weight and lignin of about 12.90% by weight was used as a feedstock. It was subjected to mechanical cutting for size reduction to less than 40 mm particles affording about 54 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 180 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was not mixed with any acids. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 180 °C and pressure of about 10.5 bar[absolute] for a period of about 45 minutes at pH of about 3.3. At the end of this pretreatment the final slurry of about 308 Kg contained about 14.32% of total solids; and about 0.03% of glucose, about 0.44% of xylose, about 0.01% of furfural, about 0.01% of HMF and about 4200 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 11.8 Kg of pentose [xylose and arabinose] and about 0.1 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 61% [however this fraction mostly contained oligomers (about 7 times over

monomers) of xylose] and that of glucan to glucose conversion was about 0.40% in this embodiment.

EXAMPLE 7

A batch of about 93 Kg of bagasse having total dry solids of about 90% by weight, cellulose of about 36% by weight, hemicelluloses of about 19% by weight and lignin of about 21% by weight was used as a feedstock. It was subjected to mechanical grinding for size reduction to less than 40 mm particles affording about 84 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 420 Kg slurry containing about 20% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 240 litres of the admixture of oxalic acid. This admixture contained about 3% by weight oxalic acid on dry biomass weight basis. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 170 °C and pressure of about 9.5 bar[absolute] for a period of about 24 minutes at pH of about 1.4. At the end of this pretreatment the final slurry of about 484 Kg contained about 16.5% of total solids; and about 0.31% of glucose, about 2.5% of xylose, about 0.01% of furfural, about 0.01% HMF and about 2300 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 13 Kg of pentose [xylose and arabinose] and about 1.5 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 72% and that of glucan to glucose conversion was about 5% in this experiment.

EXAMPLE 8

A batch of about 40 Kg of bagasse having total dry solids of about 92% by weight, cellulose of about 36% by weight, hemicelluloses of about 21% by weight and lignin of about 21% by weight was used as a feedstock. It was subjected to mechanical milling for size reduction to less than 40 mm particles affording about 36 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 180 Kg slurry containing about 20% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 80 litres of the sulphuric acid. This admixture contained about 1.8% by weight sulphuric acid on dry biomass weight basis. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 160 °C and pressure is about 7.5 bar [absolute] for a period of about 24 minutes at pH of about 1.4. At the end of this pretreatment the final slurry of about 329 Kg contained about 9.5% of total solids; and about 0.25% of glucose, about 1.5% of xylose, about 0.01% of furfural, about 0.01% HMF and about 3700 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 5.42 Kg of pentose [xylose and arabinose] and about 0.18 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 64% and that of glucan to glucose conversion was about 2% in this experiment.

EXAMPLE 9

A batch of about 247 Kg of bagasse having total dry solids of about 92% by weight, cellulose of about 35% by weight, hemicelluloses of about 21% by weight and lignin of about 22% by weight was used as a feedstock. It was subjected to mechanical chopping for size reduction to less than 40 mm

particles affording about 217 Kg of the particulate material. This particulate material was soaked in water for about 30 min. Then about 850 Kg slurry containing about 25% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 440 litres of the admixture of oxalic and sulphuric acids. This admixture of mixed acids contained about 1 % by weight oxalic acid and about 1.5% by weight sulphuric acid on dry biomass weight basis [total 2.5% of mixed acid on dry biomass weight basis]. The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 150 °C and pressure of about 5 bar [absolute] for a period of about 24 minutes at pH of about 1.2. At the end of this pretreatment the final slurry of about 1110 Kg contained about 17.2% of total solids; and about 0.32% of glucose, about 3.92% of xylose, about 0.01% of furfural, about 0.01% HMF and about 2400 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 46.50 Kg of pentose [xylose and arabinose] and about 3.52 Kg of hexose [mostly glucose] in the dissolved solids. The efficiency of xylan to xylose conversion was about 84% and that of glucan to glucose conversion was about 5% in this experiment. The insoluble solids were separated from the slurry and subjected to the enzymatic treatment. The filtered slurry with pentose sugars was further subjected to C5 fermentation to afford ethanol

EXAMPLE 10

A batch of about 60 Kg of bagasse having total dry solids of about 92% by weight, cellulose of about 35.35% by weight, hemicelluloses of about 21.39% by weight and lignin of about 21.39% by weight was used as a feedstock. It was subjected to mechanical cutting for size reduction to less than 40 mm particles affording about 54 Kg of the particulate material. This

particulate material was soaked in water for about 30 min. Then about 180 Kg slurry containing about 30% by weight total insoluble solids was prepared and continuously introduced into a hydrolyser through a plug screw reactor. Here the slurry was mixed with about 40 litres of water (no acid is added). The resultant reaction mixture was then subjected to hydrolysis in said hydrolyser at a temperature of about 180 °C and pressure of about 11 bar [absolute] for a period of about 24 minutes at pH of about 3.2. At the end of this pre-treatment the final slurry [hydrolysate] of about 285 Kg contained about 18.1% of total solids; and about 0.0% of glucose, about 0.48% of xylose, about 0.01% of furfural, about 0.01% HMF and about 4200 PPM of phenolic components along with residual cellulose and lignin as detected by the HPLC methods. This treatment afforded about 1.36 Kg of pentose [xylose and arabinose] and no hexose formed in the dissolved solids. The efficiency of xylan to xylose conversion was about 10.38% and that of glucan to glucose conversion was 0% in this experiment.

EXAMPLE 11

Table 11-1 provides the composition of the different product streams obtained by a process of the invention disclosed. Final cooked slurry [hydrolysate] was subjected to solid-liquid separation forming a solid and a liquid stream; next components of each separated stream were measured using HPLC methods. A typical range for each component is enlisted for two feedstock materials: corncobs and sugarcane bagasse.

TABLE 11-1:

| COMPONENT [W/W %] | FEEDSTOCK - CORN COB | | | FEEDSTOCK - SUGARCANE GAGASSE | | |
|----------------------|--------------------------------|-------------------------------|-----------------------------------|--------------------------------|-------------------------------|-----------------------------------|
| | HYDROLYSATE [Cooked Slurry] | SOLID STREAM [Wet Cake] | LIQUID STREAM [Supernatant] | HYDROLYSATE [Cooked Slurry] | SOLID STREAM [Wet Cake] | LIQUID STREAM [Supernatant] |
| TOTAL SOLIDS | 14-20 | 30-35 | 8.0-10.0 | 14-20 | 30-35 | 5.5-7.0 |
| GLUCOSE | 0.2-0.3 | 64-70 | 0.3-0.5 | 0.2-0.3 | 61-65 | 0.2-0.3 |
| XYLOSE | 3.0-4.0 | 3.5-5 | 4.5-5.5 | 3.0-4.0 | 3-4 | 3.0-4.0 |
| ARABINOSE | 0.1-0.2 | 0.3-0.4 | 0.3-0.4 | 0.1-0.2 | 0.1-0.2 | 0.1-0.2 |
| ACETIC ACID | 0.25-0.35 | x | 0.3-0.4 | 0.25-0.35 | x | 0.25-0.35 |
| HMF | <0.02 | x | <0.03 | <0.02 | x | <0.02 |
| FURFURAL | <0.02 | x | <0.03 | <0.02 | x | <0.02 |
| LIGNIN | x | 22-24 | x | x | 28-30 | x |
| PHENOLICS | 0.3-0.4 | x | x | 0.3-0.4 | x | x |

While the invention has been particularly shown and described with reference to embodiments listed in examples, it will be appreciated that several of the above disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different systems or applications. Also that various presently unforeseen and unanticipated alternatives, modifications, variations, or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims. Although the invention has been described with reference to specific preferred embodiments, it is not intended to be limited thereto, rather those having ordinary skill in the art will recognize that variations and modifications may be made therein which are within the spirit of the invention and within the scope of the claims.

CLAIMS

1. A process for the preparation of hydrolysate of a lignocellulosic biomass comprising:

- (a) providing a lignocellulosic biomass having a hemi-cellulose, a cellulose and a lignin;
- (b) transforming said biomass into a particulate material;
- (c) preparing a slurry of said particulate material in water;
- (d) contacting said slurry with an admixture of an organic acid and a mineral acid creating a reaction mixture;
- (e) continuously introducing said reaction mixture into a hydrolyser;
- (f) maintaining a desired temperature and pressure in said hydrolyser for a desired time to create a hydrolysate from said reaction mixture;
- (g) continuously withdrawing said hydrolysate from said hydrolyser; and
- (h) separating said hydrolysate into a liquid stream and a solid stream.

2. The process of claim 1, wherein said lignocellulosic biomass is one or more of corn cob, corn stover, sugarcane bagasse, sugarcane trash, soybean stover, wheat straw, grasses or a combination thereof.

3. The process of claim 1, wherein said biomass is transformed into said particulate material by one or more of chopping, cutting grinding or milling.

4. The process of claim 1, wherein said slurry comprises about 10% by weight to about 40% by weight said particulate material in the final composition.

5. The process of claim 1, wherein said admixture comprises oxalic acid and sulphuric acid; wherein the oxalic acid amount is between about 0.1 to about 5 percent and the sulphuric acid amount is between about 0.1 to about 5 percent of the dry biomass by weight basis.
6. The process of claim 1, wherein said temperature is from about 140⁰C to about 210⁰C and said time is from about 5 minutes to about 120 minutes.
7. The process of claim 1, wherein said process is conducted at pH of about 1.0 to about 4.0.
8. The process of claim 1, wherein hemi-cellulose present in said biomass is hydrolysed to at least 60% of original amount.
9. The process of claim 1, wherein said cellulose present in said biomass is hydrolysed to between about 0.5% to about 10% of original amount.
10. The process of claim 1, wherein said hydrolyser is a high pressure screw type digester.
11. The process of claim 1, wherein said hydrolysate contains total phenolic compounds not more than 6000 PPM and total furans not more than 1000 PPM.
12. A liquid stream according to the process of claim 1 comprising xylose.
13. A solid stream according to the process of claim 1 comprising residual cellulose.
14. A hydrolysate according to the process of claim 1 comprising at least four times more xylose than glucose and residual cellulose for an enzymatic hydrolysis process to obtain glucose.