Biochemical conversion of rice straw into bioethanol - an exploratory investigation

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INTRODUCTION

• Growing energy demands in transportation, industrial and other sectors with a simultaneous reduction of green house gas emissions.

INTRODUCTION

• Solar produced ecofriendly cheap biomass (lignocellulosics,150 billion ton/annum) renewable resource for biofuels an alternative fuel or oxygenate additive to the fossil fuels

INTRODUCTION

 Plants contain 6 x 10¹¹ tones of hemicellulose and about 3 x 10¹⁰ tonnes are photosynthesized annually. Hemicelluloses are low molecular weight compounds with DPn 200.

WHY BIOETANOL FROM BIOMASS?

- i) biomasses are geographically more evenly distributed than fossil fuels &hence the energy sourceswill be domestic and provide security of supply,
- ii) lignocellulosic wastes minimize the potential conflict between land use for food (and feed) and energy feedstock production,

WHY BIOETHANOL FROM BIOMASS?

- iii) the raw material is less expensive than conventional agricultural feedstock,
- iv) it (ex.switch grass) can also be produced with lower input of fertilizers, pesticides, and energy.
- v) biofuels from biomass- economic, environmental friendly (low emission of green house gas)
- vi) it can also provide employment in rural areas

PLANT BIOMASS



CELLULOSE



HEMI-CELLULOSE



LIGNIN



PRETREATMENT

- Saccharification of biomass- affected by porosity, fiber crystallinity, lignin and hemicellulose contents
- Lignin acts as a physical barrier should be removed to facilitate saccharification
- Pretreatment- mechanical, physical, chemical or biological- make cellulose to be more accessible to enzymes via removal of lignin and hemicellulose, reduction of cellulose crystallinity, and increase in porosity.

SCHEMATIC REPRESENTATION OF PRETREATMENT



RICE STRAW-COMPOSITION & PRODUCTION

- Rice straw(cellulose: 37%, hemicellulose:24% &lignin(14%)-an abundant biomass. Production 731 million tones/annum - produce about 205 billion litre bioethanol.
- Wheat and rice straw together : 200 million tonnes/ annum in India
- 1 kg rice straw has 350 g of cellulose which depends upon variety and the geographical location. This can theoretically yield 220 g /283 ml ethanol.

SCHEMATIC DIAGRAM FOR ETHANOL PRODCUTION FROM BIOMASS



SACCHARIFICATION OF CELLULOSE: METHODS

- Cellulose to ethanol by either SSF or SHFprocess. SSF is more favored because of its low potential costs
- Drawback of SSF : Different optimum temperatures for hydrolyzing enzymes and fermenting microorganisms. SHF method is followed here.

PRETREATMENT OF RICE STRAW

- Rice straw(Collected locally) washed and desoiled by froth-floatation in water, air dried & chopped into small pieces.
 Partially delignified using 4 % NH₄OH at 15 bar &120°C for 20 min in an autoclave at a volume ratio of 5:4 Washed with hot water repeatedly till free from alkali.
- NH₄OH treated rice straw is dipped in 1% sulphuric acid and autoclaved at 120°C for 15 min at 15 bar

RICE STRAW SACCHARIFICATION

- Done by using acid or enzyme catalyst or a combination of these two.
- Acid hydrolysis: 3 % sulfuric acid solun.
- Enzyme hydrolysis : Cellulase (liquid) enzyme (ROSSARI BIOTECH) optimum pH range :4.5-6 in 2M citrate buffer at 45oC over a period of 24 hrs.

TG Trace for virgin rice straw



TG Trace for NH₄OH treated rice straw



TG Data for Rice straw

| Rice | Weight loss at(°C) | | | %Residue |
|----------------------------|--------------------|-----|-----|----------|
| straw sample% | 100 | 250 | 350 | (400°C) |
| Desoiled (virgin) | 6 | 14 | 46 | 48 |
| Acid treated | 10 | 18 | 69 | 21 |
| Acid - NH4OH treated | 15 | 28 | 82 | Nil |

Sugar and ethanol yields per 25 g of desoiled rice straw

| Saccharificati on method | Sugar yield (g) / 25 g of rice straw | | Ethanol yield (g) from 25g of rice straw | |
|--|--------------------------------------|------|---|------|
| | Theo | Expt | Theo | Expt |
| Ethanol yield (g) from 25g of rice straw | 11 | 6.5 | 5.6 | 3.2 |
| Acid-Enzyme hydrolysis | 11 | 9.5 | 5.6 | 4.8 |
| Enzyme hydrolysis | 11 | 8.3 | 5.6 | 4.2 |

FT-IR Spectrum for virgin rice straw



FT-IR Spectrum for NH₄OH treated rice straw



FT-IR SPECTRUM

• The reductions in intensity of the peak at 1540 cm⁻¹ and reduction in $I_{1634cm-1}/I_{2924cm-1}$ intensity ratio from 1.2(virgin) to 0.766 in NH4OH treated rice straw are attributed to delignification.

FT-IR Spectral data

| Frequency | Assignment | | | |
|-----------|---|--|--|--|
| (cm-1) | | | | |
| 3416 | O-H (stretching) | | | |
| 2924 | C-H (stretching) | | | |
| 1735 | O=C-O (stretching) | | | |
| 1635 | C=O (stretching) | | | |
| 1540 | C=C (aromatic ring stretching) | | | |
| 1410 | CH2 (bending) | | | |
| 1310-1360 | C-C and C-O (skeletal vibrations.) | | | |
| 1377 | C-H (bending) | | | |
| 1200 | C-O (stretching in pyronose ring) | | | |
| 1170 | C-O(antisymmetric bridge stretching) | | | |
| 1105 | C-OH (skeletal vibrations) | | | |
| 1080 | C-O-C(pyranose ring skeletal vibration) | | | |
| 1030 | C-O (C-6 skeletal vibrations) | | | |
| 990 | C-O(sec.alcohols skeletal vibration | | | |

CONCLUSIONS

 saccharification - more effective in the combined successive acid and enzyme catalysis. The sugar and ethanol yields are 10-12% more in this method compared to those with liquid enzymatic saccharification-cum- fermentation.

CONCLUSION

This is due to better accessibility of the cellulose to cellulase enzyme by the removal of hemicellulose and lignin. Substantiated by its faster thermal degradation in the temperature range 200-400°C and nearly complete degradation at 400° C in the former case.

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