



Short Communication

Hydrolysis of biomass using a reusable solid carbon acid catalyst and fermentation of the catalytic hydrolysate to ethanol



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HIGHLIGHTS

- A glycerol based solid carbon acid catalyst found to hydrolyze biomass.
- Optimization of catalytic hydrolysis yields 31% efficiency with pretreated biomass.
- Catalyst can hydrolyze raw biomass with 20% efficiency.
- Negligible generation of fermentation inhibitors.
- Demonstrated catalyst reusability and fermentation using the catalytic hydrolysate.

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ABSTRACT

Solid acid catalysts can hydrolyze cellulose with lower reaction times and are easy to recover and reuse. A glycerol based carbon acid catalyst developed at CSIR-IICT performed well in acid catalysis reactions and hence this study was undertaken to evaluate the catalyst for hydrolysis of biomass (alkali pretreated or native rice straw). The catalyst could release 262 mg/g total reducing sugars (TRS) in 4 h at 140 °C from alkali pretreated rice straw, and more importantly it released 147 mg/g TRS from native biomass. Reusability of the catalyst was also demonstrated. Catalytic hydrolysate was used as sugar source for fermentation to produce ethanol. Results indicate the solid acid catalyst as an interesting option for biomass hydrolysis.

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1. Introduction

Simple soluble sugars can be derived through hydrolysis of biomass which can form the raw material for fermentative production of bioethanol or any bio-based chemicals (Jönsson et al., 2013). Biomass hydrolysis currently draws significant interest because large amounts of cellulosic feedstock, such as agro or forest residues are available in several countries with the possibility of utilizing them as feed stock for potential biorefineries, and the major limitation is currently the cost of its saccharification. Two of the commonly employed methods for hydrolysis are acid hydrolysis and enzymatic hydrolysis (Lee and Jeffries, 2011; Gütsch et al., 2012). However, there are many drawbacks to these processes.

The use of concentrated mineral acids is efficient at high temperature (170–240 °C), but controlling the further degradation/conversion of free sugars generated, the risk of corrosion, generation of large amounts of acidic waste water and separation of acids are major problems associated with this method (Taherzadeh and Karimi, 2007). Enzymatic hydrolysis is highly efficient, but at the same time, it is expensive and reusability of the catalyst is not practical.

Carbon acid catalysts are used extensively in organic chemical synthesis for the production of industrially important chemicals. Although sulfuric acid is inexpensive and highly active, its use has several limitations including low energy efficiency, requires separation and recycling, corrosion potential, handling hazards and also that it requires acidic waste management. The quest for environmentally sustainable chemical processing has stimulated the development of recyclable solid acid catalysts as replacements for such non recyclable systems (Kitano et al., 2009; Smith et al., 2003).

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Solid acid catalysts can be readily separated from liquid products by decantation or filtration, and the catalyst material can be reused for the reaction without neutralization, minimizing energy consumption and waste. Kitano et al. (2009) has reported a carbon-based solid acid consisting of polycyclic aromatic carbon and functional groups such as a sulfonic acid was demonstrated to act as strong solid acid catalyst for various acid-catalyzed reactions (Hara et al., 2004; Suganuma et al., 2008).

In enzymatic hydrolysis, the obvious disadvantages are the low activity, high cost of enzymes and separation problems because of the solubility in water. Due to the above mentioned disadvantages of the various methods, the development of a reusable chemical catalyst for conversion of lignocellulose to sugars with minimal generation of sugar degradation products is highly desired.

Sulfonated silica/carbon catalysts for cellulose hydrolysis have been reported which could liberate glucose in 50% yield (Van de Vyver et al., 2010). The highest reported yield of glucose is 75% which was obtained with a sulfonated carbon catalyst with mesoporous structure (Pang et al., 2010). However, most of these processes have reported hydrolysis of pure cellulose and not lignocellulosic biomass. The major challenges for a catalytic process include low cellulose/liquid ratios (eg 1:100) and the inability to convert lignin. The low biomass loading is a major limitation since this will necessitate concentration of glucose prior to the production of ethanol or other compounds which is energy-intensive. A glycerol based solid carbon acid catalyst developed at CSIR-IICT was demonstrated earlier for acid catalyzed biodiesel production (Prabhavathi Devi et al., 2009). It was speculated that the catalyst might be useful for hydrolysis of biomass since it can catalyze acid hydrolysis and at the same time will allow recovery and reuse. Hence the catalyst was evaluated for the hydrolysis of pretreated rice straw and subsequently fermentation of the catalytic hydrolysate to ethanol was performed.

2. Methods

2.1. Carbon acid catalyst, biomass feedstock and pretreatment

The glycerol based solid carbon acid catalyst was synthesized at CSIR-IICT as previously described (Prabhavathi Devi et al., 2009). The biomass feedstock (Rice Straw) was procured locally, knife milled and sieved to a maximum particle size of 2 mm. The milled biomass was pretreated using dilute alkali (4% w/w NaOH) at 120 °C for 60 min. The biomass loading was 15% (w/w). After autoclaving, the biomass slurry was neutralized by 10 N sulfuric acid followed by water wash. Pretreated materials were sun dried and stored in air tight containers until used. The compositional analysis of native and pretreated rice straw (RS) was carried out by the two stage acid hydrolysis protocol which was developed by National Renewable Energy Laboratory (Ruiz and Ehrman, 1996).

2.2. Biomass hydrolysis using the solid acid catalyst

Alkali pretreated biomass was hydrolyzed using the catalyst in acid digestion bombs to determine the efficiency of substrate conversion. Preliminary trials on hydrolysis were conducted as per the conditions specified in Table 1. The bombs were heated to the required temperature and were held at that temperature for the specified duration. After the reaction, the hydrolysate was centrifuged at 5076 g for 10 min to recover the supernatant and the total reducing sugars (TRS) were analyzed by DNS method (Miller, 1959). Individual sugar concentrations in the hydrolysate were analyzed by HPLC as per NREL protocol (Sluiter et al., 2008). Optimization of the catalytic hydrolysis was performed where the effect of biomass loading (1, 3% w/w), catalyst loading

Table 1
Biomass composition of native and alkali pretreated rice straw.

Rice Straw	Native (%)	Alkali pretreated (%)
Cellulose	32.7	59.43
Hemicellulose	15.59	17.34
Lignin	21.24	10.18
Ash	12.04	ND
Extractives	16.9	ND
Soluble proteins	4.9	ND
Total Sugars	48.29	76.77

(50%, 100%), temperature (140, 180 °C), time (2, 4 h) and mineral acid supplementation were studied following a 2^k factorial design (Table 2). Design Expert[®] software (Statease Inc., USA) was used for experiment design and analysis.

2.3. Catalyst reusability

The reusability study was studied with 3% (w/w) of biomass loading and 100% (w/w) of catalyst loading at a temperature of 140 °C for 4 h. The supernatant containing sugars were separated by centrifugation after the first cycle. The slurry containing undigested biomass and catalyst was suspended in excess volume of water and was mixed in a vortex mixer. The suspension was allowed to stand for few minutes when the catalyst settled down. It was collected by decanting the top layer and the process was repeated to remove all the undigested material. The catalyst was then given either a water or methanol wash and was used for the next cycle as above. Amount of sugar released was monitored for each cycle.

2.4. Inhibitor removal

Removal of the organic acids and sugar degradation products generated by the catalytic hydrolysis of rice straw was studied. XAD 4 and Seralite 400 resins were studied for adsorption of the inhibitors. Resins were added to the hydrolysate at 1% (w/v) and kept at 200 rpm for 8 h at 30 ± 2 °C. Supernatant was analyzed for the presence of fermentation inhibitors like organic acids, furfural and HMF by HPLC. A Rezex[®] ROA column (Phenomenex) and photodiode array (PDA) detector was used with 0.05 M H₂SO₄ as the mobile phase at a flow rate of 0.6 ml/min. The oven temperature was set at 50 °C.

2.5. Fermentation

The catalytic rice straw hydrolysate was used for ethanol fermentation. It was supplemented with yeast extract (0.25%), Ammonium Sulfate (0.5%), MgSO₄ (0.1%), KH₂PO₄ (0.2%) and pH was adjusted to 5.00. Fermentation was performed in 15 ml screw capped vials containing 10 ml hydrolysate. *Saccharomyces cerevisiae* was cultivated in YPD, centrifuged and the biomass cake was used as inoculum at 5 mg dry weight/ml level. The vials were capped and were allowed to ferment for 48 h at the end of which samples were withdrawn and centrifuged at 15400g to recover supernatant which was analyzed for ethanol by gas chromatography as outlined in NREL Laboratory Analytical protocol # 011 (Templeton, 1994).

3. Results and discussion

3.1. Rice straw pretreatment catalytic hydrolysis

Pretreatment of rice straw performed with 4% NaOH followed by neutralization and washing could remove almost 50% of the

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