

**Fuelling the Future:  
Advances in Science and  
Technologies for Energy Generation,  
Transmission and Storage**

*Edited by*  
**A. Mendez-Vilas**



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*Fuelling the Future:  
Advances in Science and Technologies for Energy Generation, Transmission and Storage*

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## INTRODUCTION

This book contains a selection of papers presented at The Energy & Materials Research Conference (EMR2012), which was held in Torremolinos, Málaga (Spain), during June 20<sup>th</sup>-22<sup>nd</sup> 2012. This new European forum was born in order to bring together researchers and professionals from a broad set of science and engineering disciplines with the aim of sharing the latest developments and advances in materials, processes and systems involved in the energy generation, transmission-distribution and storage. The organization called for research papers dealing with the following topics:

- Energy from biomass - Biofuels,
- Solar energy, photovoltaics,
- Fuel cells,
- Hydrogen,
- Wind power, wave and hydropower, geothermal energy,
- Non-renewable energy sources: nuclear and fossil fuels,
- Energy transmission-distribution and storage,
- Energy-efficient buildings,
- Energy saving and sustainability.

This first edition of the EMR Conference gathered 330 participants, coming from 65 countries. A total of 340 works were presented at the conference. This is a more than satisfactory level of attendance for a new research forum like this one, especially in the context of a global budget constraint.

The regular contributed research papers were complemented with two excellent Plenary Talks, namely:

- “From Nanometers to Terawatts. Pending Revolutions in Materials Science”, by Pedro Gómez-Romero, Research Center on Nanoscience and Nanotechnology (CIN2) (CSIC-ICN). Vice-Director of MATGAS Research Center, Barcelona, Spain.
- “Photovoltaic materials based on Small molecules: an emerging approach to organic solar cells”, by Jean Roncali, Group Linear Conjugated Systems CNRS, MOLTECH, University of Angers, France.

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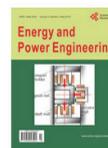
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# **Energy Production from Biomass**



# A comparison of the use of dilute aqueous *p*-toluenesulfonic acid and sulfuric acid in single step pretreatment - saccharification of biomass

Ananda S. Amarasekara\* and Bernard Wiredu

Department of Chemistry, Prairie View A&M University, P.O. Box 519, Prairie View, Texas 77446, USA

\*Corresponding author: e-mail: asamarasekara@pvamu.edu Tel: +1 936 261 3107

**ABSTRACT:** Dilute aqueous solution of *p*-toluenesulfonic acid is shown to be a better catalyst than aqueous sulfuric acid of the same H<sup>+</sup> ion concentration for the single step pretreatment - saccharification of switchgrass biomass at moderate temperatures and pressures. The highest total reducing sugar yield of 54.9% was achieved for switchgrass samples heated in aqueous *p*-toluenesulfonic acid at 150 °C for 3 hr, whereas samples heated in sulfuric acid under identical conditions produced only 41.2 % yield after 3 hr. The highest glucose yield of 20.9% was obtained at 170 °C in *p*-toluenesulfonic acid after 3.5 hr, while aq. sulfuric acid medium gave 9.8% yield under identical conditions.

**KEYWORDS:** switchgrass, *p*-toluenesulfonic acid, sulfuric acid, pretreatment, saccharification

## 1. Introduction

Saccharification of lignocellulosic biomass to fermentable sugars is an important step and the major obstacle for the large scale production of cellulosic ethanol from non-food biomass forms such as switchgrass, poplar, and corn stover [1-4]. The most efficient and widely tested procedure for this step is the pretreatment with dilute aqueous sulfuric acid at high temperature -pressure conditions, neutralization of the acid, and followed by the use of a cellulase enzyme cocktail for the saccharification step. However these operations are expensive, and constitute a major portion of the cost of cellulosic ethanol. Therefore, the whole cellulosic-ethanol process is facing major challenge in bringing the cellulosic fuel-ethanol production cost competitive with gasoline [5]. There are a number of factors that contribute to the high cost in this multi-step procedure, that includes the energy cost involved in the high pressure-temperature pretreatment [6-8], need for the neutralization of sulfuric acid with lime, inability to recycle the acid, high cost of currently available enzyme preparations, and inability to recycle the enzymes [9]. Another widely studied, and alternative method for the conversion of biomass to ethanol is the gasification route or thermochemical approach, where the syngas produced from biomass can be converted to ethanol by chemical or enzymatic catalysis. The use of enzymes or microorganisms to convert the syngas to ethanol generally suffers from poor efficiency due to inherent insolubility of these gases in water [10], and chemical catalysis method generally gives a mixture of products and poor ethanol selectivity [11], therefore this route is less efficient compared to saccharification-fermentation route.

Single step pretreatment-saccharification using a mineral acid like dilute aqueous sulfuric acid at high temperature and pressure is a feasible alternative to the acid pretreatment-cellulase two step method, and actually this is the older "Scholler process" used in World War 1 period. However, this method was abandoned with the development of efficient two-step pretreatment, enzymatic saccharification techniques. The main disadvantages of aqueous sulfuric acid direct saccharification technique are the poor sugar yields and formation of furan by products as a result of dehydration of sugars. Other disadvantage is the high energy cost associated with operating at temperatures above 250 °C at high pressures [12, 13]. Even though this direct dilute aqueous acid saccharification gives low fermentable sugar yields, in recent years a number of research groups have taken an interest [12-16] at this classical method, due to its simplicity compared to enzymatic saccharification, which nevertheless requires an energy intense pretreatment. Single step sulfuric acid saccharification can be carried out using concentrated sulfuric acid at relatively low temperature or dilute aqueous sulfuric acid at a much higher temperatures. Sun *et al.* [17] has recently studied the application of concentrated acid method on bamboo. In these experiments 75% H<sub>2</sub>SO<sub>4</sub> was used in two step hydrolysis at 85 °C (60 min.), and 120 °C (30 min.), where they reported 98.4% recovery of sugars based on the total sugar content in the biomass. Furthermore, 90.5% of acid could be recovered by passing the hydrolyzate through an anion exchange column; however the main problem in the concentrated acid method is the corrosive nature of the acid and difficulty in large scale operation. Dilute aq. sulfuric acid catalyzed single step saccharification method has attracted more attention in recent years, where a variety of biomass forms like aspen [18], balsam fir [18], basswood [18] maple wood [18, 19], sugar cane bagasse [20] corn cobs [21] and, switchgrass [18], have been studied. In these experiments, 0.07-1% dilute aq. sulfuric acid was typically used in the 160-220 °C temperature range. In the study where hydrolysis of aspen, balsam fir, basswood, red maple wood and switchgrass were compared [18] in the 160-190 °C temperature range, maximum yields for xylose ranged from 70% (balsam) to 94% (switchgrass), for glucose

from 10.6% to 13.6%, and for other minor sugars from 8.6% to 58.9%. Another approach [20] is to use extremely low sulfuric acid concentrations at high temperatures for a short period. Saccharification of sugar cane bagasse has been investigated [20] using 0.07- 0.28% H<sub>2</sub>SO<sub>4</sub> in a recent study, and the maximum glucose yields were reported as 67.6% (200 °C, 0.07% H<sub>2</sub>SO<sub>4</sub>, 30 min.), 69.8% (210 °C, 0.14% H<sub>2</sub>SO<sub>4</sub>, 10 min.), and 67.3% (210 °C, 0.28% H<sub>2</sub>SO<sub>4</sub>, 6 min.). Even though, dilute sulfuric acid has been tested with many biomass forms, comparison of sulfuric acid with other acids in the direct saccharification is rare, and is limited to small organic acids like formic acid. Kupiainen et al., [22] has recently compared the dilute sulfuric acid with formic acid for the hydrolysis of cellulose in the 180-220 °C temperature range, using the same acid concentration, and found a noteworthy difference between the reaction rates in formic and sulfuric acids. As these rate differences could not be explained unambiguously through changes in the crystallinity of cellulose, it was suggested that, in addition to hydrogen ions, cellulose hydrolysis is affected by other species found in reaction media.

Since 2009 we have been studying chemical hydrolysis of cellulose for applications in cellulosic ethanol process. These efforts have led us to explore sulfonic acid group functionalized acidic ionic liquids [23], immobilized acidic ionic liquid catalysts [24], as well as alkyl/aryl sulfonic acids [25, 26] as catalysts for the hydrolysis of cellulose. During these studies catalytic activities of a series of alkyl/aryl sulfonic acids in water were compared with sulfuric acid of the same acid strength (0.0321 mole H<sup>+</sup> ion /L) for hydrolysis of Sigmacell cellulose (DP ~ 450) in the 140-190 °C temperature range by measuring total reducing sugar (TRS), and glucose produced [26]. In 2012 we showed that aryl sulfonic acids like *p*-toluenesulfonic acid and 2-naphthalenesulfonic acid are better catalysts than sulfuric acid in water [26] for the hydrolysis of moderate molecular weight pure cellulose. For instance, cellulose samples (DP ~ 450) hydrolyzed at 160 °C for 3 hr, in aqueous *p*-toluenesulfonic acid, mediums produced total reducing sugar (TRS) yields of 28.0%, when compared to 21.7% TRS produced in aqueous sulfuric acid medium. As a continuation of this study, and in an attempt to test these results on raw biomass we have studied the direct pretreatment-saccharification of switchgrass using dilute aqueous *p*-toluenesulfonic acid. In this article we report a comparison of the use of aqueous sulfuric acid and *p*-toluenesulfonic acid of the same molar H<sup>+</sup> ion concentration for the single step pretreatment-saccharification of switchgrass.

## 2. Experimental

### 2.1. Materials and Instrumentation

Switchgrass (*Panicum virgatum*) samples were collected from USDA-ARS switchgrass biomass research plots located near Mead, Nebraska, USA, and are fully described by Dien et al. [27]. Air dried switchgrass was pulverized in a grinder to obtain a homogenous powder, and sieved through a brass mesh (Aldrich mini-sieve set, Z 675415, size 25, particle size 0.7 mm). The powder was then dried (~ 15 h) in an oven maintained at 70 °C, to a constant weight, and stored in a tightly sealed plastic bottle. Sulfuric acid (> 99.9%), *p*-toluenesulfonic acid (99.9%), were purchased from Aldrich chemicals Co., and used without further purification. Switchgrass pretreatment-saccharification experiments were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co. Ltd., Jingsu, China. These reaction kettles were heated in a preheated Cole-Palmer WU-52402-91 microprocessor controlled convention oven with ±1°C accuracy. Total reducing sugars (TRS, total of glucose, xylose, other reducing sugars, and their soluble oligomers with reducing groups) and glucose concentrations in aqueous solutions were determined using a Carey 50 UV-Vis spectrophotometer and 1 cm quartz cells.

### 2.2. General experimental procedures for pretreatment-saccharification of switchgrass samples in aqueous acid solutions

Stock solutions of the *p*-toluenesulfonic acid and sulfuric acid were prepared by dissolving appropriate amounts of these acids in deionized water to give acid concentration of 0.100 mol H<sup>+</sup>/L in each solution. The accuracy of the concentration was checked by titration with standardized aq. NaOH solution using phenolphthalein as the indicator. Pulverized, dried and sieved switchgrass (0.100 g) was suspended in 2.00 mL of aqueous acid solution in 25 mL high pressure stainless steel reaction kettles with Teflon inner sleeves. Stainless steel jackets of the reaction kettles were preheated for 30 min, before inserting Teflon sleeves, and then kettles were firmly closed and heated in a thermostated oven maintained at the desired temperature for various lengths of time. Each reactor was removed from the oven at the end of specified time period, and quickly cooled in ice-cold water to quench the reaction. The contents were transferred into centrifuge tubes, and each tube was diluted to 12.0 mL with deionized water, neutralized by drop wise addition of 0.5 M aq. NaOH. Then centrifuged at 3500 rpm for 6 min. to precipitate the solids before total reducing sugar (TRS) determination using 3,4-dinitrosalicylic acid (DNS) method [28]. The glucose formed was measured using glucose oxidase/peroxidase enzymatic assay [29,

30], which is known [31] to give glucose readings agreeable with HPLC method in the concentration range under study.

### 2.3. Analysis of hydrolyzate

#### 2.3.1. TRS assay

A 1.00 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial and 2.50 mL of deionized water was added. To this, was added 0.50 mL of DNS reagent (Breuil and Saddler 1985) and the mixture was incubated in a water bath maintained at 90 °C for 5 min. The reagent blank sample was prepared with 3.50 mL of deionized water and 0.50 mL of DNS reagent and heated similar to the samples. Then the absorbance was measured at 540 nm, against the reagent blank, and TRS concentrations in solutions were calculated by employing a standard curve prepared using glucose.

#### 2.3.2. Glucose assay

A 0.20 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial, and diluted with 1.80 mL deionized water. At zero time, reaction was started by adding 2.00 ml of glucose oxidase-peroxidase assay reagent [29, 30] to the vial and mixing thoroughly, and the vial was incubated in a water bath at 37 °C for 30 min. Then reaction was quenched by adding 2.00 mL of 6 M HCl to give a pink solution. The reagent blank was prepared by mixing 2.00 mL of deionized water and 2.00 mL of assay reagent, and was treated similarly. Then the absorbance was immediately measured at 540 nm against the reagent blank and glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

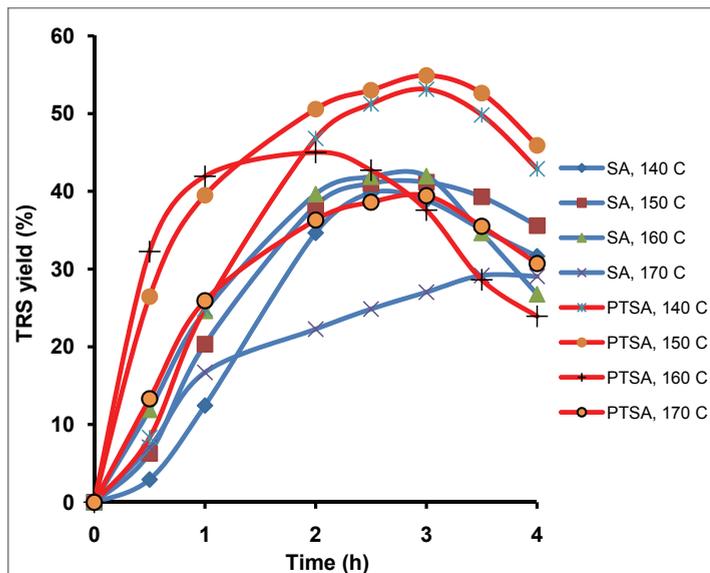
## 3. Results and Discussion

Aqueous sulfuric acid and *p*-toluenesulfonic acid were evaluated at four different temperatures for the single step pretreatment-saccharification of switchgrass by measuring total reducing sugar and glucose produced in the hydrolysis. Aqueous acid solutions of the two acids with the same acid strength (0.100 mole H<sup>+</sup> ion /L), were used in all experiments. In the case of sulfuric acid, according to Oscarson and Izatt's expression on temperature dependence of the first and second dissociation constants in aqueous medium, it is assumed that H<sub>2</sub>SO<sub>4</sub> completely dissociates to give two H<sup>+</sup> ions in the 140-170 °C temperature range [32, 33]. The average TRS yields produced in a series of experiments conducted in two acid mediums at four different temperatures (140, 150, 160, 170 °C) are shown in figure 1, whereas the glucose yields are shown in figure 2.

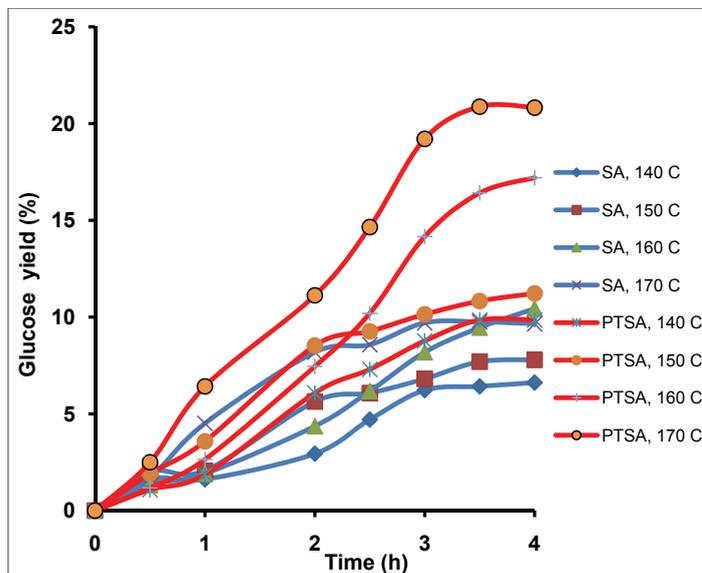
These results show that switchgrass biomass samples heated in aqueous *p*-toluenesulfonic acid at 140 and 150 °C temperature range reaches significantly higher total reducing sugar yields compared to the sample heated in aqueous sulfuric acid solution of the same molar H<sup>+</sup> ion concentration (figure 1). The highest TRS yield of 54.9% was achieved for switchgrass sample heated in aqueous *p*-toluenesulfonic acid at 150 °C, for 3 hr, whereas sample heated in sulfuric acid under identical conditions produced only 41.2 % yield after 3 hr. Similarly for 140 °C experiments, switchgrass sample heated in *p*-toluenesulfonic acid produced 53.1% yield, and aq. sulfuric acid produced 38.8% yield after 3 hr. At a higher temperature of 170 °C, both mediums gave relatively lower reducing sugars due to decomposition of the sugars in acidic mediums, however sulfuric acid medium showed more rapid decomposition and loss of TRS when compared to *p*-toluenesulfonic acid. Similar trends are reported in a comparison of glucose decomposition in sulfuric acid and organic acids like maleic acid as well [34].

Glucose produced in the series of experiments conducted at 140-170 °C temperature range are shown in figure 2, samples heated in aqueous *p*-toluenesulfonic acid at 160-170 °C range reached significantly higher glucose yields compared to the sample heated in aqueous sulfuric acid solution. Highest glucose yield of 20.9% was achieved after 3.5 hrs of heating in *p*-toluenesulfonic acid at 170 °C, and in aq. sulfuric acid the glucose yield was only 9.8% after 3.5 hr. Similarly, switchgrass sample heated at 160 °C for 3.5 hr. in *p*-toluenesulfonic acid produced 16.4% yield of glucose, whereas the sample heated in aq. sulfuric acid gave only 9.5% yield under identical conditions. The activity enhancement may be explained as a result of an adsorption of *p*-toluenesulfonic acid on to the switchgrass biomass surface, which is supported by the repulsion of the hydrophobic tolyl group from the bulk of the water phase, thereby pushing in to the lignocellulosic structure, which causes the disruption of the lignocellulosic biomass hydrogen-bonding network. This repulsion from water, sustained by the hydrophobic group is not found in sulfuric acid, therefore, H<sub>2</sub>SO<sub>4</sub> showed a relatively weaker activity compared with *p*-toluenesulfonic acid. Furthermore, in a cellulose model study we have recently shown [35] that *p*-toluenesulfonic acid interacts with the C-6', C-4' carbons of cellobiose in aqueous medium,

and a similar intermolecular interactions between cellulose and sulfonic acid may also contribute to the activity enhancement observed in these experiments.



**Figure 1.** Total reducing sugar (TRS) yields produced during the single step pretreatment-saccharification of switchgrass in aq. sulfuric acid (SA), and *p*-toluenesulfonic acid (PTSA) mediums, as a function of time, at constant temperatures of 140, 150, 160 and 170 °C. All acid solutions are 0.100 mol H<sup>+</sup>/L, 0.100 g of switchgrass (mesh size 25, particle size 0.7 mm) in 2.00 mL of aq. acid was used in all experiments. Averages of duplicate experiments.



**Figure 2.** Glucose yields produced during the single step pretreatment-saccharification of switchgrass in aq. sulfuric acid (SA), and *p*-toluenesulfonic acid (PTSA) mediums, as a function of time, at constant temperatures of 140, 150, 160 and 170 °C. All acid solutions are 0.100 mol H<sup>+</sup>/L, 0.100 g of switchgrass (mesh size 25, particle size 0.7 mm) in 2.00 mL of aq. acid was used in all experiments. Averages of duplicate experiments.

## 4. Conclusion

During the single step pretreatment - saccharification of switchgrass, aqueous *p*-toluenesulfonic acid is a better catalyst than H<sub>2</sub>SO<sub>4</sub> in the 140-150 °C temperature range. The highest TRS yields were achieved in *p*-toluenesulfonic acid at 150 °C after 3 hr, whereas the highest glucose yields for single step process were achieved in the same medium after 3.5 hr. This activity enhancement in the -SO<sub>3</sub>H function can be seen as an important lead in developing an acid catalyst better than sulfuric acid for single step pretreatment - saccharification of biomass. Furthermore, the hydrophobic group in the *p*-toluenesulfonic acid would allow recovery of the acid by solvent extraction, and we are currently studying the recovery of the sulfonic acid from biomass hydrolyzate for possible reuse in the single step process.

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## Build-up granulation of lignin sludge's as innovative process improving its energy efficiency

S. Narra<sup>\*</sup> and P. Ay

Chair of Mineral Processing, Brandenburg University of Technology, Cottbus, Germany

\*Corresponding author: e-mail: narra@tu-cottbus.de, Phone: +49 355693635

The importance of bio-products production is enhanced with the abundance and renewability of lignocelluloses biomass in comparison to the depleting fossil fuels especially in producing environment friendly energy. Lignin is obtained as a residue from the pulp industry (black liquor) as well as from the bio-ethanol / bio-diesel industries. The extracted lignin is a renewable fuel with a heating value of 17 MJ/kg, low ash content. The extracted lignin in pulp mills is usually burnt at the mill directly to cover the energy production costs of the mill. The extracted lignin undergoes a reduction in heating value from 26 MJ/kg to 17 MJ/kg due to its high moisture content (30-75 %). The high moisture content reduces the total energy efficiency of the plant and simultaneously utilizes more amount of lignin sludge in producing the required energy. The energy efficiency can be increased with the efficient utilisation of fuel and at the same time reducing the percentage of lignin sludge required for energy production. This paper explains a possibility of integrating build-up sludge pelletisation in pulp mills. The integrated sludge pelletisation techniques would lead to an optimal utilization of lignin for energy and would simultaneously save the lignin resource for materialistic utilisation. The build-up sludge pelletisation was carried out with the help of a spray-granulation apparatus. The spray-granules were then treated with H<sub>2</sub>SO<sub>4</sub> for stabilizing the lignin making it insoluble in water, regaining its original hydrophobic characteristics. The granulation process and the treatment with H<sub>2</sub>SO<sub>4</sub> solves the problem of handling, storage, explosion risks of lignin, reduction of impurities and increases the energy density of the raw materials in comparison to the present situation.

**Keywords** Lignin sulphonates; Kraft lignin; build-up pelletisation; energy efficiency; etc.

### 1. Introduction

Black-liquors /lignin sludge's (lignin-sulphonates (LS) / Kraft-lignin (KL)) are by-products of the pulping industry. The amount of black liquor obtained from the pulp cooking process is about 50 Mio t/a worldwide (FNR, 2010). Most of the black liquor is directly burnt at the pulp mill covering the energy requirement of mill partially. The materialistic utilization of black liquor is limited to less than 4 % of the total amount worldwide. The bio-polymer lignin has a high calorific value (26 MJ kg<sup>-1</sup>) almost equal to that of the anthracite coal (29 MJ kg<sup>-1</sup>). The high moisture content of the black liquor (30 to 70 %) leads in the reduction of energy efficiency to about 17 MJ kg<sup>-1</sup> (with 30 % moisture content) due to the losses in evaporation energy. The high sulphur content present in the black liquor demands a flue-gas desulphurization apparatus.

The black liquor mainly handled in liquid form is corrosive, has high energy efficiency losses due to evaporation losses, etc. The handling of black liquor after drying in the powder form is highly reactive and causes high fire and explosion risks. These are the main reasons that black liquors are always stored with a minimum moisture content of 30 %. An innovative technological processing and refinement of black liquor is required to solve the utilization problems associated in different forms (liquid, powder, sludge with 30 % moisture) in an efficient manner.

This work uses an innovative build-up granulation (spray-granulation process) of black liquor and then treating the produced granules with acid and modifying lignin. The spray-granulation was carried out with the reactor temperature below 100 °C. The granules produced are porous, dry, dense having high surface area, and the particle sizes higher than dust particles. The granules contain mainly lignin polymer along with the impurities (cooking chemicals). The impurities from granules are cleaned with the help of acid (H<sub>2</sub>SO<sub>4</sub>) treatment process. The porous granule structure offers a large surface area for the specified acid reaction (reduction in acid requirement). The acid treatment of granules leads in conversion of water soluble black liquor granules into water insoluble form regaining the original lignin characteristics and simultaneously increasing purity and yield. The particles inside the granules during the acid treatment melt and bridge with the neighbouring particles and build up into encapsulated hydrophobic lignin granules. This process carried out in a geometrically defined volume restraining filtration device (filter capsule) resulted in briquette formation due to the melting and bridging of particles inside the granules and with the surrounding neighbour granules. The briquetting process due to melting and bridging increases the efficiency of filtering process.

The briquettes increase the energy density, reduce the dust particle formation and improve storage and handling properties. The aim of this work is to investigate (i) the thermal characteristics of black liquors with varying temperatures; (ii) production of different black liquor granules with varying reactor temperatures; (iii)

particle size distribution of the produced granules using image analysis system (Camsizer); (iv) measurement of granule strength using GFP; (v) treatment of granules with different acids with varying temperatures; (vi) production of briquettes using volume restraint filtration device.

## 2. Materials and methods

Granulation of the technical lignin's was carried out with the help of spray granulator (type: 100 FSG from the company Alpine). Lignin sludge's were pumped into the reactor with the help of a pump through the two-stuff (material and air) nozzle. The evaporation process starts directly as soon as the material droplets exit the nozzle. The material is made to circulate in the reactor vertically due to the conical shape at bottom together with the air stream input. The material is also made to circulate horizontally with the help of air classifier on top of the reactor. The classifier on top filters the accumulated dust particles, serving as a control in the development of granules with certain diameter. As the granules build-up themselves into coarse granules gaining certain weight, which then fall down into the collecting container passing through zigzag de-dusting chamber. The zigzag de-dusting chamber prevents the falling down of low weight granules or dust particles (Heinrich, 2001; Heinze, 2000; Furchner and Schwechten, 1989). The goal is to produce granules having particle sizes greater than 100  $\mu\text{m}$  diameter to avoid explosion risks (Eckhoff, 2003).

The possibility to set different process parameters enables a wide range of lignin granules production. Spray granulation of calcium lignin sulphonate (Ca-LS) was carried out with increasing temperatures from 80  $^{\circ}\text{C}$  to 180  $^{\circ}\text{C}$  with an interval of 20  $^{\circ}\text{C}$ . Spray granulation of sodium lignin sulphonate (Na-LS) was only done for temperatures 80  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$ , and the Kraft lignin (KL) at 100  $^{\circ}\text{C}$  due to high moisture content present in Kraft lignin. The material input temperature was about 20  $^{\circ}\text{C}$ .

The strength indicates the quality of granules /briquettes and is defined as the force necessary to crush them with respect to time. The strength tests for granules were carried out with the help of GFP-Automatic from the company Etewe GmbH, whereas the strength tests for briquettes were carried out with ZWICK-ROELL (type: ZMART.PRO) material testing machine. The diametrical strength tests were carried out as these pressures occur during handling, transportation and storage of granules /briquettes. The elementary analysis of the raw black liquors as well as of the granules / briquettes produced with spray granulation was analysed using Elementar Vario MACRO CUBE.

The granules produced from Ca-LS, Na-LS and KL with the reactor temperatures of 80  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$  respectively have been treated with different concentrations (70 %, 80 % and 90 %) of acids ( $\text{H}_2\text{SO}_4$ ) at varying temperatures (100  $^{\circ}\text{C}$  and 130  $^{\circ}\text{C}$ ) for 15 minutes. The detailed schematic process (figure 1) in production of hydrophobic granules / briquettes with the help of acid treatment is applied for patent (patent application number 10 2012 102 327.1, Date 12.03.2012). The granules / briquettes after the acid treatment were treated with warm water (80  $^{\circ}\text{C}$ ) removing the acids adherent on the surface of the filtered granules. The washing of granules / briquettes with warm water was carried out till the pH of the filtrate stabilized. The filtrates obtained from the filtration of granules and after the washing of granules are sent to the regeneration unit, where the acids and water are regenerated and recirculated back into the process.

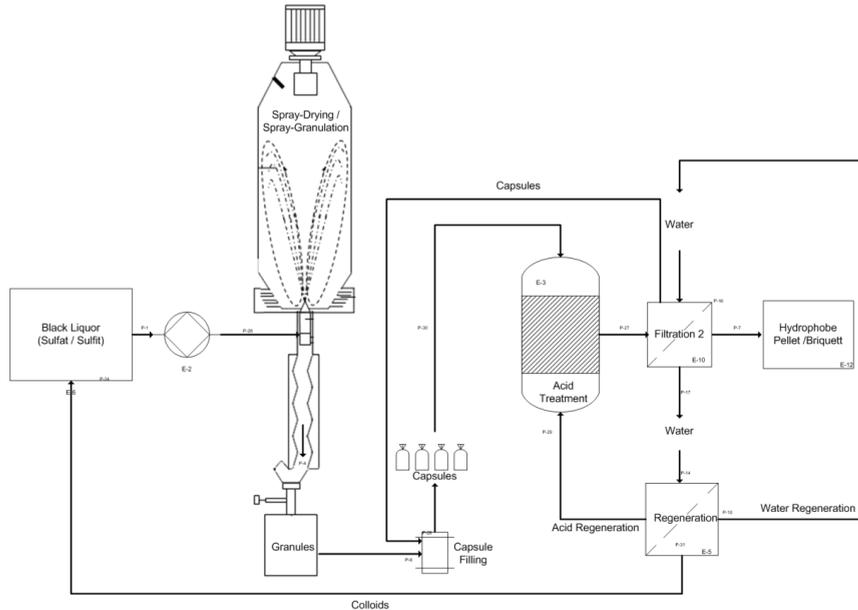
## 3. Results and discussions

The water content of LS was ranging from 50 to 55 %, whereas KL had a moisture content of 75 %. The water content of the produced granules was in between 4 % and 11 % and after the acid treatment was in between 5 % and 10 % after stabilization. The water content of the granules is either lower than or equal to that of the specified values as per solid fuel standards ( $\leq 10$  %) resulting in high combustion efficiencies and through which a high energy efficiency can be achieved (Kaliyan and Morey, 2006; Obernberger and Thek, 2004).

The drying of black liquors at different temperatures (60  $^{\circ}\text{C}$ , 80  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$ ) over 24h in oven displayed a clear thermal behavioural characteristic of the material. The black liquors displayed highly foamy structure at high temperatures, which was measured with respect to the pore sizes in the foam (85  $\mu\text{m}$  for 60  $^{\circ}\text{C}$ , 165  $\mu\text{m}$  for 80  $^{\circ}\text{C}$  and 6154  $\mu\text{m}$  for 100  $^{\circ}\text{C}$ ). The reason for this increasing pores is due to the high dynamic viscosity (changing with temperatures) of the black liquors leading in the development of a foamy structure.

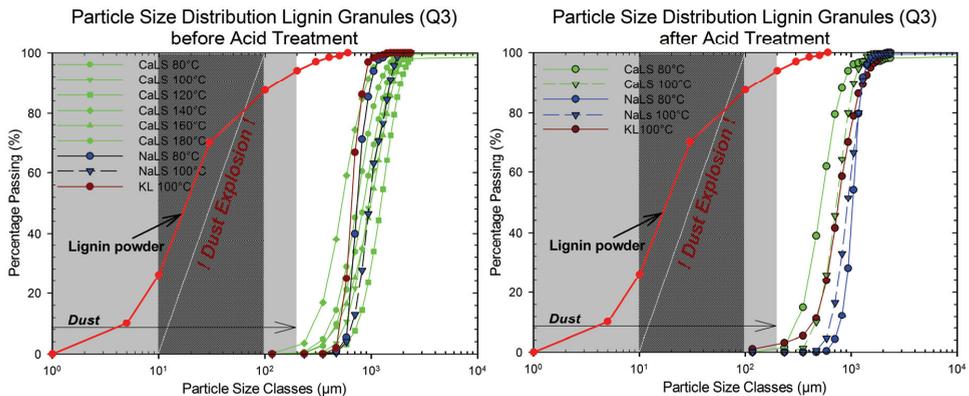
The transmissibility of the foamy behaviour of black liquors from the oven to spray granulation was clearly observed with respect to the structure, colour, particle size, density and porosity of the produced granules. The granules produced at higher temperatures ( $> 100$   $^{\circ}\text{C}$ ) resulted in highly porous, low density, bigger particle size and are light brown in colour. The granules produced at lower temperatures ( $< 100$   $^{\circ}\text{C}$ ) resulted in high density, smaller particle size, less porous and are dark brown in colour. The produced granules were build-up from sprayed droplets by the evaporation of liquid under different temperatures. The granules produced below 100  $^{\circ}\text{C}$  were almost spherical, where as the granules produced at higher temperatures had irregular size and shape due to the foamy expansion of lignin sludge. The colour difference of the granules (below 100  $^{\circ}\text{C}$  and above 100  $^{\circ}\text{C}$ )

is due to the reason that the granules produced below 100 °C have not undergone complete liquid evaporation and the drying process only takes place over the surface in spray granulation process. The presence of liquid inside the granule lets them fall through the zigzag de-dusting chamber due to the weight of the granule. The air drying of the granule produced below 100 °C increases the strength of the granules, due to the binding of the surface dried particles with liquid kernel. Based on these results, the black liquors were only granulated at 80 °C and 100 °C temperatures.



**Figure 1.** Schematic process in the production of hydrophobic granules /briquettes from black liquors.

The particle size distribution curves of different granules from different lignin sludge’s with varying temperatures before and after acid treatment are depicted in figure 2. The particle sizes and their ranges are classified in as dust (1 to 200 μm), dust explosion (10 to 100 μm) and dust free granules. The particle size distribution of lignin powder falls up to 95 % in the dust zone and 25 % to 88 % under dust explosion zone, indicating a high risk of explosion. The granules fall slightly under the dust zone (< 3 %) but not under the dust explosion zone.

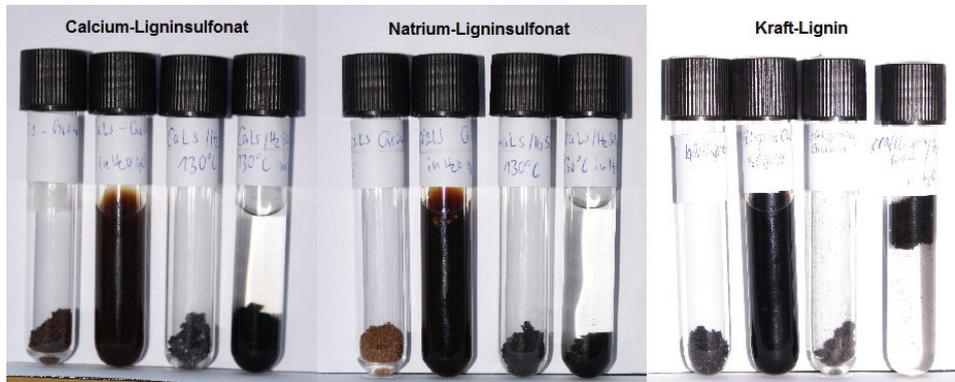


**Figure 2.** Particle size distribution of the dried lignin powder (red) and lignin sludge granules before (left) and after (right) acid treatment of i) Calcium lignin sulphonate (CaLS: green), ii) Sodium lignin sulphonate (NaLS: blue) and iii) kraft lignin (KL: dark red) with varying temperatures.

The fuel property which changes with the spray granulation /briquetisation of lignin sludge is the reduction of moisture content and production of dense granules /briquettes. The measured bulk density of the granules ranged from 490 kg/m<sup>3</sup> to 670 kg/m<sup>3</sup>, whereas the briquettes had a density of 1351 kg/m<sup>3</sup>. High density of granules /briquettes is important as this significantly reduces the storage, transportation, handling and fuel feeding costs and simultaneously increasing the energy density.

Granules /briquettes need to withstand different pressure forces as they are confronted with such pressures during handling, storage, transportation and feeding. The withstanding pressure of the granules before acid treatment was 3 N/mm<sup>2</sup> and after acid treatment was 7 N/mm<sup>2</sup>, whereas that of briquette after acid treatment was 150 N/mm<sup>2</sup>.

The acid treatment of granules and granules in geometrical defined restraint volume capsule resulted in the change of solubility characteristics along with the removal of impurities. The granules /briquettes after the acid treatment were hydrophobic. Lignin sludge granules from lignin sulphonates and Kraft lignin before (glass 1 and glass 2) and after (glass 3 and glass 4) the acid treatments were suspended in water to check their solubility (figure 3). The acid treated granules did not show any water solubility in comparison to the untreated soluble granules. Lignin polymer before the pulp cooking process is insoluble in water, and is made soluble either by breaking (Kraft lignin) or modifying (lignin sulphonate) the structure of lignin with the help of cooking chemicals and high cooking temperatures. The treatments of granules with acids regain the structure of lignin back to its original form (insoluble in water). The compact dense granules retain their structure avoiding /reducing the formation of colloids in the acid treatment process making the filtration and separation processes easier and efficient. A warm water (< 100 °C) washing process has to be carried afterwards to remove the adherent acids from the granules after their treatment with acids.



**Figure 3.** The water solubility of lignin sludge granules before (glass 1 and glass 2) and after (glass 3 and glass 4) the acid treatment

The elementary analysis of the lignin sludge's as well as the produced granules and the granules after the acid treatments (table 1) have been analysed to check the suitability of them for their different utilization purposes (materialistic as well as energetic). The sulphur and ash content analysed in the lignin sludge's were ranging in between 6.9 to 7.6 % and 13.5 to 44.4 % respectively. The sulphur and ash content in calcium lignin sulphonates, sodium lignin sulphonates and Kraft lignin granules after spray granulation before acid treatment were having the same values as that of the lignin sludge's, whereas the granules after acid treatment showed enormous reductions (Ca-LS: 13.5 to 3.9 %, Na-LS: 21.2 to 0.58 % and KL: 44.37 to 0.58 %). The water and ash free heating values of the lignin sludge's as well as the granules before and after the acid treatments and the briquettes formed during the acid treatment process are calculated based on equation 1 (Kaltschmitt et al., 2009) from the values obtained from elementary analysis. The heating values (water and ash free) of the granules before and after the treatment remained same, also indicating no losses in energy efficiency.

$$H_o(\text{waf}) = 0.3491 * X_C + 1.1783 * X_H + 0.1005 * X_S - 0.0151 * X_N - 0.1034 * X_O - 0.0211 * X_A \quad (1)$$

**Table 1.** Elemental analysis (water and ash free) of lignin sludge's spray-granulates before and after the acid treatment.

Material	T <sub>R</sub> /C /T <sub>C</sub> [°C]	Moisture [%]	Carbon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	Sulphur [%]	Ash [%]	H <sub>o</sub> (waf)
Lignin sludge's									
Calcium-LS	--	50	56,37	5,41	31,07	0,22	6,93	13,49	23,25
Sodium-LS	--	55	59,92	5,64	26,65	0,23	7,59	21,2	25,12
Kraftlignin	--	75	66,42	6,42	19,62	0,20	7,35	44,37	28,52
Calcium lignin sulphonate Granules									
Before Acid	80	8,65	56,27	5,41	31,30	0,22	6,80	13,52	23,17
Treatment	100	8,70	56,47	5,41	30,84	0,22	7,07	13,46	23,32
After Acid Treatment	80 /80 /100	5,54	61,30	2,88	30,02	0,19	5,60	3,93	22,16
	80 /80 /130		62,73	0,35	32,65	0,26	4,01	4,52	19,23
	100 /80 /100		66,01	4,31	24,90	0,20	4,58	5,77	25,88
	100 /80 /130		64,62	3,76	26,61	0,39	4,63	5,88	24,57
Sodium lignin sulphonate Granules									
Before Acid	80	3,95	60,02	5,93	25,93	0,27	7,86	22,20	25,57
Treatment	100	8,99	59,81	5,34	27,36	0,18	7,31	20,20	24,64
After Acid Treatment	80 /80 /100	8,65	61,73	4,10	27,58	0,21	6,37	1,18	24,14
	80 /80 /130		63,36	3,48	28,33	0,15	4,67	0,32	23,75
	100 /80 /100		62,77	4,00	26,77	0,20	6,26	1,61	24,45
	100 /80 /130		62,95	4,66	25,94	0,20	6,25	4,84	25,30
Kraft lignin Granules									
Before Acid Treatment	100	10,20	66,42	6,42	19,62	0,20	7,35	44,37	28,52
After Acid Treatment	100 /70 /100 100 /70 /130	5,00	62,80 63,99	5,08 5,07	22,43 22,07	0,20 0,22	9,48 8,65	0,24 0,58	26,54 26,88

#### 4. Conclusions

The challenging / restricting issues in utilization of black liquors are the high moisture content, presence of harmful cooking chemicals, high reactivity in powder form, high emissions, etc. The utilization of black liquors is restricted mainly due to their high presence in cooking chemicals and sulphur content. The disadvantage in the handling and combustion of black liquors is the high amount of water content, reducing the calorific value due to evaporation losses. The calorific value of the lignin sludge can be increased by producing granules /briquettes respectively.

The granules /briquettes of black liquors produced with the help of spray-granulation and their acid treatments increased the calorific value from 15 MJ kg<sup>-1</sup> to 28 MJ kg<sup>-1</sup>. The acid treatment of granules resulted in removing the impurities, sustaining the particles as granules. The granules in the acid treatment have undergone a structural modification due to the melting and bridging of particles in the granule. The acid treatment of granules in a volume restrained device resulted in the development of briquettes. Briquettes have doubled the density (1351 kg m<sup>-3</sup>) compared to that of the granule density (670 kg m<sup>-3</sup>). The produced granules /briquettes were stable and hydrophobic. The granules or briquettes show a reduction in sulphur and ash contents from 13.5 to 3.9 % and 44.37 to 0.58 % after the acid treatment respectively, indicating the removal of impurities along with the stabilization of granule structure.

The production of granules /briquettes following an acid treatment is considered as more economical and ecological way of lignin sludge treatment due to their (i) increased filtration efficiency, (ii) reduction in acid requirement compared to traditional flocculation systems, (iii) regaining its original insoluble characteristic, (iv) increase in calorific value, (v) reduction of impurities and (vi) reduced handling and maintenance costs. This process can be easily implemented in the existing paper and pulp industries without major modifications, making the process more economical, ecological and environmental friendly.

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