Intensification of alkaline delignification of sugarcane bagasse using ultrasound assisted approach

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ABSTRACT

Ultrasound-assisted approach has been investigated for delignification so as to develop green and sustainable technology. Combination of NaOH with ultrasound has been applied with detailed study into effect of various parameters such as time (operating range of 15–90 min), alkali concentration (0.25 M –2.5 M), solvent loading (1:15–1:30 w/v), temperature (50–90 °C), power (40–140 W) and duty cycle (40–70 %) at fixed frequency of 20 kHz. The optimized operating conditions established for the ultrasonic horn were 1 M as the NaOH concentration, 1 h as treatment time, 70°C as the operating temperature, 1:20 as the biomass loading ratio, 100 W as the ultrasonic power and 70% duty cycle yielding 67.30% as the delignification extent. Comparative study performed using conventional and ultrasonic bath assisted alkaline treatment revealed lower delignification as 48.09% and 61.55% respectively. The biomass samples were characterized by SEM, XRD, FTIR and BET techniques to establish the role of ultrasound during the treatment. The morphological changes based on the ultrasound treatment demonstrated by SEM were favorable for enhanced delignification and also the crystallinity index was more in the case of ultrasound treated material than that obtained by conventional method. Specific surface area and pore size determinations based on BET analysis also confirmed beneficial role of ultrasound. The overall results clearly demonstrated the intensification obtained due to the use of ultrasonic reactors.

1. Introduction

The lignocellulosic biomass contains up to 30 percent of lignin which performs the vital role of binding hemicellulose and cellulose [1]. The removal of lignin from lignocellulosic biomass is one of the challenging part because lignin is a complex phenolic polymer [2]. Despite the challenge, delignification is necessary as it hinders the processing of biomass to any value added chemical [3]. For example, lower sugar yields are obtained by subjecting biomass directly to saccharification process whereas delignification step improves the accessibility of cellulose to the medium giving enhanced sugar production [4]. Pretreatments of lignocellulosic material can be of different types such as steam explosion, dilute acid hydrolysis, alkaline treatment, and wet oxidation [5]. Pretreatment processes can improve the digestibility of lignocellulosic biomass as pretreatment removes lignin and hemicelluloses from lignocellulosic materials [6]. It can also can improve the hydrolysis efficiency of various lignocellulosic materials as well as give higher conversion of the cellulose [7,8]. Pretreatment commonly gives higher sugar and also prevents the growth of inhibitory products during the subsequent hydrolysis and fermentation processes. Alkaline pretreatment plays more vital role in the delignification than the diluted acid and it is also possible to recover and recycle alkaline reagents, potentially reducing costs associated with pretreatment [9]. Acid pretreatment also causes higher corrosion therefore making it unsuitable for the scale up [10] and also the formation of large amount of fermentation inhibitors such as furfural and HMF reduces the efficiency of further steps. One of the major problems with alkaline delignification is the slowness of the process and limitations on using much higher alkali strength or the required treatment times. For example, Sun and Coworkers [11] reported the optimal conditions as 1.5% sodium hydroxide applied for 144 h at 20 °C, that resulted in 60% delignification. It was also reported that using higher temperature or pressure was not advantages mostly due to the higher energy input and higher capital/operating cost [12]. In the recent years, ultrasound based pretreatment is also considered efficient for the removal of lignin from the biomass. Ultrasound along with alkaline pretreatment has many advantages including less pretreatment time and alkaline concentration requirement as well as higher reducing sugar yield in the subsequent hydrolysis stages. Considering this
analysis, the present study conjugates alkaline assisted treatment with ultrasound. The ultrasonic treatment of aqueous media produces cavitation, which generates conditions of high temperature, pressure and intense shear forces. Ultrasound irradiation causes hemolysis of lignin–carbohydrate bonds releasing lignin [13]. The combination of ultrasound and alkali treatment can give synergetic effect leading to higher removal of lignin, and this leads to more reducing sugars or in general higher yields of other value added products such as levulinic acid or ethanol depending on the subsequent processing. Ultrasound assisted process can hence be a successful process intensification approach helping to reduce the drawbacks of conventional processing [14].

The focus of the current work is on the use of sugarcane bagasse as sustainable biomass for the delignification processing. Sugarcane bagasse, being a widely available agricultural residue, especially in India, was chosen as representative source of waste lignocellulose [15]. Sugarcane bagasse has low ash content with high cellulose and hemicellulose contents than the paddy straw, rice husk, wheat straw [16]. The general composition of sugarcane bagasse is cellulose as 40–43%, hemicellulose as 21–25%, lignin as 15–21% and other extractives as 4–6% [17,18]. The sugarcane bagasse is currently used for burning in boiler and domestic purpose but can be harnessed as a value added resource for the different chemical products provided suitable green processing methods are developed. Considering this analysis, current work was focused on developing improved method for delignification of sugarcane bagasse in the presence of ultrasound. There have been some studies reporting the use of ultrasound for alkaline delignification. For example, Velmurugan et al. [5] reported 92% lignin removal from sugarcane bagasse using ultrasound assisted alkaline pretreatment based on simple probe type configuration operating at 400 W power, 100% duty cycle and fixed 24 kHz frequency using 100 mL Erlenmeyer flask as a reactor operated at 70°C as the temperature and treatment time of 50 min. The analysis revealed that only fixed ultrasonic configuration was used whereas the differences in the cavitation activity in different ultrasonic configurations can lead to different delignification extents. In addition the earlier works related to sugarcane bagasse did not focus on analyzing the structural changes in the processed bagasse with an objective of elucidating the role of ultrasound. Considering this analysis, the present work was directed into detailed optimization study for the effect of operating conditions followed by comparison of two different ultrasonic reactors as ultrasonic horn and ultrasonic bath and also with the conventional method as well as establishing the surface morphology and crystallinity of the processed samples. The work also presents analysis of the processing cost required for the delignification. Overall, the main aim of the present study is to establish the best conditions of sonication time, alkali concentration, biomass loading, temperature, sonication power, and duty cycle to maximize the efficiency of ultrasound-assisted alkaline pretreatment in terms of maximum delignification and comparing the ultrasonic horn with ultrasonic bath in terms of delignification extent and cost of treatment.

2. Materials and methodology

2.1. Materials

Sugarcane bagasse was procured from Warana Sugar Industry, Kolhapur, Maharashtra. Collected sugarcane bagasse was air-dried for one day followed by oven-drying for one night and then grounded and screened to 0.5 mm size screen. The raw material lignin composition was found to be 17.33% as per the standard method described by NREL method [19]. The overall composition of the obtained sugarcane bagasse as established in the analysis has been mentioned in Table 1. Total carbohydrate content includes the cellulose and hemicellulose. The other used chemicals in the work as Sodium hydroxide (NaOH) and sulfuric acid (98% purity) (AR grade) were purchased from Thomas Baker Pvt. Ltd, India.

2.2. Experimental methodology

A specially designed 100 mL three neck round bottom glass reactor was used for the delignification experiments, with a fixed working volume as 60 mL. The use of round bottom flask helps to eliminate the formation of dead zones commonly seen in flat bed vessels [20]. For the ultrasound assisted experiments based on direct irradiation, ultrasonic horn used operate at a fixed frequency of 20 kHz with 1.2 cm as horn tip diameter and 100 W as the power dissipation. The schematic representation of the experimental setup is given in Fig. 1.

Typically in the experiment, a uniform suspension of known quantity

![Experimental setup for alkaline pretreatment using a) ultrasonic horn b) ultrasonic bath c) Conventional method.](image-url)
of biomass in deionized water was taken in the reactor before addition of known quantity of sodium hydroxide solution and switching on the sonication for the desired time of treatment. The ultrasonic horn was dipped about 0.5 cm deep into the reaction mixture taken in the round bottom reactor [21]. The reaction temperature was maintained using a water bath. During the treatment, the samples were collected at the end of experiments (each experiment was performed independently for the specified time and under the required operating conditions so that power dissipated per unit volume remains constant for all experiments), neutralized using water wash with deionized water and filtered using the Maslin cloth. A square shaped white Maslin cloth with double-deck cotton cloth material and dimensions of 50 cm by 50 cm was used in the study. For the filtration, using Maslin cloth has advantage as it requires less time, and also less amount of water with no losses of particles compared to the vacuum filtration. The obtained filtrate color was black as shown in Fig. 2(a) attributed mainly to lignin, similar to that reported by Zhang et al. [22]. The filtered sample residue was oven dried at 60°C overnight. The neutralized and dried sugarcane bagasse sample appearance was white in color as shown in Fig. 2(b) elucidating lignin removal and that delignified solid sample mainly contained cellulose and hemicellulose. The various parameters investigated in the work included time (15–90 min), alkali concentration (0.5–3 M), biomass:

400 RPM speed was applied. In the case of ultrasonic bath, pitched blade impeller with 6 blades and diameter of the impeller as 2 cm was used to have uniform mixing in the reactor.

2.3. Analysis methods

2.3.1. Analysis of lignin.

NREL method [19] was used for the lignin analysis. During the analysis, 300 mg of dried sample was mixed with 72 % H₂SO₄ having density 1.64 g/mL in the ratio of 1:10 and stirred for a period of 1 h at 30°C. Subsequently the mixture was diluted to 4% H₂SO₄ by adding 84 mL of DI water. The resultant solution with volume as 87 mL was kept in autoclave at 121°C temperature for 1 h, and after cooling the solution to ambient conditions, it was filtered and the residue washed 2–3 times using 150 mL DI water. The filtrate contains acid soluble lignin and residue contains acid insoluble lignin. The acid insoluble lignin (residue) was kept in oven at 105°C until we get the constant weight and then at 575°C ± 25°C for 18 h. The acid soluble lignin (in the filtrate) was analyzed using UV-Spectrophotometer at 240 nm with 4 % H₂SO₄ used as a reference.

The formulae used for calculation of lignin content in the analysis are:

Acid insoluble lignin(%) = \( \frac{(\text{sample weight}) \text{ at } 105^\circ C - (\text{sample weight}) \text{ at } 575^\circ C}{\text{ODW}} \times 100 \)

Acid soluble Lignin (%) = \( \frac{UVabs \times \text{Total Volume} \times \text{Dilution}}{\epsilon \times \text{ODW Sample} \times \text{Pathlength}} \times 100 \)

Where, \( \epsilon \) = Absorptivity of biomass at 240 nm wavelength; ODW = Oven dry weight; Total Lignin (%) = Acid insoluble lignin (%) + Acid soluble Lignin (%); Delignification extent (%) = \( \left( \frac{W_f - W_i}{W_i} \right) \times 100 \),

Where, \( W_f \) = weight of untreated sugarcane bagasse in g and \( W_i \) = weight of treated sugarcane bagasse in g.

2.3.2. Carbohydrate analysis

Carbohydrate analysis was also performed using NREL method [19]. The obtained filtrate as per the process described in section 2.3.1 was...
neutralized using CaCO$_3$ by adding 0.6 g of CaCO$_3$ in 10 mL of filtrate (sample) with continuous stirring. The neutralized sample was analysed using UHPLC (Thermofisher) equipped with RI detector and Sodex SH 1821 column operated with 5 mM H$_2$SO$_4$ as mobile phase at flow rate 1 mL/min. The column temperature was kept at 60 °C and detector temperature kept at 30 °C.

2.3.3. Fat content analysis

Soxlet method was used for quantification of fat content in sample with hexane used as extraction solvent. Weighed sugarcane bagasse sample was taken into the thimble and extraction process using hexane continued for 5 h. The equation used for the fat analysis is:

\[
\text{Fat content} \% = \frac{\text{Weight of flask with oil} - \text{weight of empty flask}}{\text{weight of sugarcane bagasse sample}} \times 100
\]

2.3.4. Reproducibility of the obtained data and statistical analysis

Multiple experiments were performed to check the reproducibility of the experimental data and it was found that percentage error was within ± 2% of the reported average value in the figures or used in the discussion. ANOVA test was also used to check the statistical significance of the obtained data and it was found that the p-values were always less than 0.05 indicating the proper variation in the trends and reproducibility of the data.

2.3.5. Analyzing the effects of ultrasound on biomass

2.3.5.1. FTIR. FTIR analysis was carried out using ATR-FTIR Shimadzu IR Prestige-21 Kyoto Japan instrument, coupled with the Specac Golden Gate GS10500 ATR assembly. Air was kept as background. FTIR spectroscopy analysis was performed to study the changes in chemical structure of biomass obtained using various pretreatment methods

2.3.5.2. XRD. X-ray diffractometer D8 Advance Bruker was used with an operating condition of 2θ range of 5-80° at 0.02 step interval with step time of 0.4 s [23]. XRD is useful to know the proportions of amorphous and crystalline cellulose component in the biomass and helps to explore the nature of molecular structure as well as the change in cellulose crystallinity for different applied pretreatment methods [24]. Crystallinity index (CI) estimates the relative amount of crystalline material in cellulose material [25] which was quantified using the following equation:

\[
CI(\%) = \frac{I_{002} - I_{AM}}{I_{002}} \times 100 - (1), \text{ Where, } I_{002} - \text{Maximum intensity at}
\]

3. Results and discussion

3.1. Optimization of process parameters

3.1.1. Effect of treatment time

Fig. 3 shows the obtained results for changes in the delignification of sugarcane bagasse at different treatment times (over the range of 15–90 min with each experiment performed independently for the required time duration) with the experiments performed at fixed frequency of 20 kHz, 70 % as duty cycle, 100 ± 5 W as the ultrasonic power, 70 ± 3 °C as the temperature, 1 M as the alkali concentration and 1: 30 (w/v) solid to solvent loading. It was observed that the delignification increased from 26.66 % to 57.34 % when the time was increased from 15 min to 60 min and subsequently only marginal variation was seen for further increase in treatment time to 75 and 90 min. Initially increment in the extent of delignification is due to the enhanced exposure to the effects of cavitation over the extended treatment times. The collapse of cavitating bubbles generates high energy and turbulence which helps in lignin breakage and enhanced activity of the alkali for lignin removal. Cavitation effects also increases the rate mass transfer [26] and hence the extent of delignification increases. With a higher treatment time, the solvent becomes saturated with lignin and hence there is no further lignin removal from the sugarcane bagasse. Balachandran et al. [27] reported similar trends for ginger processing to extract gingerol where the application of ultrasound up to 200 min resulted in linear increase in the concentration of gingerol to maximum of 0.1 kg/m$^3$ and after that further increase to 400 min resulted in no further increase in concentration. Gomes et al. [28] studied delignification of brewer’s spent grain...
using varied NaOH concentrations of 4%, 6% and 8% and varying time and 100 \( \times \) solid to liquid ratio, 2.0 W/mL power density, 20 kHz frequency, 60 min as the treatment time, 1 M as the sodium hydroxide concentration over the range of 0.25 M to 2.5 M with 1.5 N demonstrated as an optimized concentration as 0.5 N to 2.5 N with 1.5 N demonstrated as an optimized concentration.

### 3.1.2. Effect of alkali concentration

Effect of alkali concentration over the range of 0.25 M to 2.5 M on the delignification was studied at 60 min as the fixed treatment time, frequency of 20 kHz, 70 °C as the duty cycle, 100 ± 5 W as the power, 70 ± 3 °C as the temperature and 1:30 as solid to solvent loading. As per the reported results in Fig. 4, it was seen that delignification increased from 33.2% to 70% with a change in concentration from 0.25 M to 1 M. Use of sodium hydroxide solution in combination with ultrasound helps to disrupt the bond between C–H based on generation and subsequent attack of OH radicals. Higher strength of sodium hydroxide further helps in enhancing the radical formation and breakdown of the structure of lignin [11]. The combination of ultrasound with alkali enhances the rate of disruption of lignin due to the cavitational effects which results in higher surface area based on lowering of the particle size and also better utilization of the alkali. When the concentration of alkali increased further beyond the optimum it may be possible that there was no further increase in the mass transfer between biomass particle and alkali solvent as the reaction mixture attained saturation [29]. The effect of alkali concentration is seen dominant till 1 M as the alkali concentration with maximum extent of delignification as 68.9% and further increase in the concentration to 2.5 M resulted in marginally lower extent of delignification attributed to excess alkali that is not able to effectively react with lignin based on reaching of equilibrium [30]. Similar trend was also elucidated by Saratale et al. [31] who studied the effect of sodium hydroxide concentration over the range of 0.5% to 3% combined with the ultrasound for delignification of wheat waste. It was demonstrated that there was no significant difference in the extent of delignification seen for alkaline strength between 2% and 3%. Optimum alkaline concentration of 2% resulted in 70% as the extent of delignification at 1:20 solid to liquid ratio, 2.0 W/mL power density, 20 kHz frequency, 60 min time and 100 °C temperature. Patil et al. [32] also reported similar trend of delignification of saw dust for the study over range of alkali concentration as 0.5 N to 2.5 N with 1.5 N demonstrated as an optimized alkali concentration after which there was no significant difference in the delignification. It is important to note that though the trends are similar, the exact value of optimum alkali concentration is different elucidating the importance of the presented work.

### 3.1.3. Effect of solid (Sugarcane Bagasse) to solvent loading

Sugarcane bagasse (solid) to alkali (1 M sodium hydroxide solution) ratio was varied from 1:15 (w/v) to 1:30 (w/v) at fixed frequency of 20 kHz, 60 min as the treatment time, 1 M as the sodium hydroxide concentration, 70 °C duty cycle, 100 ± 5 W as power and 70 ± 3 °C temperature. Fig. 5 shows the obtained results where it is seen that the delignification increases up to ratio of 1:20 (w/v) after which it becomes constant at 1:25 (w/v) and 1:30 (w/v). Actual delignification was observed as 55.56%, 60.9%, 60% and 59.2% at various ratios as 1:15, 1:20, 1:25 and 1:30 (w/v). Delignification increased with a change in ratio from 1:15 to 1:20 (w/v) due to enhanced mass transfer base on the more amount of solvent and also higher cavitational activity due to higher presence of the solvent in the system [33]. Role of higher cavitational activity is again to improve the mass transfer rate and reduce the particle size which gives higher removal of lignin [34]. However increase in the amount of solvent beyond 1:20 ratio did not give significant difference compared to 1:20 (w/v) because the enhanced effects of mass transfer and higher cavitational activity reach a saturation and hence no changes in the driving force are seen [35,26,36]. Xu et al. [37] studied the effect of ratio of the ethanol: Limonium sinuatum flower over the range of 10:1 to 70:1 mL/g and they also found similar trend attributed to mechanism that the increment in the ratio of solvent to solid till an optimum leads to increment in the contact area between material and solvent and enhances the solubility of antioxidant components within the plants cells. It was also reported in their study that when the ratio of solvent to solid reached to 40:1 (mL/g), the dissolution process reached its equilibrium and thus solvent to solid ratio of 40:1 was considered as optimum. It is interesting to see that the optimum ratio is indeed dependent on the type of biomass and the system used for study elucidating the importance of the work.

### 3.1.4. Effect of temperature

Effect of temperature on delignification was studied by using different operating temperatures as 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C. It was found that with an increase in temperature from 50 °C to 70 °C, the delignification increases though subsequently it was observed that the delignification decreases as per the trend shown in Fig. 6. Quantitatively, the delignification increased from 55.44% to 66.64% with a change in temperature from 50 °C to 70 °C mainly attributed to favored kinetics at higher temperatures. Beyond 70 °C, delignification reduced significantly to 46.66% and 13.34% at temperatures of 80 °C and 90 °C respectively due to the significant reduction in the cavitational effects based on the cushioned collapse of the vaporous cavities. The cavitational and thermal effects play an important role in the ultrasound assisted processing [38] and hence optimum temperature is seen. Due to the dominant thermal effects, deformation in the lignin structure also occurs which leads to increase in the mass transfer rate and hence
delignification increases up to temperature of 70 °C. At much higher temperatures, reduction in cavitation effects is dominant implying that less amount of energy is available and hence delignification decreases [39]. Similar trend was reported by Kim and Holtzapple [40] who studied effect of temperature from 25 to 55 °C for the delignification of corn stover with the optimum temperature being reported as 45 °C. Subbedar et al. [41] reported similar trend for the study of delignification of waste newspaper using ultrasound where it was seen that extent of delignification increases from 16 % to 44 % with a change in temperature from 313 to 373 K with optimum temperature being established as 353K, beyond which the increase in the temperature has marginal effect on the delignification. It is interesting to note that optimum temperature is different for various biomass making it important to study the effect of temperature for sugarcane bagasse for the specific ultrasonic reactor configuration.

### 3.1.5. Effect of power

Effect of power on delignification of sugarcane bagasse was studied using different power dissipations as 40 W, 60 W, 80 W, 100 W, 120 W and 140 W. It was observed that the delignification increases from 40 W to 100 W, and then decreases for further increase to 120 W and 140 W as per the data shown in Fig. 7. Increasing the power from 40 W to 100 W increases the extent of delignification from 48.86 % to 66.67 % whereas subsequently delignification decreases to 57.74% and 56.67 % for higher power as 120 W and 140 W respectively. With an increase in the power till an optimum, the cavitation activity is higher driving the higher extent of delignification based on the effects such as enhanced penetration of the solvent or the higher rates of mass transfer [26]. Beyond the optimum power, increase in actual power dissipation leads to too much cavitation because of huge amplitude of ultrasound through the solvent medium which leads to cushioned collapse of the cavities giving lower intensity of cavitation and hence the extent of delignification also reduces [42]. Similar results were also reported by Olughu et al. [13] at 180 W power reported as the optimum with 21 % as the extent of delignification. Further increase in power to 240 W reduced the extent of delignification to only 13% under conditions of 1:25 as the solid to solvent ratio and 50 min as time elucidating 180 W as optimum power.

### 3.1.6. Effect of duty cycle

Effect of duty cycle on delignification of sugarcane bagasse was studied using different duty cycles as 40%, 50%, 60% and 70% within the total cycle time of 10 s. Duty cycle is adjusted by changing the ON and OFF time of sonicator and operation in pulse mode has a positive effect on the operation of the reactor as continuous mode operation can lead to erosion of tip. It was observed that delignification increases as duty cycle increases as per the trends shown in Fig. 8. Quantitatively 63.6%, 65.46%, 68.87% and 70.47% as delignification was seen to occur at 40%, 50%, 60% and 70% duty cycle respectively. Based on the obtained results, it can be said that 70% duty cycle is considered as the best condition as operating at higher duty cycles beyond 70% was not feasible based on the overheating of horn and possible erosion effects. It is important to note that though higher duty cycle were not used in the current work, literature has confirmed the existence of the optimum duty cycle which is attributed to the coalescence effect based on too many cavitating bubbles being generated at much higher duty cycle. The formation of cavitating bubble clouds due to coalescence effect results in reduced intensity of cavitation collapse [43].

Similar trend was reported by Subbedar and Gogate [13] who observed that duty cycle till optimum increment causes increment in delignification with maximum delignification of 70.92 % elucidated at 70% duty cycle. Mohapatra et al. [44] also reported that increment in duty cycle and time resulted in higher yields only till an optimum condition of 50% duty cycle and 30 min as the time with maximum yield as 135.8 mg/g for denanath grass as the substrate.

### Table 2

Comparative study of ultrasonic horn approach, ultrasonic bath approach and conventional approach.

| Process                        | Extent of delignification (%) | Operating parameters conditions                        | Units of electric energy required per gram of delignification (kWh) | Process Cost for delignification per gram (Rs/g) |
|--------------------------------|-------------------------------|-------------------------------------------------------|---------------------------------------------------------------------|-----------------------------------------------|
| Ultrasonic horn                | 67.30                         | 1 h as Time, 70 °C as Temperature, 100 W as power, 70% as duty cycle, 1 M as alkali concentration, 1:20 as Solid to solvent ratio. | 0.622                                                               | 5.46 (0.073)*                                |
| Ultrasonic bath               | 61.55                         | 1 h as Time, 70 °C as Temperature, 100 W as power, 70% as duty cycle, 1 M as alkali concentration, 1:20 as Solid to solvent ratio. | 0.68                                                                | 6.2 (0.083)*                                |
| Only alkali (conventional)     | 48.09                         | 1 M as alkali concentration, 1 h as Time, 70 °C as temperature and 1:20 as Solid to solvent ratio.                      | 0.032                                                               | 0.28 (0.0038)*                               |

*in US dollars.
3.2. Comparison of different approaches for delignification

The optimized conditions established with detailed experiments in the ultrasonic horn as 1 M NaOH concentration, 1 h treatment time, 70°C temperature, 1:20 biomass loading ratio, 100 W power and 70% duty cycle resulted in 67.30% as delignification. At optimized treatment parameters, the experiments performed with conventional method (only alkali) and ultrasonic bath resulted into 61.55% and 48.09% of delignification respectively as per the data shown in Table 2. Ultrasound-assisted approach definitely gave higher delignification compared to conventional method and also delignification for ultrasonic horn was higher compared to bath. The main role of ultrasound in observed intensification was attributed to higher mixing or mass transfer due to the physical effects of cavitation [45,46] which helps in removing more amount of lignin compared to the conventional method. Use of ultrasound gives more penetration of the applied alkali based on enhanced rate of mass transfer [47] leading to higher delignification. Application of ultrasonic horn is a direct mode of operation giving higher delignification compared with ultrasonic bath where indirect mode of operation is applied. Ultrasonic horn tip has direct contact with the surrounding particles of biomass and hence higher cavitation exposure, whereas in the case of ultrasonic bath, transducers are not in direct contact with the processed particles leading to lesser effects for intensification.

Energy and cost required for the ultrasonic horn assisted alkaline treatment approach, ultrasonic bath approach and only alkaline

Fig. 9. FTIR spectra for untreated and pretreated sugarcane biomass using different methods (Conditions of 1 h time, 1M alkali concentration, 70°C temperature, 1:20 w/v solvent loading, 100 W power, and 70% duty cycle) a) Conventional only alkali b) Ultrasonic horn with alkali c) Ultrasonic Bath with alkali d) Untreated (Raw material).

Fig. 10. XRD patterns for untreated and pretreated sugarcane biomass using different methods (Conditions of 1 h time, 1M alkali concentration, 70°C temperature, 1:20 w/v solvent loading, 100 W power, and 70% duty cycle) a) Untreated b) Conventional method c) Ultrasonic Bath d) Ultrasonic horn.
treatment approach was compared and the obtained data have been shown in the Table 2 with the details of calculations of the energy cost mentioned in the annexure I. Ultrasonic bath based approach resulted in higher energy cost per unit gram, which was 6.2 Rs/g as compared to ultrasonic horn with the cost as 5.2 Rs/g. For ultrasonic horn, higher extent of delignification has also been seen. It can be thus said that ultrasonic horn assisted alkaline approach of delignification of sugar-cane bagasse is efficient compared to ultrasonic bath assisted alkaline approach based on the extent of delignification achieved, energy consumption, and process cost.

Fig. 11. SEM images for untreated and pretreated sugarcane biomass using different methods (Conditions of 1 h time, 1M alkali concentration, 70°C temperature, 1:20 w/v solvent loading, 100 W power, and 70% duty cycle) a) Untreated b) Conventional method c) Ultrasonic Bath d) Ultrasonic horn.
Delignification Efficiency Comparison of present study with literature reports.

| Pretreatment Method | Lignocellulosic biomass | Optimized reaction Conditions | Delignification (%) |
|---------------------|-------------------------|--------------------------------|---------------------|
| Ultrasound + alkali | Sugarcane bagasse       | 400 W power, 24 kHz Frequency, 100% duty cycle, time 50 min, 70°C temperature, 1 M alkali concentration | 92                  |
| Only US             | switchgrass             | Power 180 W, Frequency 24 kHz, time 50 min, Solvent used as distilled water, 90% duty cycle | 21                  |
| Only Alkaline       | Sugarcane bagasse       | 1 N alkali concentration, 100°C temperature, 1 bar pressure, Time 45 min. | 58                  |
| US + Alkaline       | Groundnut shells        | 100 W power, 20 kHz frequency, 1 alkali concentration, 80% Duty cycle, 70 min time, 80°C temperature. | 80                  |
| US + Alkaline       | News paper              | 100 W power, 20 kHz frequency, 1 alkali concentration, 80% Duty cycle, 70 min time, 80°C temperature | 71.1                |
| US + Alkaline       | Palm kernel             | 100 W power, 20 kHz frequency, 1 alkali concentration, 80% Duty cycle, 70 min time, 80°C temperature | 89.5                |
| Ultrasound + Alkaline| Sugarcane bagasse       | 1 M alkali concentration, 70°C temperature, 100 W power, 20 kHz frequency, 70% duty cycle, 60 min time. | 67.3                |

3.3. Analyzing the effects of ultrasound on biomass

3.3.1. FTIR analysis

FTIR spectra of untreated and pretreated sugarcane bagasse using different methods such as ultrasonic horn, ultrasound bath and conventional approaches was recorded to analyze the changes in the functional groups. The broad absorption peak related to the stretching vibration of –OH functional group was seen at around 3400 cm⁻¹. A small band at 2919 cm⁻¹ was found in all pretreated samples attributed to the C-H vibration of the –CH₂ and CH₃ groups while C-H vibration of the –CH₂O group was seen at 2849 cm⁻¹ as shown in Fig. 9(b) [48]. The absorption bond at 1610 cm⁻¹ and 1537 cm⁻¹ shows the aromatic C=C vibrations whereas the absorption peak at 1033 cm⁻¹ is attributed to C-O vibrations [49]. It was observed that after pretreatment of sugarcane bagasse, the peak intensity of 1610 cm⁻¹ and 1537 cm⁻¹ reduced while at peak intensity increased at 3400 cm⁻¹ and 1033 cm⁻¹. Moreover, in the ultrasound assisted method, C-H vibration peak at 2919 cm⁻¹ reduced to a greater extent as compared to conventional method. It was thus inferred that ultrasound assisted alkaline pretreatment results in dominant changes as compared to the conventional method.

3.3.2. XRD analysis

The solid delignified sugarcane bagasse subjected to different pretreatment approaches involving ultrasonic horn, ultrasound bath and conventional approach as well as the untreated bagasse was also subjected to XRD analysis and the obtained results are shown in Fig. 10.

The CI was calculated by the equation 1 whereas the intensity graph was drawn using the origin 9.0 software over the 2θ range of 21.91°-22.04° and 15.91°-16.04°. For the 21.91°-22.04° range, the height peak was 0.02 whereas 15.91°-16.04° corresponded to the amorphous peak of 101. Observed CI of untreated sample, conventionally treated sample, sample treated using ultrasonic bath, and sample treated using ultrasonic horn were 36.48%, 46.59%, 52.21%, and 53.66% respectively. It was evident that CI increased after delignification and maximum CI was seen for the sample treated using ultrasonic horn. Lignin is amorphous in nature [13,50] and pretreatment leads to decrement in the amorphous nature and hence increment in nature of crystallinity. CI obtained with application of ultrasonic bath as well ultrasonic horn was higher than CI of conventionally treated material. Similar results were also reported Zhao et al. [51] with 53.3%, 58.5%, 67.9% and 68.2% as the observed CI for raw bagasse, alkali treated bagasse, alkali-PAA treated pulp and Kraft pulp respectively.

3.3.3. SEM analysis

The surface morphology of the untreated and ultrasound-assisted alkali pretreated samples was determined using SEM analysis. SEM analysis results for sugarcane bagasse exposed to various pretreatments such as ultrasonic horn (Fig. 11(d)), ultrasound bath (Fig. 11(c)), and only alkali method (Fig. 11(b)) are shown in Fig. 11. It can be seen from Fig. 11(a) that the untreated sugarcane bagasse shows compact nature with strong binding of the cell wall. After pretreatment using only alkali (conventional method), the structure just swells with weak binding of the cell wall. Treatment using ultrasonic bath in combination with alkali further opens the structures and loosens the cell wall also leading to increased surface area and pore volume as shown in images in Fig. 11 (c1) and (c2). The cell matrix completely breaks down and entire structure appears as separate fibers because of much higher effects of ultrasonic horn combination with alkali treatment as shown in images in Fig. 11 (d1), (d2). For the treatment of ultrasonic bath combination with alkali, similar images were reported by Donovan et al. [52] for the treatment of the grass used as sustainable biomass. It was also reported that ultrasound assisted alkali treatment shows breakdown of the cell matrix because of cavitational effects also yielding the reduction in the particle size and increased surface area.

3.3.4. BET analysis

The surface area and pore size of sugarcane bagasse before and after treatment was measured using BET analysis. The results obtained for raw sample and alkali pretreated samples (using ultrasonic horn, ultrasonic bath and conventional method) are shown in Table 3. It was observed that for untreated raw material, specific surface area was 52.914 m²/g which increased after treatment to 77.73 m²/g (ultrasonic horn), 73.63 m²/g (ultrasonic bath) and 58.89 m²/g (conventional method). The median pore diameter (based on volume) of the samples was found as 4.852 nm for the untreated raw material which changed marginally to 4.549 nm (ultrasonic horn), 4.809 nm (sonication bath) and 4.812 nm (conventional method) after the treatment. Similarly the median pore diameters (based on surface area) were 3.16 nm for the untreated raw material, 3.01 nm for the treated material using ultrasonic horn, 3.09 nm for the treated material using sonication bath, and 3.12 nm for the treated material using conventional method. It was thus observed that the pore size distribution remains similar for the untreated and pretreated samples. The pore size (based on volume and area) is in the range of 2–50 nm meaning that it is mesopore surface as per the IUPAC definitions [53]. Importantly there was a favorable change in the nature of the pure cellulose during the treatment.
The pretreatment results in increased specific surface area of sugarcane bagasse compared to the ultrasonic bath. Under same optimized treatment conditions of 1 M NaOH, 70°C temperature, 100 W power, 20 kHz frequency, 70% duty cycle and 60 min was found to be 68%. Thus, overall work presents positive effects of ultrasound in combination with the alkaline treatment and also it was elucidated that maximum amount of lignin was removed at lower pretreatment time and at less treatment cost using ultrasonic horn.

4. Conclusions

Sonication has been explored for enhancing delignification of sugarcane bagasse also presenting the comparison of the two reactor configurations as ultrasonic horn and ultrasonic bath. It was observed that efficacy of ultrasonic horn is superior compared to ultrasonic bath. Effective delignification resulted in enhanced surface area as well as the crystallinity of the sample which can be beneficial in the subsequent processing for the value added products. Detailed optimization study enabled establishing the optimized reaction conditions as 1 M NaOH concentration, 1 h time, 70°C temperature, 1:20 biomass loading ratio, 100 W power and 70% duty cycle, which resulted in process intensification of delignification with actual value as 67.30% for the ultrasonic horn and 61.55% for the ultrasonic bath. Under same optimized treatment parameters, conventional method resulted in only 48.09% of delignification clearly establishing the benefits due to the use of ultrasound.

The cost analysis of ultrasonic horn and ultrasonic bath pretreatment demonstrated that ultrasonic horn pretreatment was more economical than ultrasonic bath. Overall, an effective delignification methodology was presented in the work also elucidating the higher efficacy of ultrasonic horn for process intensification.

CRediT authorship contribution statement

Madhuri M. Kininge: Methodology, Writing – original draft. Parag R. Gogate: Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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