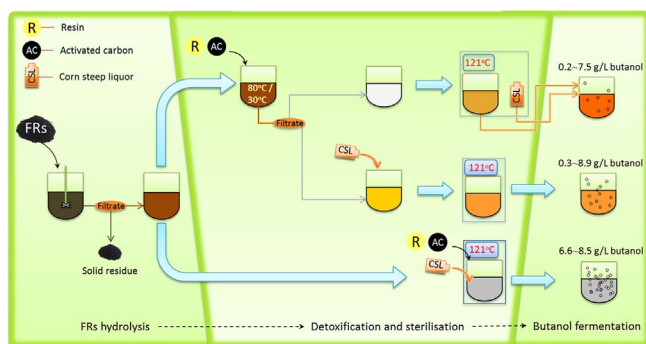# Detoxification of furfural residues hydrolysate for butanol fermentation by *Clostridium saccharobutylicum* DSM 13864

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The toxicity of furfural residues (FRs) hydrolysate is a major obstacle in its application. This work focused on the detoxification of FRs hydrolysate and its application in butanol fermentation. Combination of activated carbon and resin 717 was appropriate for the detoxification of hydrolysate. Mixed sterilization of FRs hydrolysate and corn steep liquor (CSL) was better than the separate ones, since proteins in CSL could adsorb and remove toxic components during sterilization. The results further confirmed that simultaneous sterilization of activated carbon + resin and fermentation medium was more efficient for detoxification and butanol production, in which 76.4% of phenolic compounds and 99.3% of Maillard reaction products were removed, 8.48 g/L butanol and 12.61 g/L total solvent were obtained. This study provides feasible and economic approaches for the detoxification of FRs hydrolysate and its application in butanol production.

1. Introduction

Economic and environmental concerns have stimulated worldwide interest in the utilization of renewable biomass, such as bio-butanol, bioethanol, furfural and derivative of furfural (Baral et al., 2014; He et al., 2017a,b,c,d; Procentese et al., 2017). As a promising alternative energy source, butanol could be produced from lignocellulosic materials, especially low-cost waste materials (Baral et al., 2014; Ni et al.,

2013; Procentese et al., 2017; Trindade & dos Santos, 2017).

Furfural produced from corn cobs is one of the largest agricultural industries in China (Mamman et al., 2008). During the entire furfural production process, furfural residues (FRs) is one major waste by-product from corncobs after heat and acidic treatments (Yu et al., 2013). It has been estimated that about 2.3 million tons of FRs is generated annually in China (Bu et al., 2011). Commonly, fresh FRs usually contain high moisture content (above 50%), rich carbon and

other valuable nutrients. For instance, it typically contains 5.0–6.0 g/kg of N, 360 g/kg of humic acids, and more than 980 g/kg of organic matter. At present, FRs are mainly used for the preparation of organic fertilizer, soil conditioner, culture media to cultivate edible fungi, activated carbon, biofuels (Zheng et al., 2016). Meanwhile, FRs also contain abundant cellulose (45%) (Bu et al., 2012), which could be potential biomass after pretreatments. Utilization of FRs for biofuel production would be significant for waste regeneration and environmental protection. There is also high content of unfermentable lignin in FRs, which may also inhibit enzymatic hydrolysis (Ma et al., 2014; Wang et al., 2013). Therefore, biomass delignification is a critical approach to increase the available cellulose for butanol production. Various chemical and physicochemical delignification methods have been reported, such as NaOH, NaClO, NaOH/H$_2$O$_2$, NaOH/ultrasound, NaOH/microwave, etc (Ji et al., 2016; Lee et al., 2009; Lin et al., 2014; Ma et al., 2014).

There have been several reports on the utilization of FRs for bioethanol production (Ji et al., 2016; Wang et al., 2013), whereas none has reported the bio-butanol fermentation from FRs. In preliminary study, untreated FRs hydrolysate could not be directly used for butanol production due to its inhibitory effect on cell growth. These inhibitors may contain: weak acids, furan derivatives, and phenolic compounds (Oliva et al., 2006; Palmqvist & Hahn-Hagerdal, 2000), as well as dark-brown polymeric compounds (melanoidins) produced during Maillard reaction (Wijewickreme et al., 1998). Detoxification of FRs hydrolysate was therefore investigated. Activated carbon and resin 717 were chosen as detoxification reagents in this work, and the detoxified FRs hydrolysate was successfully applied in butanol fermentation (Fig. 1).

2. Materials and methods

2.1. Raw materials, strains and enzymes

Furfural residues (FRs) was kindly provided by Heze Yikang Chemical Technology Co., Ltd (Shandong Province, China). FRs, with an initial pH 2.0, was dried at 70 °C for 8 h and stored in a closed container.

Activated carbon and strongly basic anion exchange resin 717 were purchased from Sinopharm Chemical Reagent Co., Ltd. Resin 717 was pretreated according to the instructions and dried at 60 °C in an oven for 12 h before use.

Clostridium saccharobutylicum DSM 13864 was purchased from DSMZ and stored as spores in Reinforced Clostridial Medium (10.0 g/L meat extracts beef, 3.0 g/L yeast extract, 1.0 g/L soluble starch, 5.0 g/L, glucose, 3.0 g/L sodium chloride, 10.0 g/L peptone, 0.5 g/L cysteine hydrochloride, 3.0 g/L sodium acetate) at room temperature before

inoculation.

ACCELLERASE® 1500 cellulase was a generous gift from Genencor (Wuxi) Bio-Products Co.

2.2. Pretreatment of FRs

FRs was rinsed with water to pH > 5 to remove acids and inhibitors, such as 5-HMF and furfural (Cantarella et al., 2004). Then, 4 M NaOH was added to adjust pH to 11. After soaked in water at room temperature for 12 h, the FR slurry was rinsed with water to pH < 8.5, and then adjust to pH 7 with 4 M NaOH. The FRs filtered through 250 meshes filter cloth was collected and dried at 80 °C for 12 h for further usage.

Three different pretreatment methods were evaluated as follows: (1) 5 g NaOH-pretreated FRs. (2) 5 g NaOH-pretreated FRs + 50 ml of 0.6% H$_2$O$_2$ solution, then incubated at 80 °C for 3 h (Yu et al., 2013). After 3 h, the system was rapidly cooled with tap-water, and the solids were removed and washed with distilled water. (3) 5 g NaOH-pretreated FRs + 50 ml solution of 2 g/L NaClO, then incubated for 30 min, at pH 8 (Lee et al., 2009). After 30 min, the solids were removed and washed with distilled water.

2.3. Enzymatic hydrolysis of FRs

The pretreated FRs (9.0–13.0 g) were soaked in 100 ml of citrate buffer (50 mM, pH 4.8) in 250-ml conical flasks with plugs. Then, 10–50 FPU/g FRs cellulase was added to the mixture. The mixture was further incubated in a water bath at 50 °C and 150 rpm for 48 h.

Samples were taken at 0, 2, 4, 6, 10, 14, 26, 36, 48 h, and then subjected to centrifugation at 12,000 rpm for 5 min. The glucose concentration was determined using HPLC analysis as described in Section 2.6. The glucose yield was calculated by dividing the actual glucose obtained in hydrolysis process by theoretical glucose converted from cellulose.

2.4. Detoxification of FRs hydrolysate

2.4.1. Resin detoxification
Resin (0.2–1.5 g) was added into a 150-ml shake flask, then 50 ml of FRs hydrolysate was transferred to the same flask, corresponding to a resin concentration of 4–30 g/L. The flask was capped and incubated at 30 °C and 120 rpm for 8 h for detoxification.

2.4.2. Activated carbon detoxification
Activated carbon (0.05–1 g) was added into a 150-ml shake flask with 50 ml of FRs hydrolysate. The flask was capped and incubated at
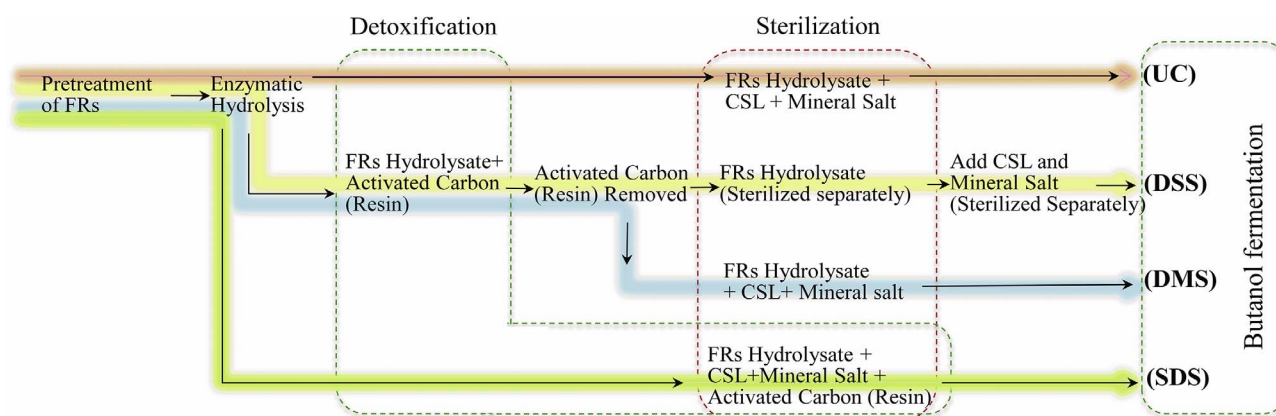

Fig. 1. Scheme of the experimental procedures. UC represents fermentation from un-detoxified FRs hydrolysate; DSS represents fermentation from FRs hydrolysate pretreated by detoxification with separate sterilization; DMS represents fermentation from FRs hydrolysate pretreated by detoxification with mixed sterilization; SDS represents fermentation from FRs hydrolysate pretreated by simultaneous detoxification and sterilization.

80 °C and 150 rpm for 1 h for detoxification.

Control experiments were performed without the addition of activated carbon or resin.

Samples were taken after the detoxification to measure $OD_{280 \, nm}$ and $OD_{420 \, nm}$. Detoxified FRs hydrolysates were used for butanol fermentation.

2.5. Butanol fermentation

Butanol fermentation medium was composed of 45 g/L sugar, 10 g/L corn steep liquor (CSL), 4 g/L $CaCO_3$, 2 g/L $(NH_4)_2SO_4$, 0.5 g/L K_2HPO_4, 0.01 g/L $MnSO_4·H_2O$ (Ding et al., 2016). *Clostridium saccharobutylicum* DSM 13864 cultured at 37 °C for 16–18 h was used as seed culture for butanol fermentation at an inoculum size of 10% (v/v). The butanol fermentation was conducted in 3 different manners as follows.

2.5.1. Undetoxified control (UC) and detoxification with separate sterilization (DSS)

About 40 ml of undetoxified and detoxified (by resin or/and activated carbon) FRs hydrolysate was adjusted to pH 6.5 with 4 M NaOH, and then transferred into a 150-ml anaerobic bottle for sterilization, respectively. Mixture of CSL and mineral salts [$CaCO_3$, $(NH_4)_2SO_4$, K_2HPO_4, $MnSO_4·H_2O$] were adjusted to pH 6.5 and sterilized. The sterilized CSL and salts mixture was then transferred into sterilized undetoxified or detoxified FRs hydrolysate to prepare the fermentation medium as described above, and then inoculated with 10% (v/v) seed culture for butanol fermentation.

2.5.2. Detoxification with mixed sterilization (DMS)

About 40 ml of undetoxified and detoxified (by resin or/and activated carbon) FRs hydrolysate was mixed with CSL and mineral salts [$CaCO_3$, $(NH_4)_2SO_4$, K_2HPO_4, $MnSO_4·H_2O$] and adjusted to pH 6.5 with 4 M NaOH in a 150-ml anaerobic bottle for sterilization. Then, inoculated with 10% (v/v) seed culture for butanol fermentation.

2.5.3. Simultaneous detoxification and sterilization (SDS)

About 40 ml of un-detoxified FRs hydrolysate was mixed with resin or/and activated carbon, CSL and mineral salts [$CaCO_3$, $(NH_4)_2SO_4$, K_2HPO_4, $MnSO_4·H_2O$] and adjusted to pH 6.5 with 4 M NaOH in a 150-ml anaerobic bottle for sterilization. Then, inoculated with 10% (v/v) seed culture for butanol fermentation.

2.6. Analytical methods

The components of the cellulose, hemicellulose, lignin and ash in raw and pretreated FRs were analyzed using NREL Laboratory Analytical Procedure (LAP) – Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter et al., 2008).

The FRs hydrolysate was filtered through qualitative filter paper and diluted for 40 folds. The UV absorption at 280 nm of the diluted furfural residue hydrolysate was used to evaluate the content of phenolic compounds formed from the degradation of lignin (Li et al., 2014). The visible absorption at 420 nm of the furfural residue hydrolysate was monitored to evaluate the Maillard reaction products formed during the furfural production (Wijewickreme et al., 1998; Yang et al., 2015). Above assays were performed using an absorbance microplate reader (Biotek, USA). Optical density was determined after centrifugation (12,000 rpm, 5 min) (Orozco et al., 2012). $OD_{280 \, nm}$ value of FRs hydrolysates was determined after diluted for 80 times.

The total reducing sugar and monosaccharides in FRs hydrolysate were measured as previous report (Ding et al., 2016; Xu et al., 2016). The concentrations of butanol, acetone, and ethanol were determined by gas chromatography as previous report (Ni et al., 2013).

3. Results and discussion

3.1. Pretreatment of FRs

Various methods for the pretreatment of FRs have been reported (de Frias & Feng, 2014; Yu et al., 2014, 2013). In this study, FRs were soaked in NaOH solution under room temperature. Then pretreated with 2 g/L NaClO or 0.6% H_2O_2 separately. As shown in E-supplement, delignification effect of NaOH + NaClO pretreatment was the best, the glucose concentrations of FRs hydrolysate pretreated by NaOH or NaOH + H_2O_2 were almost the same, approximately 3% lower than that by NaOH + NaClO. However, considering that the corrosive effect of chloride ion on stainless steel reactor and hard removal of NaClO, NaOH pretreatment was chosen for further FRs hydrolysis study. The glucose concentration of 42.8 g/L was obtained from NaOH-pretreated FRs in 48 h.

3.2. Hydrolysis and detoxification of FRs

Enzyme loading was critical in hydrolysis. At 10 FPU/g FRs, the glucose concentration was merely 20.2 g/L at 48 h. The highest glucose concentration of 42.5 g/L was achieved at 40 FPU/g FRs, and no further improvement was observed with higher enzyme loadings (> 40 FPU/g FRs) (Fig. 2A).

To obtain higher reducing sugar concentration, the effect of FRs loading was investigated (Fig. 2B). The glucose concentration increased along with the increasing FRs loading from 90 g/L to 130 g/L. Although the highest glucose concentration (46.5 g/L) was achieved at 130 g/L FRs, the yield of glucose is lower than that of 120 g/L. For economic considerations, 120 g/L was regarded as the appropriate FRs loading. In addition, other hydrolysis conditions such as pH and temperature were also studied.

Utilization of resin and activated carbon as detoxifiers have been reported (Berson et al., 2005; Cheng et al., 2015; Gao & Rehmann,
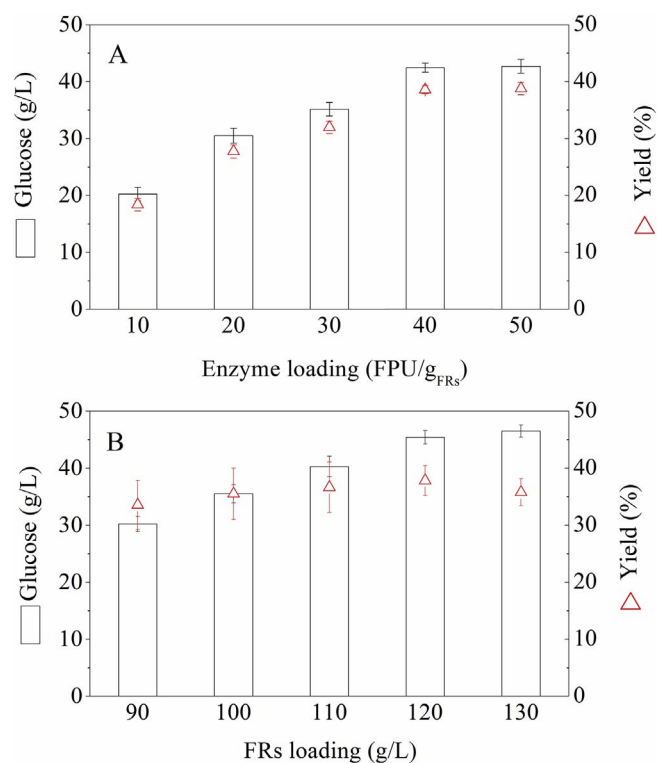

Fig. 2. Effect of enzyme (A) and FRs loading (B) on the hydrolysis of FRs. The hydrolysis reaction was carried out at pH 4.8, 50 °C, 150 rpm for 48 h. The loading of FRs (A) and enzyme (B) were 100 g/L and 40 FPU/g FRs respectively.
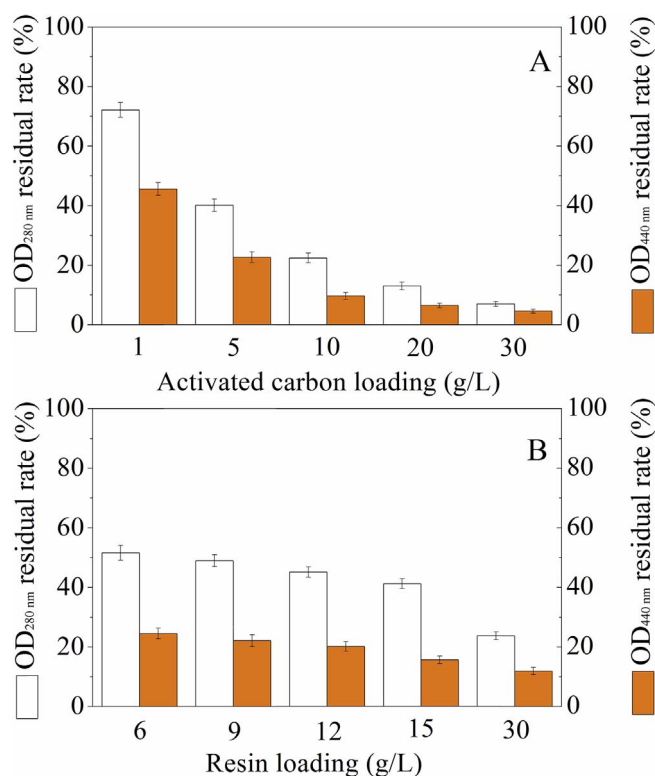
Fig. 3. Detoxification effect of activated carbon (A) and resin 717 (B). The activated carbon detoxification (A) was carried out at 80 °C, 150 rpm for 1 h. The resin detoxification (B) was carried out at 30 °C, 120 rpm for 8 h.

2016; Orozco et al., 2012; Wong et al., 1977). Resin (L-493) has been applied to remove furfural content and total phenolic compounds from water (Gao & Rehmann, 2016; Rege et al., 1998). Activated carbon (2.5%) was able to remove 42% of formic acid, 14% of acetic acid, 96% of hydroxyl methyl furfural (HMF) and 93% of the furfural in woody hydrolysate (Lee et al., 2011). In this study, the influence of resin 717 and activated carbon on detoxification of FRs was investigated. $OD_{280\ nm}$ of the hydrolysate was used to evaluate the content of phenolic compounds (Li et al., 2014). $OD_{420\ nm}$ was monitored to evaluate the Maillard reaction products (Wijewickreme et al., 1998; Yang et al., 2015). In Fig. 3A, the values of $OD_{280\ nm}$ and $OD_{420\ nm}$ decreased along with the increasing activated carbon loading from 1 g/L to 30 g/L. Considering the cost of activated carbon and its sugar adsorption (Berson et al., 2005), about 10 g/L was regarded as the appropriate activated carbon loading. The values of $OD_{280\ nm}$ and $OD_{420\ nm}$ also decreased along with the increasing resin 717 loading from 6 g/L to 30 g/L (Fig. 3B). Compared with resin 717, the detoxification effect of activated carbon was more obvious at the same loading. Resin 717 loading of 30 g/L exhibited similar detoxification effect as activated carbon of 10 g/L in this study, and their effect on butanol fermentation was compared in further study.

3.3. ABE fermentation with FRs hydrolysate pretreated by detoxification with separate sterilization (DSS)

Straw contains 2.2% of crude proteins (Dong et al., 2016), which is hydrolyzed into free amino acid in the process of furfural production. Maillard reaction often occurs between free amino acid and xylose, glucose or furfural (Beckel & Waller, 2010; Obretenov et al., 2010; Yen et al., 1993), which produces darkbrown polymeric compounds named melanoidins (Wijewickreme et al., 1998). Melanoidins contain a number of enzyme inhibitors (El-Morsi et al., 1997), and antibacterial agents against *Escherichia coli* and *Staphylococcus aureus* (Rufián-
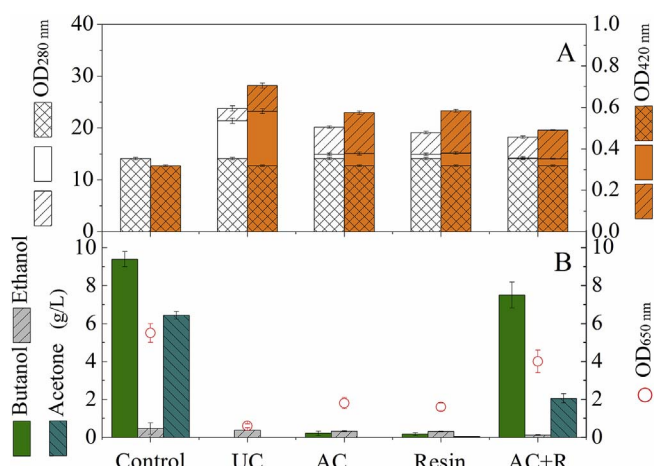

Fig. 4. Butanol fermentation from FRs hydrolysate pretreated by detoxification with separate sterilization (DSS). A: Absorbance ($OD_{280\ nm}$ and $OD_{420\ nm}$) of sterilized CSL (▨ ▧), FRs hydrolysate before sterilization (☐ ■), and increased optical density of FRs hydrolysate after sterilization (▨ ▨). B: Butanol fermentation with different hydrolysates. Control: glucose and separately sterilized CSL; UC: un-detoxified FRs hydrolysate and separately sterilized CSL; AC: FRs hydrolysate detoxicated with 10 g/L activated carbon; Resin: FRs hydrolysate detoxicated with 30 g/L resin 717; AC + R: FRs hydrolysate detoxicated with 5 g/L activated carbon and 15 g/L resin 717.

Henares & Morales, 2008a,b).

As shown in Fig. 4B, only 0.37 g/L ethanol and no butanol was produced when undetoxified hydrolysate (UC) was used. It suggests that certain components in FRs hydrolysate inhibited the cell growth. $OD_{280\ nm}$ and $OD_{420\ nm}$ of FRs hydrolysate detoxified by activated carbon (AC) were 2.36 and 0.02, which were reduced by 77.6% and 89.0% compared with that without detoxification (UC) (Fig. 4A). $OD_{280\ nm}$ and $OD_{420\ nm}$ of FRs hydrolysate detoxified by resin 717 (Resin) were 2.45 and 0.02, representing 76.7% and 89.0% decrease than that of control (UC). When FRs hydrolysate was detoxified by both 10 g/L of activated carbon and 30 g/L of resin 717 (AC + R), the absorbance values further reduced by 87.1% and 98.4% at 280 nm and 420 nm, respectively. Sterilization of FRs hydrolysate caused a significant increase in the values of $OD_{280\ nm}$ and $OD_{420\ nm}$. The $OD_{280\ nm}$ value of UC, AC, Resin, and AC + R treated FRs hydrolysates were increased for 4.95, 7.88, 8.15, and 5.54, respectively, while the $OD_{420\ nm}$ values were also slightly increased by 0.06–0.13 (Fig. 4A). It is speculated that impurities (enzyme, metal ions, etc) in the hydrolysate could promote the production of toxic components during sterilization. The butanol titers of AC, Resin, and AC + R treated hydrolysates were 0.21 g/L, 0.17 g/L, 7.5 g/L, respectively (Fig. 4B). Despite of the increase in $OD_{280\ nm}$ and $OD_{420\ nm}$ values after sterilization, the toxicity of untreated FRs hydrolysate is much higher than that produced during sterilization process. Thus, butanol titer was mainly influenced by the detoxification degree of FRs hydrolysate.

3.4. Butanol fermentation with FRs hydrolysate pretreated by detoxification with mixed sterilization (DMS)

Considering that the detoxification with separate sterilization of hydrolysate and CSL/salts (DSS) was not necessarily effective in reducing the Maillard reaction (Fig. 4A), mixed sterilization of hydrolysate and CSL/salts (DMS) was attempted. Remarkably, butanol titers of mixed sterilization were higher than those of separate sterilization (Fig. 5B). The butanol concentrations of AC, Resin, and AC + R detoxified FRs hydrolysates were 4.42 g/L, 0.28 g/L, 8.86 g/L, which were increased by a striking 20-fold, 64% and 18% than those of separate sterilization, respectively. It was also noticed that $OD_{280\ nm}$ and $OD_{420\ nm}$ values of mixed sterilized UC, AC, Resin, and AC + R detoxified hydrolysates were 17.5–21.6% and 3.6–21.7% lower than those of separate sterilization (Fig. 5A). It is speculated that the proteins in CSL
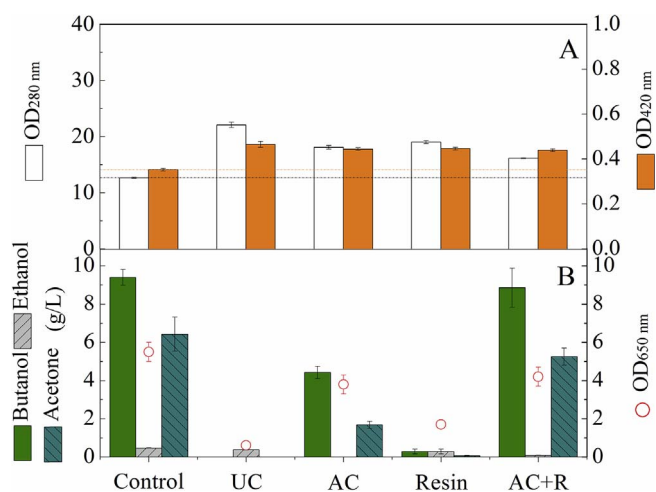
Fig. 5. Butanol fermentation from FRs hydrolysate pretreated by detoxification with mixed sterilization (DMS). A: Absorbance ($OD_{280\ nm}$ and $OD_{420\ nm}$) of mixed sterilized medium (□ ▬). B: Butanol fermentation with different hydrolysates. Control: glucose (as carbon source) and separately sterilized CSL; UC: un-detoxified FRs hydrolysate and separately sterilized CSL; AC: FRs hydrolysate detoxicated with10 g/L activated carbon; Resin: FRs hydrolysate detoxicated with 30 g/L resin 717; AC + R: FRs hydrolysate detoxicated with 5 g/L activated carbon and 15 g/L resin 717.
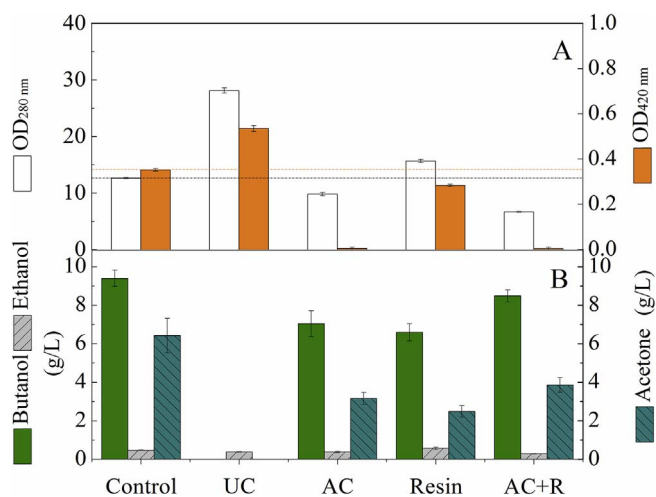

Fig. 6. Butanol fermentation from FRs hydrolysate pretreated by simultaneous detoxification and sterilization (SDS). A: Absorbance ($OD_{280\ nm}$ and $OD_{420\ nm}$) of mixed sterilized medium (□ ▬). B: Butanol fermentation with different hydrolysates. Control: glucose and separately sterilized CSL; UC: un-detoxified FRs hydrolysate and separately sterilized CSL; AC: FRs hydrolysate detoxicated with10 g/L activated carbon; Resin: FRs hydrolysate detoxicated with 30 g/L resin 717; AC + R: FRs hydrolysate detoxicated with 5 g/L activated carbon and 15 g/L resin 717.

could absorb and thereby remove toxic components (detected at 280 nm and 420 nm) during sterilization. It has been reported that proteins could adsorb different chemicals depending on the physical and chemical properties of the protein surface. For example, albumin exhibits a stronger affinity toward hydrophobic (CH_3) surface, while fibrinogen adheres better to both hydrophobic (CH_3) and hydrophilic (OH) surfaces (Roach et al., 2005). Similar phenomenon was observed in succinic acid production from cane molasses and CSL in previous study (Liu et al., 2008). Therefore, mixed sterilization of hydrolysate and organic nitrogen sources could be an efficient approach for reducing toxic impurities.

3.5. Butanol fermentation with FRs hydrolysate pretreated by simultaneous detoxification and sterilization (SDS)

When the FRs hydrolysate were sterilized after detoxification, the

melanoidins produced in the process of sterilization could not be removed. Simultaneous sterilization of medium and AC/Resin was therefore attempted (Fig. 6). Mixed sterilization of AC, CSL and FRs hydrolysate resulted 7.04 g/L butanol, 3.16 g/L acetone, and 0.37 g/L ethanol (Fig. 6B). For mixed sterilized resin, CSL and FRs hydrolysate, 6.59 g/L butanol, 2.48 g/L acetone, and 0.56 g/L ethanol were produced. When both resin and AC were added, the highest butanol titer of 8.48 g/L was achieved. The results suggest that SDS operation could not only remove phenolic compounds in FRs hydrolysate, but also toxic components generated during the mixed sterilization of CSL and hydrolysate. Detoxification efficacy of AC was better than that of Resin (Fig. 6A). Compared with UC, the toxins measured at 280 nm was removed by 65.1% (AC), 44.4% (Resin) and 76.4% (AC + R), and 99.3% of toxins determined at 420 nm were removed by both AC and AC + R (Fig. 6A).

Consequently, the mixed sterilization of resin or/and activated carbon with culture medium was proved to be more economic and efficient in butanol fermentation from furfural residues by *C. saccharobutylicum*.

4. Conclusions

Butanol production from FRs was investigated for the first time. Various detoxification procedures were attempted to remove the toxic compounds in FRs hydrolysate. Detoxification effect of activated carbon/resin 717 combination was better than that of activated carbon or resin alone. Mixed sterilization of hydrolysate and CSL (DMS) was confirmed to be beneficial for the detoxification and butanol production. It is presumed that the proteins in CSL could help absorbing and removing toxic compounds during the mixed sterilization. Simultaneous detoxification and sterilization (SDS) is a more practical and efficient approach for butanol fermentation from FRs hydrolysate by *C. saccharobutylicum* DSM 13864.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.biortech.2018.02.098.

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