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# Process for calcium xylonate production as a concrete admixture derived from in-situ fermentation of wheat straw pre-hydrolysate



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#### ABSTRACT

One of the major obstacles in process of lignocellulosic biorefinery is the utilization of pre-hydrolysate from pretreatment. Although lignocellulosic pre-hydrolysate can serve as an economic starting material for xylonic acid production, the advancement of xylonic acid or xylonate is still limited by further commercial value or applications. In the present study, xylose in the high concentration wheat straw pre-hydrolysate was first in-situ biooxidized to xylonate by *Gluconobacter oxydans*. To meet the needs of commercialization, crude powdered calcium xylonate was prepared by drying process and calcium xylonate content in the prepared crude product was more than 70%. Then, the calcium xylonate product was evaluated as concrete admixture without any complex purification steps and the results demonstrated that xylonate could improve the performance of concrete. Overall, the crude xylonate product directly produced from low-cost wheat straw pre-hydrolysate can potentially be developed as retarding reducer, which could subsequently benefit lignocellulosic biorefinery.

# 1. Introduction

Lignocellulosic materials are the most abundant renewable sources, with an annual global production of approximately 200 billion metric tons (Lange 2007). Currently, biorefining of lignocellulosic materials for commercial processes is gradually being realized due to the increasing selection of techniques available for converting lignocellulosic resources into valuable fuels, high value-added chemicals, and polymers (Ragauskas et al., 2006). Wheat straw, which is the second largest lignocellulosic resource in the world after rice straw (Kim and Dale, 2004), usually contains 33-40% cellulose, 20-25% hemicellulose and 15–20% lignin (w/w) (Prasad et al., 2007). Although lignocellulosic materials can serve as an abundant potential feedstock for production of value-added chemicals, lignocellulosic solids are usually dense cellulose structures with hemicellulose and lignin in the cell wall, which shields cellulose from enzymatic hydrolysis (Talebnia et al., 2010). However, pretreatment can break down the plant cell wall and the crystalline structure of cellulose whilst increasing cellulose porosity and improving enzymatic hydrolysis. Thus, several procedures have been developed to reduce the recalcitrance of lignocellulosic biomass, such as dilute acid hydrolysis, steam explosion and ammonia fiber expansion (Wyman et al., 2005; Jin et al., 2016). Dilute acid hydrolysis, a

relatively cheap and straightforward method for hydrolysis of lignocellulosic materials, has been extensively explored to enhance cellulose digestibility and effectively hydrolyzes hemicellulose and yields a xylose-rich liquor (Martin et al., 2007; Schell et al., 2003). Most hemicellulose can be degraded during the dilute acid pretreatment process, with the degradation products, which contain an abundance of xylose, being released into the pretreatment waste liquor ("pre-hydrolysate"); therefore, the relatively high amount of hemicellulose stresses the need for subsequent utilization of xylose. During the pretreatment, not only free sugars are released, but also various degradation chemicals. These degradation chemicals usually contain small molecular organic acids, furan compounds and lignin derivates, these degradation chemicals can inhibit the microbial capability for conversion of sugars or growth (Palmqvist and Hahn-Hagerdal, 2000a,b). Thus, some valued-products from conversion of xylose in pre-hydrolysate are not presently utilized in an efficient manner (Wyman 1994). In one word, bioconversion of xylose in pre-hydrolysate is still a major bottleneck in the advancement of industrial lignocellulosic biorefinery (Rodriguez and O'Connell, 2011).

Xylonic acid (XA) has been identified as a valuable platform chemical and is currently ranked in the top 30 high-value chemicals (Werpy et al., 2004). Microbial production of xylonic acid from xylose

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has been extensively studied and is a promising future biorefinery technique (Toivari et al., 2012). For example, G. oxydans has been useful for the bioconversion of soluble carbohydrates by efficiently performing incomplete oxidation of xylose in pre-hydrolysate (Buchert et al., 1988; Zhou et al., 2017). XA is a valuable chemical compound with wide potential applications, including as chelating agent, dispersant, precursor of 1,2,4-butanetriol and retarder for oil wells (Deppenmeier et al., 2002). In addition, one of the biggest potential uses for XA is supposed to be admixture that improves the performance of concrete, one of the most used and viable construction materials (Chun et al., 2006). Concrete admixtures are formulated products that are added in small amounts during the mixing process to selectively modify and enhance the properties of concrete or cement (Siddique and Khan, 2011). Global cement output in 2010 was more than 30 billion ton, and cement trade has been growing intensively in recent decades (Selim and Salem, 2015). Apparently, there is a large market for concrete admixtures due to the common usage of concrete. One of the most important classes of concrete admixture is called water reducer. Fundamentally, the water reducer is a cement-dispersing chemical that improves the strength and durability of concrete (Mario and Collepardi, 1996). Most water reducers and retarders are organic, water soluble products, such as lignosulfonates, hydroxycarboxylic acids or carbohydrates. A commonly used water-reducing chemical, known as lignosulfonate, is found in spent sulfite liquor from sulfite pulp mills; however, hydroxycarboxylic acids, particularly gluconate, are known to be superior inorganic-dispersing chemicals (Mario and Collepardi, 1996). Additionally, gluconate has already been used in the cement and concrete industries as a cement-dispersant and a retarding agent for prolonging the setting time of concrete (Chun et al., 2008). The structure of XA is similar with gluconate and it is expected to become one kind of water reducer because it is a hydroxycarboxylic acid that has several hydroxyl (OH) groups and one terminal carboxylic acid (COOH) group attached to a relatively short carbon chain (Mario and Collepardi, 1996).

In this study, hemicellulose hydrolysate from wheat straw was used as a low-cost starting material for production of xylonic acid by *G. oxydans* fermentation. The main objectives of this work were to in-situ bio-converted the xylose in pre-hydrolysate to xylonate and evaluate its potential as a water reducer in concrete.

#### 2. Materials and methods

#### 2.1. Preparation of lignocellulosic pre-hydrolysate

Wheat straw was harvested from North Jiangsu, China, in the autumn of 2016. The contents of cellulose and hemicellulose in wheat straw was 35.38% and 22.62%, respectively. The wheat straw samples were chopped up into small pieces (1-3 cm) by hand-cut with scissors and the composition was measured using two-step sulfuric acid hydrolysis, according to the laboratory analytical procedure from the National Renewable Energy Laboratory (Sluiter et al., 2012). Briefly, wheat straw (1 kg) was combined with the sulfuric acid solution (1%, 10 L) at a mass ratio of 1/10 (w/v). The reaction was conducted in a 15 L digester (ZT1-01, Zhongtong Corporation, Shanxi, China) at 150 °C for 30 min before separating the solid and liquid fractions. The liquid fraction was named as lignocellulosic pre-hydrolysate. Next, concentrated pre-hydrolysate was prepared using a BÜCHI rotary evaporator (R-200, BÜCHI Shanghai Trading, LLC, Shanghai, China) at 70 °C and 1.60  $\times$  10<sup>4</sup> Pa until the xylose concentration reached approximately 100 g/L. The pH of pre-hydrolysate was adjusted to 6.5 with Ca(OH)<sub>2</sub> powder and the suspension was filtered through glass fiber filter with a 2.7 µm pore size (Whatman). The concentration of main aldoses in the pre-hydrolysate is shown in Table 1.

Table 1

|--|

Compositions	Component	Pre-hydrolysate (g/L)		
		Initial	Concentrated	
Sugars	Xylose Glucose Arabinose	26.82 6.22 5.49	101.23 22.81 20.34	
Carbohydrate- degradation products	Formic acid Acetic acid Levulinic acid 5-Hydroxymethylfurfural Furfural	$\begin{array}{c} 0.41 \\ 0.94 \\ 6.01 \times 10^{-2} \\ 3.14 \times 10^{-1} \\ 1.66 \times 10^{-1} \end{array}$	$\begin{array}{c} 1.01 \\ 1.91 \\ 2.12 \times 10^{-1} \\ 9.85 \times 10^{-1} \\ 8.02 \times 10^{-3} \end{array}$	
Lignin-degradation products	Vanillin Syringaldehyde Syringic acid 4-Hydroxybenzaldehyde 4-Hydroxybenzoic acid	$\begin{array}{c} 1.75\times10^{-1}\\ 1.41\times10^{-2}\\ 4.56\times10^{-3}\\ 1.79\times10^{-2}\\ 5.12\times10^{-3} \end{array}$	$\begin{array}{l} 6.31\times10^{-1}\\ 5.11\times10^{-2}\\ 1.62\times10^{-2}\\ 7.01\times10^{-2}\\ 1.97\times10^{-2} \end{array}$	

#### 2.2. Microorganism and culture conditions

*G. oxydans* NL71, originating from the strain ATCC 621, was maintained on sorbitol-agar (sorbitol 50 g/L, yeast extract 5.0 g/L, agar 20 g/L) at 4 °C. The *G. oxydans* NL71 inoculum was prepared in a 250-mL Erlenmeyer flask containing 50 mL medium (sorbitol 80 g/L, yeast extract 8 g/L), and cultured for 18–24 h with shaking (220 rpm) at 30 °C. The cell pellet was harvested by centrifugation at 5000g for 8 min (Miao et al., 2015).

The biotransformation medium contained MgSO<sub>4</sub> (0.5 g/L), KH<sub>2</sub>PO<sub>4</sub> (1 g/L), K<sub>2</sub>HPO<sub>4</sub> (2 g/L), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (5 g/L), yeast extract (5 g/L), and pure mixed aldoses or pre-hydrolysate. The density of the initial *G. oxydans* cell inoculum was 4 g/L (Zhou et al., 2017). Calcium carbonate powder was used to control the pH. Fermentation was conducted in a 3.0-L compressed oxygen supplied sealed stirred tank reactor (COS-SSTR). Oxygen (purity  $\geq$  99.9%) was supplied to the COS-SSTR at a gas inlet pressure of 0.02–0.05 MPa (Zhou et al., 2017), and the temperature was controlled at 30 °C.

#### 2.3. Analytical methods

Aldoses (glucose, xylose, and arabinose) and aldonic acids (XA, gluconic acid (GA), arabonic acid (AA) and 2-ketogluconic acid (2-KGA)) were analyzed on high performance anion-exchange chromatography (HPAEC) (Dionex ICS-5000) linked to a CarboPac<sup>TM</sup> PA 10 column with NaOH and sodium acetate as eluants at a flow rate of 0.3 mL/min (Wang et al., 2014). The XA/AA yield (%) was calculated from the concentration of XA/AA divided by the total xylose concentration and multiplied by the constant of 0.904. The volume productivity (g/L/h) of XA/AA was calculated from the concentration of XA divided by the reaction time.

# 2.4. Concrete test

Calcium lignosulfonate (CL) was made in South Africa from Borregaard Corporation, calcium gluconate (CG) from Shanghai Sangon Biotech Corporation and calcium xylonate from lignocellulosic prehydrolysate (CXL) and pure xylose conversion (CXX) by our group were used as admixtures in concrete testing. Concrete was prepared for performance testing. The concrete was composed of cement (Conch cement P-O42.5; 4.96 kg), silica sand (10.66 kg), small stones (5–19 mm; 6.84 kg), medium stones (10–20 mm; 10.26 kg), and admixture and water as required. The dosages of CXL were 0, 0.05, 0.1, 0.15, 0.2, 0.3, and 0.4%. For comparison, 0.2% CL, CG, CXX were also used for testing. For each treatment, three separate batches were used for concrete testing (fresh and hardened concrete test) according to Chinese National Protocol GB8076-2008. Briefly, (1), fresh concrete test was determined in accordance with the GB/T50080 standard: The slump values (100 mm) were maintained in the concrete mixtures prepared for determining and comparing the amount of water reduction. Moreover, setting time and air content were measured in accordance with GB/T50080-2002. (2). hardened concrete test was determined in accordance with the GB/T50081 standard. Concrete mixes were made in the laboratory while forming the specimens in  $100 \times 100 \times 100$  mm metal forms. After 24 h the specimens were taken out from the forms and kept in water of  $20 \pm 2$  °C for 28 days. Cubes were used for compressive strength and the compressive strength of concrete cubes was tested after 3, 7 and 28 days. In order to reduce the effect of sampling bias in qualitative results, each of three samples was analyzed for concrete properties.

# 3. Results and discussion

# 3.1. In-situ fermentation of crude wheat straw pre-hydrolysate by G. oxydans

Lignocellulosic pre-hydrolysate typically contains large amounts of plant monosaccharides (mainly xylose, arabinose and glucose) derived from lignocellulose hydrolysis and provides an economic raw material for sugar acids production. Apart from some carbohydrates, various degradation products derived from the degradation of lignocellulose during acid pretreatment in of the original and the concentrated prehydrolysate are also listed in Table 1. These degradation chemicals always are described as key inhibitors for microbial fermentation (Palmqvist and Hahn-Hagerdal, 2000a,b). Although, some degradation products could be partly removed after concentration, there were still plenty of degradation products preserved in the pre-hydrolysate. Thus far, some studies on xylonic acid production from lignocellulosic hydrolysate have been reported by using G. oxydans. Buchert et al. (1988) used G. oxydans to convert steamed hemicellulose hydrolysate, containing 25 g/L xylose, to 27 g/L XA by using a mixed bed resin treatment. More recently, Zhang et al. (2017) used G. oxydans to produce, by means of detoxification, 66.42 g/L of XA from 65.39 g/L xylose. Evidences showed that G. oxydans possessed a desired and a great ability to convert xylose to XA. In this study, crude pre-hydrolysate was directly used for in-situ fermentation. Initially, in-situ fermentation was difficult to achieve in the traditional aeration and agitation reactor because colloidal and aggregative components in the pre-hydrolysate resulted in uncontrollable foam issue. Further experimentation revealed that the compressed pure oxygen gas with sealed stirred bioreactor (COS-SSTR) system, provided by Zhou et al. (2017), significantly enhanced the performance of G. oxydans. Importantly, the issue of foam formation was eliminated or decreased in the pressurized system, thereby avoiding the necessity for antifoam agents and aerobic fermentation of pre-hydrolysate could be implemented successfully.

To determine the ability of XA bioconversion with G. oxydans NL71, pure aldoses medium which contain 100 g/L xylose, 20 g/L arabinose and 20 g/L glucose (the concentration ratio was similar with those of the pre-hydrolysate) was first tested. As shown in Fig. 1a, it could be found that all aldoses could be completely and efficiently utilized by 4 g/L G. oxydans (dry biomass concentration). Here, observations suggested that further metabolism of pentonic acids (XA and AA) was difficult. XA showed a slight decline during prolonged fermentation, we speculated that a small portion of XA could be utilized by Dahms pathway to support the subsistence of the cells (Zhang et al., 2013). Anyway, after 8 h fermentation, 106.5 g/L xylonic acid and 19.5 g/L arabonic acid were accumulated in the broth, with corresponding yields of 96.3% and 88.1%, respectively. Conversely, glucose was converted to GA, which was then further metabolized to 2-KGA (at a yield of 41.2%) and small amount of 5-ketogluconic acid. Although GA can be converted to ketogluconic acids, these acids, as polyhydroxy organic acid,



**Fig. 1.** Reaction process of *G. oxydans* fermentation in COS-SSTR (a) pure aldoses medium (b) pre-hydrolysate.

also can be used as a concrete admixture (Kasai 1967). Thus, preservation of ketogluconic acids in the fermentation broth also can be used for the next process.

Then, the capability of XA bioconversion with *G. oxydans* NL71 in pre-hydrolysate was also tested in COS-SSTR. The profile obtained was shown in Fig. 1b. It could be seen that the production and volumetric productivity of XA all decreased. Generally, crude pre-hydrolysate contains various lignocellulosic degradation products will hinder the bioprocesses. As predicted, the results indicated that the bioconversion of the pre-hydrolysate was more difficult than that of the pure aldoses. Nonetheless, 98.6 g/L xylose also could be converted to 104.4 g/L XA at a yield of 95.7% within 12 h. Meanwhile, 16.9 g/L AA was also accumulated simultaneously. All observations indicated that *G. oxydans* NL71 in COS-SSTR possessed excellent biocatalysis performance for conversion of the crude pre-hydrolysate, even if the concentration of xylose in the pre-hydrolysate was more than 100 g/L. To be sure, the design of the COS-SSTR is an efficient and ideal method for in-situ fermentation of pre-hydrolysate.

Generally, dry powder is safer to store and transport, and products in liquid form are more expensive than powders and are also more difficult to store, package and transport, due to their bulk, weight and refrigeration requirements (Gharsallaoui et al., 2007). Additionally, because XA is a sugar-derived acid, it may easily be contaminated by microorganisms. Therefore, to satisfy commercial needs, the fermented pre-hydrolysate was dried after fermentation (Trophardy 2014). After spray drying, the crude bioconverted pre-hydrolysate product (calcium salt of mixed acid) was prepared from wheat straw pre-hydrolysate, which still contained about 7.6% moisture. The content of calcium xylonate and calcium arabonate accounted for approximately 70% and 10% of the powdered solid product (dry basis), respectively, as determined by HPAEC analysis. In addition, the products also contained some lignin, proteins, colloids and degradation product and together these accounted for about 5–8%.

#### 3.2. Effect of calcium xylonate loading for concrete property

Fresh concrete is a very useful and flexible material that can be poured in formwork. The mixture consists of cement, sand, stone and admixtures. Admixtures are one of the most important components used for improving the performance of concrete (Baru et al., 2014). Concrete use is increasingly prevalent and in line with economic growth, thus admixtures have a huge market (Ouyang et al., 2006). Moreover, the use of admixtures in concrete production can be reduced by using alternative materials, such as renewable or discarded waste, that's to say, it can protect natural resources to some extent. During biorefining, large amounts of pre-hydrolysate as waste liquor are generated. Currently, the utilization or dispose of waste liquor still limits the advancement of biorefinery. Xylonate product as concrete admixture put forward a new idea for utilization of pre-hydrolysate.

Here, CXL produced from lignocellulosic pre-hydrolysate was tested in concrete assays for its potential as a water reducer in concrete industry. Water is necessary in concrete mixtures to obtain the proper slump value for concrete with greater fineness. Thus, the slump value (100 mm) was maintained in the concrete mixtures that were prepared for determining and comparing the amount of water reduction. It is widely accepted that reduced water consumption under the same concrete fluidity conditions can improve the properties of hardened concrete and/or increase strength and durability (Ouyang et al., 2006; Surhone et al., 2010). As shown in Fig. 2, the incorporation of CXL (0.05-0.4%) led to a significant reduction in water (5-16%), compared to the unmodified mix. Generally, commercial water reducers can decrease mixing water requirements up to 10-15% (Siddique and Khan, 2011), therefore, the water reduction efficiency of CXL is comparable to known reducers. Table 2 showed the results of setting-time (initial and final), which could improve the workability of concrete and was important for the temporary transport and storage of concrete. Settingtime significantly increased with increasing CXL dosages. Additionally, CXL from pre-hydrolysate could prolong the time of setting and the



CXL addition dosage (%)

Fig. 2. Percentage of water reduction at different CXL addition dosages.

results of setting-time in agreement with the change of water reduction. This may be due to the lower hydration rate of cement during the first hours in the presence of a water reducer (Ouyang et al., 2006). The results of the water reduction and setting-time assays indicated that XA performs satisfactorily and could be used alone as a retarder or water reducer.

The effectiveness of concrete admixtures was not only determined by a reduction in water consumption or an increase in setting time, but also determined by increased compressive strength after adding the admixture. Hence, the effect of different CXL addition dosages on air content and compressive strength was investigated after 3, 7 and 28 days. Results in Table 2 indicated that increasing CXL addition dosages (0.05–0.3%) resulted in an increased concrete air content and compressive strength. Furthermore, the reduction of water consumption significantly enhanced the compressive strength of the concrete. The use of 0.3% CXL permitted a 13.4% water reduction and a remarkable 65.8% increase in the 28 days compressive strength. However, a 0.4% CXL content in the concrete resulted in a sharp rise in air content. Generally, higher air content would increase the amounts of pores in the concrete, thereby decreasing its strength (Ouyang et al., 2006). Thus, the 28 days compressive strength of the 0.4% CXL addition showed a seriously decline when compared with the 0.3% addition. The above results suggested that 0.2-0.3% CXL was ideal addition dosage for concrete preparation.

# 3.3. Comparison of different admixtures for effect of the concrete property

In this study, CL, CG and CXX were all used in the assays of concrete property test and all assays were tested under the same conditions. As shown in Fig. 3a, CXL, CXX, CG and CL all could improve the capability for prolonging initial and final setting times of concrete. At a dosage of 0.2% admixture (by weight of concrete), delays of the initial and final set were more than 3 and 2 h, respectively. Therein, the concrete by adding CG and CL exhibited slightly better performance than the concrete which added CXL and CXX in water reduction and concrete setting. Generally, lower w/c ratio in the concrete permits better hydration (El-Hosiny and Gad, 1995), and the CG or CL contained more hydroxy which resulted in slight increase of the 3 days compressive strength of concrete as Fig. 3b. However, the 7 and 28 days compressive strength of CL and CG concrete was lower than the CXL and CXX concrete, which was a result of higher air content in CL concrete. According to the test results, the CXL is comparable to CXX, that's to say, complex purification steps is not necessary for CXL as concrete admixture application. In addition, the result showed that the property of concrete mixed with flour admixtures was basically similar. In summary, CXL from pre-hydrolysate can potentially be applied in concrete manufacturing instead of CL or CG. In addition, as reducer or retarder, the calcium xylonate exhibits superior characteristics and greater functionality, and can be manufactured by compounding with other admixtures to improve the performance of concrete.

# 4. Conclusions

In this work, crude powdered CXL was successfully prepared from wheat straw pre-hydrolysate. Improved characteristics were obtained for water reduction or retardation capacity and compressive strength reinforcement. In short, all observations allowed us to term CXL as a potentially useful water reducer or retarder. Preliminary results of this study confirmed that low-cost wheat straw pre-hydrolysate was a promising commercial precursor for concrete admixture. That's to say, cost-competitive xylonate product from pre-hydrolysate can boost comprehensive utilization of lignocellulosic materials.

#### Table 2

Concrete properties testing results of CXL as admixture.

CXL Content /%	Water addition <sup>a</sup> /kg	Air content <sup>b</sup> /%	Compressive strength <sup>c</sup> /MPa			Setting time <sup>d</sup> /h	
			3 d	7 d	28 d	Initial	Final
0.00 0.05	2.97 2.80	/ 0.8	12.6 14.7	20.9 25.2	25.2 32.8	5.33 6.08	7.83 8.25
0.10	2.69	0.9	16.4	27.1	35.4	+0.75 6.83 +1.50	+0.42 8.75 +0.91
0.15	2.66	1.0	17.1	29.0	38.7	7.82 + 2.48	9.82 + 1.98
0.20	2.61	1.5	15.7	28.3	41.1	8.47 + 3.13	10.13 + 2.30
0.30	2.57	1.9	15.0	26.1	41.8	10.90 + 5.56	12.82 + 4.98
0.40	2.51	3.2	11.9	22.6	27.8	12.55 +7.21	15.38 +7.53

The data was average of separated and duplicate tests.

+ numerical value: prolonged setting time compared with 0% CXL addition test.

- <sup>a</sup> Water Reduction Test.
- <sup>b</sup> Air Content Test.
- <sup>c</sup> Compressive Strength Test.
- <sup>d</sup> Setting Time Test.







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