



## Production of carboxymethyl lignin from sugar cane bagasse: A cement retarder additive for oilwell application



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### ABSTRACT

The use of residues generated during agro-processing to produce valuable products is in the concept of biorefinery applied in recent times. This concept is attractive for being an alternative to solve disposal issues while processing a more added value product to residues. This work suggests a process to produce Carboxymethyl Lignin using Sugar Cane Biomass (SCB) as raw material and to test its efficiency as retarder additive for oil well cement slurry. The soda/anthraquinone pulping process was used to extract lignin from cellulose present in biomass. The lignin was isolated and chemically modified to produce Carboxymethyl Lignin (CML). The CML was tested through Thickening Time tests. The linear increment on the thickening time of cement slurries containing different concentrations of CML was observed reaching up to 104% of increase on thickening time in relation to a reference. Two mechanisms of action were proposed to explain its effect as cement paste set retarder. The results showed that Carboxymethyl Lignin production from sugar cane biomass can be an interesting process to a line of biorefinery associated to sugar industry. That process can reduce the disposal issues with crops and bagasse, avoiding its burning and generating more valuable biochemical.

### 1. Introduction

The sugar cane biomass is a by-product of the sugar-alcohol industry that represents a large volume of up to 30% of the harvested cane in South Africa (Mashoko et al., 2013). Brazil is the largest sugar cane producer with about 39% of world sugar cane production (Silalertruksa et al., 2017). According to UNICA (Brazilian Sugarcane Industry Association), the amount of sugar cane produced in the harvesting period 2015/2016 was 666.824 tons (UNICA, 2016), with estimated bagasse generation around 200.047 tons. Sugar mills only operate during harvesting, whence the seasonality and storage of bagasse cause problems related with its degradation. Most of the bagasse is currently used as fuel in sugar mills and ethanol distilleries (Clauser et al., 2016). In recent years, the burning of lignocellulosic materials has been used as cleaner alternative to coal in the production of electricity, with sugarcane bagasse being one of the biomasses with highest potential (Mashoko et al., 2013). Environmental gains would be greater if the burning of the surplus were avoided and the biomass become feedstock for the production of new materials.

Biorefinery concept is therefore gaining interest as a promising approach for enhancing competitiveness of the sugarcane industry, which is recognized as a key agribusiness in many emerging economies, by production system that integrates biomass conversion processes to produce fuels, heat, electricity and value-added products e.g. materials or chemicals from biomass (Clauser et al., 2016; Fontoura et al., 2015; Ma et al., 2016; Patrizi et al., 2015; Pereira et al., 2015; Silalertruksa et al., 2017, 2015). The wide variety of chemical structures present in lignocellulosic materials make these versatile for application in various industrial areas (Maziero et al., 2012).

The building process of an oil well is based on cycles of drilling, casing and cementing job going down section by section until the interest zone. For each section a cement slurry is designed and displaced to fulfill the annulus space between formation and case. The slurry design is required to meet operational and wellbore conditions as pressure and temperature. Chemical additives are used to modify cement slurry's behavior in order to meet those requirements.

Additives called retarders are used to increase thickening time (ThTi), thus postponing cement set and allowing more operational time

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for placement of slurry on annulus space. Sodium and calcium lignosulfonates are the most common retarders found in cementing jobs, with a wide range of application temperature and low production cost when compared with other synthetic retarders. Although it is known that lignin is the chemical base used in the composition of this additive, little is reported about chemical composition and the effect of additive in the cement matrix, since lignin has a variable and complex molecular structure, as well as the production of these additives is intellectual property of the major service companies in oil well cementing.

Generally, lignosulfonates used in oil well cementing are unrefined sodium or calcium salts. The presence of unwanted components, usually low molecular weight carbohydrates such as pentoses, hexoses, and aldonic acids, derived from hemicelluloses and sugars that make up the biomass (Angelini et al., 2017), leads one to believe that the retarding effect in the cement slurry is largely attributed to those components, since lignosulfonates that pass through the purification process lose much of the retarding potential (Nelson and Guillot, 2006). Attributing the effect of a chemical additive to its unwanted components has a big associated risk that can interfere in several spheres of the production chain. Restricting the production of lignosulfonates only to biomasses whose carbohydrates have the retarding effect or, on the other hand, not ensuring a reproducibility in the performance of these products is not desirable since lignin has a wide compositional and structural variety depending on the origin of the biomass (Horst et al., 2014; Li and McDonald, 2014) and extraction method (Mansouri and Salvador, 2006; Maziero et al., 2012; Zhang et al., 2017).

Controlling the cement set is a key element in the success of the cementing job. An oversized thickening time (Th.Ti.) increases the costs with waiting on cement (time needed to wait for cement sheath to develop compressive strength) and delays the development of the oil well construction process. Similarly, very short operational times also generate associated risks and costs, due to premature set risk during displacement of the slurry inside the case which, in extreme cases, can lead to total loss of investments in the well. The purpose of this work is to produce a retarder additive from sugarcane biomass and to elucidate the effect of this retarder associated with the lignin origin, product purity.

## 2. Experimental

### 2.1. Biomass pre treatment

Sugar cane bagasse (SCB) collected in Northeastern Brazil (6°13'59.6"S 35°12'59.2"W) was sun-dried and then crushed with a knife mill. Biomass were sieved for sand and residues removal and selected size between 1.41–0.354 mm, as shown in Fig. 1. The SCB was washed with water at 70 °C under agitation for sand, sugars and residues removal and dried at 50 °C for 12 h. Compositional analysis of cellulose and hemicellulose content were determined by acid detergent fiber (ADF) and neutral detergent fiber (NDF) (Van Soest and Wine, 1967), and lignin by Klason method (Theander and Westerlund, 1986). All analyses were performed in triplicate.

### 2.2. Sugar cane bagasse delignification

The delignification process was made through soda/anthraquinone method based on the procedures reported by (Sharma et al., 2015). For each 10 g of SCB, 120 mL of a 0.2 g/mL NaOH (CPQ<sup>o</sup>, 98%) and 0.15% (m/V) of anthraquinone (VETEC<sup>o</sup>, 99%) were used. The reaction was conducted in a closed stainless steel reactor at 160 °C during 1 h under constant mixing. At the end of the process, the cellulose-rich pulp was filtered in a 0.044 mm sieve to separate from the black liquor. Lignin was extracted from black liquor by precipitation at pH close to 3. A solution of H<sub>2</sub>SO<sub>4</sub> 30.0% (V/V) was slowly added to the black liquor until lignin precipitation. Then, the extracted lignin was filtered and washed with the same H<sub>2</sub>SO<sub>4</sub> acidic solution and dried in a hothouse at

50 °C for 12 h.

### 2.3. Carboxymethyl lignin (CML) synthesis

A dispersion of 0.08 g/mL ratio of lignin in isopropanol was prepared. The process must be at pH 8–10 by constant adjust with a solution 0.2 g/mL NaOH. After pH set, dispersion was kept in constant mixing during 30 min to produce the lignin alkali. Subsequently, 15 mL of 0.32 g/mL of monochloroacetic acid in isopropanol was added dropwise over 30 min. The lignin modification reaction was kept in constant mixing, light heating (until low reflux) overnight. The product Carboxymethyl-Lignin (CML) can be retrieved by paper filtering. The CML solid were washed with isopropanol and dried in hothouse at 50 °C during 2 h.

### 2.4. CML conversion tracking

Fourier-transform infrared spectroscopy (FT-IR) scans were performed to track the extraction process of lignin from cellulose and to verify lignin modification through new bands characteristic of inserting group. Due to the fact that no commercial sugar cane lignin was found, commercial kraft lignin (Sigma Aldrich) was used to compare with SCB lignin. A Spectrum 65 FT-IR Spectrometer Perkin Elmer with Universal ATR sampling accessory was used. Spectrum from 650 to 4000 cm<sup>-1</sup>, 12 scans for each sample.

### 2.5. Thickening time tests for retarder additive validation

The CML was evaluated as retarder additive for cement slurries containing API Class G cement. Slurries containing CML concentrations of 4.68, 8.69 and 13.37 L/m<sup>3</sup> (Liter of retarder per cubic meter of cement) in SI units or 0.035, 0.065 and 0.100 gals (gallon per sack of cement) in industrial units were used, respectively. All slurries had fix density of 1.89 g/cm<sup>3</sup> (15.8 lbm/gal). Formulation, mixing and testing the cement slurries followed API (American Petroleum Institute) RP (Recommended Practice) 10B. Heating and pressuring ramps were set according to schedule 9.7 of API RP 10B, simulating a well condition of 3050 m (10000 ft), 82 °C (180°F) and 43.44 MPa (6300 psi). Thickening Time tests were performed on a Pressurized Consistometer model 8040D Ametek Chandler Engineering.

## 3. Results and discussion

### 3.1. Lignin extraction

The soda/anthraquinone pulping process was efficient on lignin extraction from sugar cane bagasse with yield of 90.75%. Table 1 shows the amounts of cellulose, lignin and hemicellulose present on SCB and the relative extraction yield by the process.

### 3.2. FT-IR spectra analysis of SCB lignin and carboxymethyl lignin

The lignin extracted from sugar cane biomass (SCB lignin) showed vibrational stretches similar to commercial Kraft lignin (Sigma Aldrich) (Fig. 2). Similar FT-IR spectrum lignin were reported for SCB lignin (Mancera et al., 2010). An enlargement of the phenolic and aliphatic hydroxyl bands was noticed, which can be attributed to water physically adsorbed by the material. The C–H stretches of methyl, methylene and methoxyl groups of the side chains were attributed to the band around 2909 cm<sup>-1</sup>. It was possible to detect a “shoulder” at 1692 cm<sup>-1</sup>, near the typical band of carbonyl conjugate at 1672 cm<sup>-1</sup>. This overlapping of bands is typical of lignins with low degree of oxidation (Mancera et al., 2010). The displacement of the carbonyl band to the 1692 cm<sup>-1</sup> region can be attributed to unbound interactions, such as hydrogen bonds. It was also possible to notice the absorptions corresponding to the aromatic ring (S) stretches in 1603, unit rings (G) in

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