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**LIGNIN-BASED COATINGS FOR
CONTROLLED RELEASE FERTILIZERS BY
COATING SINGLE SUPERPHOSPHATE**

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Tribunal:

Los miembros del Tribunal hacen constar que en el día de la fecha el **Sr. Ing. Quím. Felipe Rotondo Suárez** ha sido **APROBADO/REPROBADO** en la defensa de su **Tesis de Maestría** en Ingeniería de Celulosa y Papel titulada: **“RECUBRIMIENTOS EN BASE A LIGNINA PARA FERTILIZANTES DE LIBERACIÓN CONTROLADA EN BASE A SUPERFOSFATO DE CALCIO”**.

La resolución del Tribunal se fundamenta en los puntos detallados a continuación:

(A modo de guía y sin necesidad de ceñirse estrictamente a los lineamientos detallados debajo se sugiere que la fundamentación contenga los siguientes puntos:

1. La importancia/originalidad del trabajo realizado, del aporte, de los métodos empleados, y de los resultados obtenidos.
2. La ubicación del tema en el marco del conocimiento actual de la disciplina.
3. La calidad de la Tesis, teniendo en cuenta su correcta redacción como trabajo científico.
4. La presentación oral
5. Otros)

Para que conste,

Firmas originales

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Resumen

La industria de procesamiento de la celulosa genera lignina, la cual se utiliza como combustible para producir vapor y energía eléctrica. En los últimos años el precio de la energía eléctrica que obtienen los generadores se ha reducido como consecuencia de la instalación de parques eólicos. En consecuencia resulta de interés encontrar aplicaciones de mayor valor agregado para la lignina, mejorando así la eficiencia de la cadena forestal.

El fertilizante superfosfato de calcio fue recubierto utilizando recubrimientos con lignina como material principal. De esta manera se prepararon fertilizantes de liberación controlada. El objetivo de este trabajo fue estudiar diferentes recubrimientos en base a lignina y el comportamiento del fertilizante recubierto al ser sumergido en agua.

En la parte experimental de esta tesis la lignina fue modificada químicamente para ser incorporada eficazmente en el recubrimiento. Se ensayó con dos clases distintas de recubrimiento: 1) una resina compuesta de lignina hidroximetilada y resina fenol-formaldehído, con talco como relleno; y 2) material termoplástico compuesto de lignina acetilada y acetato de celulosa. En todos los casos se ensayaron diferentes condiciones de reacción para modificar la lignina y se seleccionó la mejor condición para preparar el recubrimiento.

Los fertilizantes fueron ensayados en agua y se hizo un seguimiento de la curva de liberación de fósforo. Su comportamiento se adecuó al modelo de difusión propuesto por Shaviv et al. (2003). Todos los fertilizantes ensayados mostraron semejante magnitud en su permeabilidad al fósforo. Sin embargo, el comportamiento se alejó del modelo durante la etapa final de la liberación, porque ésta comenzó mucho antes de la que la mayor parte del fósforo hubiera sido liberado.

Se atribuye este fenómeno a la presencia de sulfato de calcio, cuya baja solubilidad y lenta liberación limita indirectamente la disolución del fosfato monocálcico. De esta manera el fosfato ocluido dentro del sulfato de calcio no sería liberado.

Palabras clave: lignina Kraft, fertilizante de liberación controlada, materiales en base a lignina

Abstract

Pulp mills generate dissolved lignin as a by-product, which is currently burnt to produce steam and electric energy. In recent years, the price of electric energy in Uruguay has reduced as a consequence of the installation of wind farms. As a result there is a greater interest in finding more valuable applications for lignin, thus improving the efficiency of the forest value chain.

In this master's thesis work single-superphosphate fertilizer was coated using lignin as the main material of the film. In this way coated controlled release fertilizers (CRF) were prepared, controlling the diffusion of phosphorus through the film. The objective of this work was to study different lignin-based coatings and the phosphorus release behaviour of the resulting fertilizer.

Lignin was chemically modified to be incorporated into the coating solution. Two different groups of coating materials were prepared: 1) thermoset resin composed of hydroxymethylated lignin and phenol-formaldehyde (PF) resin, with talc as a filler; and 2) thermoplastic blend of acetylated lignin and cellulose acetate. In the first material aqueous sodium hydroxide solution was used as a solvent, while the second was dissolved in acetone. During lignin modification several experimental conditions were tested in order to improve the resulting material.

The fertilizers were submerged in water and their phosphorus fractional release curve was determined. Its behaviour adjusted well to the diffusion mechanism proposed by Shaviv et al. (2003). All tested coatings had similar phosphorus permeability values and no significant difference was found between the two groups of lignin-based materials. However, the release behaviour departs from the model during the decaying phase, because the release rate reduced long before most of the fertilizer had been released.

These findings were attributed to the presence of calcium sulphate, which low solubility and slow release indirectly limit calcium phosphate monobasic dissolution. In this way the phosphorus occluded inside the calcium sulphate matrix would not be released.

Keywords: Kraft lignin, controlled release fertilizers, lignin-based materials

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1 INTRODUCTION

The excessive or inefficient nutrient application is a serious environmental concern because it contributes to the eutrophication of rivers and lakes. All major river basins in Uruguay are suffering from eutrophication, whose leading cause is the excessive use of phosphate fertilizers (*Chalar et al., 2017*). This is so because phosphorus is the limiting nutrient for the algal growth in surface waters.

Uruguayan economy relies heavily on food production, as the agricultural sector accounted for 78% of uruguayan exports in 2016. Nowadays Uruguay produces enough food for 28 million people, and this figure is expected to increase to 50 million in the coming years (*Uruguay XXI, 2017*). Therefore, a higher fertilizer volume will be applied in the future, and the current environmental problems will grow.

In addition, mineral phosphorus is a non-renewable resource. Phosphorus reserves are concentrated in a limited number of countries, and Uruguay is not among them. The European Commission added phosphate rock to its critical raw material list in 2014, which means that its supply is critical to UE economy (*March et al., 2016*). The European Sustainable Phosphorus Platform was created in 2013 to facilitate discussions, policy proposals and long-term visions to phosphorus sustainability. Nutrient recovery and optimisation practices are being actively discussed (*ESPP, 2017*).

Any excess of nutrient not absorbed by the crop can suffer different processes that makes them unavailable to plants. Phosphorus is gradually immobilized in the soil, especially if iron and aluminium are present, forming very stable compounds. For this reason great excesses in their

application are employed to ensure a high fertilizer concentration for the whole crop cycle. Conversely, the soil can be saturated in phosphorus if the land has been fertilized for a long time (*Hernández, 1999*). In this case, the excess may stay in the water contained in the soil, and can then be leached to the groundwater.

Excessive nutrient application leads to an excess of nutrients immediately after the application and a deficiency later when the crop reaches its highest nutrient demand. In the case of seasonal crops, the nutrient demand is 'sigmoidal'. It needs a small amount during germination, then it requires more as it grows, and at last the demand decreases when the harvest time is near (*Trenkel, 2010*).

One alternative to match fertilization with nutrient demand is to make many fertilizer applications, with different amounts according to the stage of development of the crop. However, this practice has higher costs because it needs more labor, fuel, monitoring and soil analysis. In addition the applications may have to be postponed due to bad weather, thus affecting its efficiency. The fertilizer industry is on the lookout for solutions to control the availability of the nutrients that the fertilizer releases. In that way the nutrient efficiency would increase without incurring in the costs explained above.

This master thesis is concerned specifically with coated controlled release fertilizers (CCRF), where the fertilizer is covered by a film that controls its release. Ideally the release rate matches the nutrient requirement of the crop. In this work different lignin-based materials were prepared to be applied on single superphosphate. The fertilizers thus prepared were tested in water to determine its phosphorus release behaviour.

Single superphosphate is manufactured by reacting phosphate rocks with sulfuric acid. It was selected for this work because of its being a highly water-soluble phosphate fertilizer which is currently produced in Uruguay, so that the manufacturing process could be modified for the application of the lignin-based coating.

Controlled release formulations for agricultural applications generally include significant amounts of petroleum-derived polymers that accumulate in the soil. Natural polymers have the advantage of being biodegradable, so that no polymeric residue accumulates (*Cotteril et al., 1996*).

Lignocellulosic biomass is the most abundant renewable raw material available and it has been recognized as a potential feedstock for the production of chemicals, fuels and plastic materials. Recently, plantation forest area has been steadily growing in Uruguay up to a current value of 1 million ha, and a wood annual harvest of 14 million m³ in 2016 (*Dirección General Forestal- MGAP, 2016*). The pulp industry produces 2.6 million ton per year of *Eucalyptus spp Kraft* pulp (*Uruguay XXI, 2017*).

In particular, lignin is a promising material for the development of CRF coatings because of its relative hydrophobicity compared to other natural substances (*Azeem et al., 2016*). In spite of this, lignin needs to be modified in order to be incorporated into an effective coating. Kraft lignin current price is higher than other bio-polymers, 600- 800 U\$S/ton (*Dieste et al., 2016*), which is an important disadvantage. In this work lignin was hydroxymethylated to improve its reactivity towards phenol-formaldehyde resin (PF resin), while the acetylation of lignin allowed it to be blended with cellulose acetate.

LITERATURE REVIEW

2 Background on Controlled Release Fertilizers

Coated controlled release fertilizers (CCRF) are the most widespread controlled release fertilizers because the amount of material required by the coating (4-15%) is much lower than when the fertilizer is contained inside a matrix (up to 40%). This is so because the added material reduces the nutrient concentration of the fertilizer.

Sulfur coated fertilizer is the oldest and most economical CCRF (*Trenkel, 2010*). However, sulphur is impermeable to water, so that no fertilizer is released until the coating breaks, abruptly liberating all its nutrients to the soil. The behaviour of the fertilizer is determined by the distribution in which each particle fails in time. As a consequence its behaviour is very difficult to control, and a third or more of its content may still be unavailable after the crop season.

Polymer-coated fertilizers have been developed to deliver a higher precision in its nutrient release. The release behaviour of these fertilizers can be predicted much more reliably than sulphur coated fertilizers. In addition, they are insensitive to soil properties such as pH, salinity and microbial ability. Their behaviour is affected by temperature and soil moisture (*Trenkel, 2010*). Some of the materials used as coatings are ethylene-vinyl-acetate, polyethylene and polyurethane.

The main obstacle to the widespread use of CCRF is its high price compared to conventional fertilizers. Its use is more easily justified for high value crops. As a result CCRF are seldom used in large scale crops, while having a higher penetration in horticulture and gardening markets. The

factors that explain its high price are:

- Complex production process and low scales
- Expensive coating materials relative to the fertilizer (10 to 30 times more expensive)
- Complex sales strategy with specialised vendors and more information regarding its properties to justify its use

In 2004 the estimated consumption of CRF did not amount to a 0.2% of the global fertilizer consumption (*Trenkel, 2010*). In spite of this CRF is a fast growing market segment, with an estimated annual growth higher than 6% during the period 2016-2021 (*Global Marker Insight, 2017*).

Some polymer-coated fertilizers are not biodegradable and leave a coating residue that remains in the soil, which may represent up to 50 kg/ha year. This poses the challenge of developing biodegradable coating materials, while at the same time retaining its properties during the crop season (*Trenkel, 2010*).

3 Coated Controlled Release Fertilizer Release Models

The controlled release mechanism depends on the coating material. In general, polymer-coated fertilizers behave according to a diffusion model, while sulfur-coated fertilizers follow a 'failure' mechanism'. Polymeric coatings endure the osmotic pressure and allow for the nutrients to diffuse across the membrane after the particle has completed its hydration (*Azeem et al., 2014*).

A successful multi-stage diffusion model explaining the release behaviour for polymer-coated fertilizers was developed by Shaviv (2003) consisting of three stages.

At first the fertilizer particle hydrates, this means that water diffuses across the membrane into the particle. The driving force for hydration is the difference in water vapor concentration between the outside medium (soil or water) and the inner core of the particle. This stage is defined as 'lag' phase because no fertilizer is released.

Once all the internal voids of the particles have been filled with water, the nutrient begin to diffuse across the membrane away from the particle. At first the concentration inside is constant because the particle contains both saturated nutrient solution and solid fertilizer. Assuming that the outside concentration is negligible, then the concentration profile reaches a steady state in the membrane. As a result the nutrient flux is constant and this period is known as 'linear release stage'.

The constant stage ends when all nutrient in solid state has been consumed. At this point the solution inside the granule is no longer saturated and its concentration starts to decrease. This period is known as 'decaying phase'. Although the release rate decreases, all nutrient should be released if given enough time.

The fractional release is defined as the proportion of the initial fertilizer mass that has been released at a given time. Equation 1 predicts nutrient fractional release, which is composed of three equations, each one corresponding to a different phase of the model. The equations are listed in chronological order.

$$g(r, l, t) = \left\{ \begin{array}{l} 0, t < t' \\ \frac{3P_s A C_{sat}}{rl} (t - t'), t' \leq t < t^{\circ} \\ \left(1 - \frac{C_{sat}}{\rho_s}\right) \exp\left[\frac{-3P_s}{rl} (t - t^{\circ})\right], t^{\circ} \leq t \end{array} \right\} \quad \text{Eq. 1}$$

The parameters involved are: a) the product rl (where r is the particle radius and l is the coating thickness); b) the concentration of a saturated fertilizer solution (C_{sat}); and c) the permeability of the coating to both water and solute (P_s).

The solute permeability is the relation between the flux of nutrient and its driving force, which is the different in concentration between the inside of the particle and the outside medium. The permeability depends on the membrane, the fertilizer involved and temperature.

During the linear release stage the release rate (nutrient released per unit of time) can be calculated by Eq. 2.

$$\frac{\partial m(t)}{\partial t} = \frac{P_s}{l} A C_{sat} \quad \text{Eq. 2}$$

Where $\partial m(t)/\partial t$ is the release rate, P_s is the solute permeability, l is the coating thickness, A is the surface area of the particle and C_{sat} is the concentration at saturation. This equation has been used to estimate the solute permeability.

Shaviv calculated the urea permeability of modified polyolefin ($1.0 \times 10^{-5} \text{ cm}^2 \text{ d}^{-1}$) and polyurethane-like coating ($2.5 \times 10^{-5} \text{ cm}^2 \text{ d}^{-1}$). Du *et al.* (2006) studied phosphate release of the Multicote® fertilizer, finding longer lag-times and slower release than for nitrogen and potassium fertilizers, suggesting strong interactions among nutrients in the fertilizer granule.

In practice, the fertilizer that is applied to the soil is composed of different granules whose size and thickness may vary. A statistical analysis showed that a population of granules behaves in the same way as a single granule with average properties if the standard deviation of size and thickness are low enough (Shaviv, 2003). The coefficient of variation of these properties should be lower than 10-20%.

4 Background on Kraft Lignin

Lignin is the second most abundant natural renewable polymer after cellulose. It is found in all vascular plants, Gymnosperm species contain more lignin (30%w) than angiosperm species (20-25%w), followed by Gratiaceae (Duval and Lawoko, 2014). For instance, Eucalyptus Grandis has a lignin content of 25%w (Cebreiros *et al.*, 2017), being one of the most widely cultivated species in uruguayan plantations.

Kraft pulp mills separate lignin from the pulp, in the form of a lignin-rich black liquor which is currently being burnt to generate electric energy. Since the price of electric energy in Uruguay has reduced as a consequence of the installation of wind farms, the profitability of electric generation from biomass resources has reduced (Paseyro, 2012). For this reason, the development of more valuable lignin products will have a stronger impact on the economics of pulp production in years to come.

Only a 5% of lignin produced worldwide is destined to valuable applications, while the majority is used to produce energy (Cazacu *et al.*, 2012). Therefore, a huge potential remains for its valorisation in chemical products.

Lignin is an amorphous phenolic polymer with a non-defined structure and a high molecular weight, from 1000 to 20000 kDa (Duval, Lawoko, 2014). The variability in the molecular weight is a consequence of the random order of its monomers. Lignin is made of three basic phenylpropane units (monolignols): *para*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The difference between them lies in the number of methoxy groups in the meta positions. Its structure has two different parts, one is aromatic and the other is a three carbon chain. The relative abundance of the monomers in lignin depends on the vegetable specie and the particular tissue (García Calvo-Flores *et al.*, 2010).

The main linkages between phenylpropane units of lignin are aryl ether linkages, the more important of which are β -O-4 aryl ether bonds. Hardwood lignin contains about 1.5 times more β -O-4-linkages than softwood lignin. Other major linkages include β -5-, 5-5-, 4-O-5-, β -1-, α -O-4- and β - β linkages (Chakar *et al.*, 2004).

Lignin has the following functional groups: aliphatic hydroxyl, phenolic hydroxyl, methoxy, carbonyl and carboxyl groups (Duval and Lawoko, 2014). Its glass transition temperature ranges between 70°C and 170°C, depending on its structure and molecular weight distribution (Glasser *et al.*, 2000).

Lignin properties do not depend only on the vegetable specie, but also on

the extraction and purification process. The majority of lignin produced industrially comes as a by-product of wood pulp production, generally obtained by the Kraft or sulfite processes. The first one is known as Kraft lignin, while the second one produces lignosulphonates. Kraft lignin is relatively free from sulfur. Conversely, lignosulphonates contain polar sulphonate groups and a higher average molecular weight (*Pandey, 2010*). Lignocellulosic bioethanol production does also generate lignin as a by-product. Other lignin extraction processes include organosolv, where lignin is extracted from wood with an organic solvent, and alkali lignin, where wood chips are cooked in an a sodium hydroxyde solution.

The Kraft process for the production of wood pulp involves a high temperature treatment with aqueous sodium hydroxyde and sodium sulfide. Under these conditions most β -O-4 linkages are hydrolysed and the resulting lignin is dissolved in the alkaline solution (approximately 90-95% of the lignin present in wood) (*Chakar et al., 2004*).

Kraft lignin is recovered by acidifying the black liquor with a mineral acid or carbon dioxide. A lignin slurry precipitates, which must be washed to remove salts and then dried (*Dieste et al., 2016*). This principle has been proven in large scale operations, there is a Kraft lignin recovery plant using a patented LignoBoost process working in Canada. The lignin generated in this process is highly modified, insoluble in water and soluble in strong alkaline solutions.

The lignin structure is modified during the Kraft cooking process in many ways. The molecular weight of Kraft lignin reduces as a result of its degradation. Phenolic content increases due to the cleavage of β -O-4 linkages and demethylation. Condensation give rise to new carbon-carbon

bonds between phenyl propane units, including stilbene structures. Carboxylic acid groups are generated through oxidation and cleavage of lignin-carbohydrate linkages.

5 Lignin in Controlled Release Fertilizers

Lignin is being actively investigated as a raw material for different applications such as emulsifiers, antioxidants, adhesives, thermoplastic materials and bio-fuels (*García Calvo-Flores et al., 2010*). Much work is still necessary to develop valuable applications for lignin that could be produced in large scale. Some studies have tested lignin as a component in coatings and matrixes for the controlled release of fertilizers.

Mulder et al. (2011) coated urea granules with soda-flax lignin (Bioplast), together with plasticizers (acronal¹), hydrophobic compounds (ASA²) and cross-linkers (formaldehyde). Different lignin varieties were tested, Bioplast was selected because its films showed better water resistance relative to Indulin AT and lignosulphonate. The last one was found to be completely soluble in water.

Lignin was dispersed in 0.5 N sodium hydroxyde to prepare a solution containing 25 wt% lignin together with 6.25 wt% acronal (relative to lignin) and another additive (ASA or formaldehyde). Particles were sprayed with the solution inside a pan coater, the temperature was adjusted at 70°C. The particles were submerged in water and the urea release measured with a refractive index meter. The most effective coating tested had 3.3 wt % ASA, where a 60% fractional release was observed at 30 minutes after immersion. The urea release rate was reduced but did not meet industrial

1 Acronal® is an all acrylic liquid plasticizer manufactured by BASF

2 Alkenyl succinic anhydride

standards. It was suggested that the chemical modification of lignin could improve the performance of the film.

A fertilizer was prepared by coating triple superphosphate with a solution containing pine Kraft lignin (Indulin AT) and natural rosins³, with ethanol as a solvent. The coating content ranged between 5 and 26%w. A test was performed introducing the fertilizer in water and measuring phosphorus release. The release curves adjusted well to a kinetic equation of first order, including a linear behaviour during the first 4 days of the experiment. It is noteworthy that the release rate decreased sharply long before all the fertilizer passed to the solution (*García et al., 1997*).

Lignin has been blended with urea in liquid state (*Fernández-Pérez et al., 2007*). Although this fertilizer is not coated, it was included here because it uses lignin as the matrix of a controlled release fertilizer. Urea and pine Kraft lignin (Indulin AT) were mixed in a glass reactor, then heated at 120°C for 20 min. At this temperature urea is in liquid state. Two formulations were prepared, one with 80 wt% urea and the other with 88%. After cooling the resulting material was milled and sieved to obtain granules in the 0.5-5 mm range. At 2 hours after immersion in water the 80% of urea had been released from the granules.

6 Lignin Applications in Resins and Plastic Materials

It has been stated that the hydrophobicity and water resistance of a coating are fundamental properties for the success of a CRF membrane. Likewise, these characteristics are also desirable for many applications,

³ Pine extractives; Natural, dimerized (Residys Polymer) and esterified (Resiester T) rosins were used as the lignin's adhesive in that work

such as adhesives and plastic materials. As a result, the strategies developed for Kraft lignin modification in these areas might be useful for making CRF coating. Some of them were pursued in the experimental part of this thesis.

Lignin can be used as a co-monomer in the production of phenol-formaldehyde resins, epoxide resins and polyurethanes. Nowadays, all these resins are produced from petrochemical feedstocks. Some polymerization reactions such as the manufacturing of polyurethanes and polyesters involve any hydroxyl group of lignin. Other resins, such as PF and epoxides, react only with the phenolic hydroxyl groups.

Most studies revised during this literature review modified lignin before synthesizing the polymers. Many papers commented that the low reactivity of lignin required it, as lignin has only a moderate amount of phenolic hydroxyl groups and contains steric hindrances that slow to the polymerisation reactions.

6.1 Phenol-formaldehyde resins

Phenol-formaldehyde (PF) resins has been the most investigated area for lignin use as a co-monomer. The largest users of PF resins are the plywood and reconstituent wood products industries, which employ mainly resols (*Malutan, 2008*).

Although there is an important amount of work published on the use of lignin to prepare PF resins, there are few records of its practical applications. The principal limitation to the use of lignin in PF resins is the pressing time of the final wood product, which is a consequence of its low reactivity. Mixes of PF resin and hydroxymethylated lignin have been used

in some plywood mills, with substitutions up to 30 %wt. However, the long pressing times made impractical its application in particleboards and panels (*Stephanou Pizzi, 1993*).

6.2 Polyurethanes, polyesters and epoxy resins

Polyurethanes are useful for both rigid components as well as foams. In this case lignin can substitute the usual petrochemical polyols. Nowadays, little success has been reported in the use of lignin in polyurethanes because lignin decreases the flexibility of the material. It is important to point out that flexible foams are the biggest application of polyurethanes. *Bernardini et al. (2015)* obtained a suitable polyurethane for packaging purposes containing 12 %wt lignin. Lignin was liquefied with polyols (glycerol and EJ 300) at 140°C and 2 minutes prior to its use in polyurethanes.

Lignin offers the potential of substituting bisphenol-A in the manufacturing of epoxy resins, as lignin contains free phenolic groups that can react with epichlorohydrin. Epoxy resins play a key role in the electronics and composite materials industries. In most studies lignin was chemically modified before the epoxidation reaction because the direct use of lignin would be challenging due to its low reactivity (*Ferdosian et al., 2014*).

7 Chemical Reactions to Increase Lignin Reactivity

Possible lignin modifications should increase its reactivity. There are different methods available, the most promising ones are phenolation, depolymerisation and hydroxymethylation (*Malutan, 2008*). Others such as demethylation and fractionation have been less studied.

7.1 Phenolation

Phenolation refers to the reaction of phenol with lignin in acid medium and high temperatures. The incorporation of phenols takes place through the hydroxyl groups in the α and γ carbons of the lignin structure (*Podschun et al., 2015*). This process directly increases lignin reactivity if lignin is to be incorporated in PF or epoxy resins. In addition, a reduction in molecular weight was reported, so that it should have less steric hindrances and hence be more reactive.

Podschun et al. (2015) reacted organosolv lignin with 6.7% sulphuric acid (relative to L+P) at 110°C for 20 min. The aliphatic hydroxyl group content reduced from 4.1 to 0.2 mmol g⁻¹, resulting in a lignin with almost exclusively aromatic OH groups. The process created 4.5 mmol g⁻¹ of new phenolic OH groups. Meanwhile, the average molecular weight reduced from 4100 to 2200 g mol⁻¹. The maximum degree of phenolation was achieved with a phenol/lignin ratio of 2.0.

7.2 Depolymerisation

Lignin depolymerisation has been extensively studied, generally with the aim of producing fuels and value-added chemicals. Thermochemical

methods include pyrolysis (thermolysis), gasification, hydrogenolysis, chemical oxidation, and hydrolysis under supercritical conditions (*Padney et al., 2011*). The substances produced by some of these methods have a higher phenolic content than lignin, particularly hydrogenolysis and base-catalysed depolymerisation.

Lignin hydrolysis is known to take place in aqueous alkaline medium, probably by the same mechanisms than in the pulping process (*El Mansouri, 2006*). El Mansouri cooked calcium lignosulphonate at 170°C for 90 min. at an initial pH of 12.7. Phenolic OH groups increased from 2 mmol g⁻¹ to 2,6 mmol g⁻¹ while the average molecular weight reduced from around 1400 to 1086 g mol⁻¹. The aqueous solution to be hydrolysed contained 10 %wt lignin and 2 %wt sodium hydroxyde.

Ferdosian et al. (2014) subjected organosolv lignin to an alkaline hydrolysis with the purpose of making epoxy resins. The best pre-treatment was 8h, 55°C and 6.3 NaOH/L molar ratio for hydrolysis, according to the epoxy content of the products.

7.3 Hydroxymethylation

Hydroxymethylation is the simplest method for the chemical modification of lignin to be used in PF resins. During this reaction hydroxymethyl groups are introduced in the lignin structure. Lignin reacts with formaldehyde in an alkaline medium at a temperature range of 40- 60°C. Although lignin hydroxymethylation does not increase the number of reactive sites, it facilitates the formation of methylene and ether bridges with the PF structure.

Under these conditions the Lederer-Manasse reaction occurs (*Malutan,*

2008), whereby the hydroxymethyl groups are introduced in the aromatic rings of lignin. On the other hand, two undesirable reactions take place. One is the Cannizaro reaction, where formaldehyde reacts with itself. The other is the Tollens reaction, where formaldehyde reacts with the carbonyl groups in the aliphatic chains of lignin (*Marion et al., 1966*). According to the results of Zhao et al. (1994), the Tollens reaction has a modest extent in the hydroxymethylation of Kraft lignin. They found that 0.36 mol of formaldehyde was introduced per unit of lignin monomer (C9), with 0.33 mol CH₂OH/C9 corresponding to the Lederer-Manasse reaction. In that work pine Kraft lignin was reacted with formaldehyde at pH 12 and 50°C, with a CH₂OH/C9 molar ratio of 1.

Malutan et al. (2008) studied the reaction conditions for the hydroxymethylation of alkali Sarkanda grass lignin. A substantial addition of lignin hydroxymethyl groups was achieved at 50°C and pH 10.5. Increasing amounts of NaOH resulted in higher formaldehyde losses without an improvement in the hydroxymethylation efficiency.

After a hydrolysis pre-treatment, El Mansouri (2007) hydroxymethylated a lignosulphonate by adding formaldehyde in a 0.12 NaOH/lignin mass ratio and reacting it at 58°C for 8 h. It was found that the optimum degree of hydroxymethylation depends on the lignin molecular weight. If too much formaldehyde is reacted, the resin hardens too fast, causing a lower density of crosslinking and lower strength in the PF-lignin blends (*El Mansouri, 2007*).

8 Lignin in Thermoplastic Polyblends

The physical blend of different polymers offers the potential of improving its properties while reducing costs. The incorporation of lignin in polymers has been investigated for a long time with the aim of improving its properties or reducing its environmental impact, although there have been limited practical results.

The components of a blend might be miscible or not. In the case of non-miscible blends, its stability depends on the size of the particles of the dispersed phase and the interfacial adhesion, being possible to achieve a reasonable mechanical resistance. Non-miscible blends show more than one glass transition temperature. The miscibility between two polymers depend on the interaction forces such as hydrogen bonds, dipole-dipole or Van der Waals (*Feldman, 2002*).

The blends of lignin with non-polar materials such as polyolefins generally result in a low interfacial energy, and hence poor mechanical properties (*Feldman, 2002*). The experiments with polyethylene and polypropylene have not shown promising results. In addition, lignin has been studied as an additive for UV protection or antioxidant in these polymers, with concentrations lower than 5 %wt. Pouteau et al. (2003) reported that the main challenge for lignin as an antioxidant in polyethylene was its low solubility in the polymer. The compatibility improves with lower molecular weights and lower hydroxyl group content.

Polymers that contain polar groups establish stronger interactions with lignin. Industrially, polyester are an important group of polymers containing polar groups, and blends with lignin have been prepared at laboratory

scale. A blend of lignin (85 %wt), polyvinyl acetate and two plasticizers was prepared with reasonable mechanical properties (*Li et al., 1997*).

Many studies have experimented with blends of lignin together with biopolymers such as cellulose, polysaccharides and proteins, playing an important role as a hydrophobic agent (*Baumberger, 2002*). Lignin has been observed to improve the water, UV and microbial resistance of soy protein (*Arancibia et al., 2014*).

A thermoplastic material composed of cellulose, lignin and natural additives has been developed and produced at industrial scale under the trademark Arboform. This material can be molded with conventional technology, and the final product resembles wood (*Nägele et al., 2002*).

8.1 Acetylated lignin

The compatibility of lignin with other materials can be improved through chemical modification, although the associated costs may render it non-competitive with other polymers.

One approach to modify the polarity of lignin is to esterify its hydroxyl groups using organic anhydrides. The product becomes more hydrophobic as lignin as hydroxyl groups are removed, facilitating its blending with other polymers. However, its compatibility with synthetic polymers is still far from being acceptable (*Jeong et al., 2011*).

Lignin acetylation has been the most studied esterification method. In the work of Jeong, lignin and acetic anhydride were heated together. Afterwards water was added to stop the reaction and hydrolyse the remaining acetic anhydride. The acetylated lignin decanted in the bottom

phase and was washed with water until it became neutral. Finally it was washed with methyl alcohol and then vacuum-dried.

Gordobil et al. (2015) achieved a 93% conversion of hydroxyl groups in the acetylation reaction. In that experiment Kraft lignin was dissolved in formamide and pyridine was added as a catalyst before the reaction with acetic anhydride. The product had a higher molecular weight and lower polydispersity than the original lignin, indicating it was more homogeneous. The glass transition temperature reduced from 115-125°C to 105°C.

Films of acetylated lignin are very brittle and voids were observed inside the surface, although it had been vacuum-dried at 60°C. Therefore, it was assumed that some gas products were produced by thermal degradation (*Jeong et al., 2011*).

Membranes were casted with acetylated lignin and cellulose acetate. The solvent used was acetone and the non-solvent was water. Cellulose acetate gave elasticity to the membrane while lignin acetate controlled the surface hydrophobicity (*Musa, 2016*).

EXPERIMENTAL WORK

9 OBJECTIVES

The aim of these experiments was to develop and test the barrier properties of different lignin-based coatings applied to single superphosphate. The objectives of this master thesis work are:

- Develop lignin-based coatings for single superphosphate fertilizers, including the appropriate chemical modifications for lignin, necessary additives and choice of solvent.
- Compare the performance of fertilizers resulting from coating single superphosphate with different films
- Adjust the release behaviour of phosphorus in water to a suitable model
- Compare the behaviour of the fertilizers under different temperatures.

Two different paths were followed to improve lignin properties:

- Thermoset resin (HML-talc-PF) composed of hydroxymethylated lignin and phenol-formaldehyde (PF) resin, with talc as a filler. These materials were dissolved/dispersed in a sodium hydroxyde aqueous solution that was sprayed on the fertilizer particles.
- Thermoplastic blend (AL-CA) of acetylated lignin and cellulose acetate. Acetone was used as a solvent and the particles were painted manually with a brush.

In both cases lignin had to be modified before making these coating materials. In the case of HML-talc-PF coatings the most important reaction is hydroxymethylation in order to increase its reactivity towards PF resin. In addition, a hydrolysis pre-treatment was performed to increase the phenolic content of lignin. Likewise, lignin had to be acetylated to reduce its barrier properties for the AL-CA coating.

10 MATERIALS AND METHODS

Lignin was precipitated from *Eucalyptus spp* Kraft black liquor by acid precipitation with sulfuric acid. The lignin produced was 96,4% purity; lignin properties are listed in Table 1 (*Dieste et al., 2016*). Black liquor was

Table 1: Lignin properties

lignin property (unit)	(unit)
LHV (MJ kg ⁻¹)	2.2
bulk density (freely settled dry lignin) (kg m ⁻¹)	804
particle density (kg m ⁻¹)	1010
acid-insoluble lignin (%wt, dry basis)	86.7
acid-soluble lignin (%wt, dry basis)	7.4
carbohydrate content (%wt, dry basis)	0.7
elemental analysis (%wt, dry basis)	
C	60.4
H	5.3
N	0.2
S	3.5
O	28.5
ash content (%wt, dry basis)	2.1
Na (ash %wt, dry basis)	13.7

Molecular weight was assumed to be 180 g mol⁻¹
 LHV (Low Heating Value)
 (*Lin and Dence., 1992*)

obtained from a local pulp mill. Single superphosphate granules were obtained from a local fertilizer company. The phenol-formaldehyde (PF) resin was provided by Hexion, Uruguay (water content 57 ± 1 %, viscosity 800 ± 300 cPs, pH 11.5 ± 0.5 , specific weight 1.190 ± 0.01 gcm⁻³). Cellulose acetate was kindly provided by Prof. Dr. Stéphan Barbe from TH Köln, Germany, (average Mn 50.000 by GPC; density: 1.3 g mL⁻¹; N20/D: 4.475; wt% Acetyl: 39.2-40.2; water by Karl Fischer: <3%).

Single superphosphate is a mixture of calcium phosphate monobasic, (Ca(H₂PO₄)₂·H₂O), and gypsum (CaSO₄·2H₂O). The phosphorus content and the phosphorus solubility in water of the fertilizer were analysed during this study. The phosphorus concentration of water saturated in single superphosphate was found to be 23.2 g L⁻¹.

Single superphosphate had 7.8 %wt elemental phosphorus content (17.8 %wt, P₂O₅). Fertilizer granules were milled in a mortar until it became a powder. 0.25 mg fertilizer were added to a 500 ml volumetric flask, which was filled with distilled water. The phosphorus concentration was analyzed and the mass of phosphorus released was calculated. The method used for phosphorus analysis is described in detail later in this chapter. According to the manufacturer superphosphate had a 51 %wt calcium sulphate content.

The granules were sieved before the coating process to obtain 2 mm particles. The granules had a mean weight of 40 mg (average of 26 granules).

10.1 Hydroxymethylated Lignin Coatings

10.1.1 Hydrolysis

Lignin was hydrolyzed in alkaline solution with a NaOH/L molar ratio of 0.8 (Alonso *et al.*, 2001). An aqueous lignin solution was prepared by dissolving 44.93 g lignin in 100 ml aqueous sodium hydroxide (8%wt). 5 ml of this solution was poured in a closed vessel, which was submerged in a controlled temperature water bath. The temperatures and times were selected in the 80-160°C and 30-120 minutes range, respectively. These ranges are based on bibliography (El Mansouri, 2006), whose range was 120-170°C and 30-90 min. The experimental setup is described in Table 2. At the end of the reaction the vessel was cooled by submerging it in ambient temperature water. The pH of the solution was adjusted to pH 7 and the resulting solid dried at under vacuum overnight at 40°C.

Table 2: Conditions for lignin hydrolysis

Trial	H ₈₀₋₁	H ₈₀₋₂	H ₈₀₋₃	H ₈₀₋₄	H ₁₀₀₋₁	H ₁₀₀₋₂	H ₁₀₀₋₃	H ₁₀₀₋₄
Temperature (°C)	80	80	80	80	100	100	100	100
Time (min)	30	60	90	120	30	60	90	120

Trial	H ₁₂₀₋₁	H ₁₂₀₋₂	H ₁₂₀₋₃	H ₁₂₀₋₄	H ₁₄₀₋₁	H ₁₄₀₋₂	H ₁₄₀₋₃	H ₁₄₀₋₄
Temperature (°C)	120	120	120	120	140	140	140	140
Time (min)	30	60	90	120	30	60	90	120

Trial	H ₁₆₀₋₁	H ₁₆₀₋₂	H ₁₆₀₋₃	H ₁₆₀₋₄
Temperature (°C)	160	160	160	160
Time (min)	30	60	90	120

The amount of free phenolic hydroxyl groups was determined by a UV absorption technique (Gärtner *et al.*, 1999), as an assessment of the improvement in reactivity. 20 mg hydrolyzed lignin was dissolved in 10 ml dioxane with 10 ml sodium hydroxide solution 0.2 M. A 1 ml aliquot of this solution was diluted to a final volume of 25 ml with NaOH 0.2 M in a volumetric flask. Its absorbance was determined at 300 nm and 350 nm in a UV-Vis spectrophotometer Shimadzu UVMINI-1240 (Japan), using a pH 6 buffer as a reference. The total content of phenolic groups in hydroxymethylated lignin was calculated by Eq. 3.

$$\text{Total OH content} = (0.25 \cdot A_{300\text{nm}} + 0.107 \cdot A_{350\text{nm}}) / (c \cdot l) \quad \text{Eq. 3}$$

Where the total phenolic group content is measured in mmol g⁻¹, A_{300 nm} and A_{350 nm} are the difference between the absorbances at 300 and 350 nm and the absorbance of the pH 6 reference solution. c is the concentration (g L⁻¹) and l is the path length through the sample (cm). Three replicates of this technique were performed starting from different samples of dried modified lignin, and the results were averaged.

10.1.2 Hydroxymethylation

Lignin was hydroxymethylated at 45°C and 5 hours with the following chemicals: analytical grade sodium hydroxide, technical grade formaldehyde 40 %v/v, lignin and water. A blank was performed with all the chemicals except lignin to evaluate the impact of the Canizzaro reaction. Lignin was not hydrolyzed before this experiment.

Three different runs were performed to evaluate the influence of the sodium hydroxyde to lignin molar ratio (NaOH/L ratio). The reaction conditions were based on bibliography (*Alonso et al., 2001*). The composition of the solutions used in this experiment is described in Table 3.

Each lignin solutions was poured in a three-neck flask, which was connected to a condenser to avoid losses of formaldehyde by evaporation. The temperature was adjusted using a laboratory heater with magnetic agitation.

Table 3: Composition of solutions used in the hydroxymethylation experiment

Solution	NaOH (%wt)	Formaldehyde (%wt)	Lignin (%wt)	Water (%wt)
M1	5.6%	7.9%	18.2%	68.3%
M2	4.2%	8.0%	18.6%	69.2%
M3	2.1%	8.2%	18.8%	70.9%

A sample was taken from the flask at certain times: 150 min, 240 min and 300 min. The formaldehyde content of these samples was analyzed following a sodium sulfite method (*TAPPI Test Methods T600.,1983*). 25 ml distilled water were added to 3 ml of sample together with 4 drops of thymolphthalein. Afterwards 0.1 N sulphuric acid was added until the disappearance of blue color. 50 ml of 1 M sodium sulphite was added. This solution was tritrated immediately with 0.5 N sulphuric acid to the colorless endpoint of the indicator. A blank was performed by titrating the reagents used without the addition of a specimen. Two duplicates were performed for each sample.

Reacted formaldehyde was calculated by subtracting the formaldehyde

content of the sample from the initial formaldehyde concentration.

At the end of the hydroxymethylation reaction lignin was precipitated with the dropwise addition of chloric acid. The precipitate was filtrated in a 400 mesh paper filter and washed four times with distiller water to remove formaldehyde and chloric acid.

The relative amount of hydroxymethyl and phenolic groups of hydroxymethylated lignin was calculated with a infrared spectroscopy method (*Malutan et al., 2008*). Lignin samples were milled to a particle size appropriate for ART-FTIR spectroscopic analysis. The spectrum was obtained from a range of 400– 4000 cm^{-1} and 4 cm^{-1} resolution. 32 scans were accumulated employing a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer (Japan). The ratios of relative absorbance for different groups were calculated by Eq. 4 and Eq. 5.

$$\text{Mean value of hydroxymethyl groups} = \text{average}(A_{2890}, A_{1460}, A_{1420}) / A_{1510} \quad \text{Eq. 4}$$

$$\text{Mean value of phenolic groups} = A_{1370} / A_{1510} \quad \text{Eq. 5}$$

Where the A_x are the peak intensities at their respective wave length. The spectrum data was processed by assigning a value of zero to the minimum value of peak intensity.

Three replicates of this technique were performed starting from different samples of dried hydroxymethylated lignin. The results from the replicates were averaged.

10.1.3 Coating of particles

Coating solutions were prepared by adding PF resin and talc to the solution that resulted from the lignin hydroxymethylation reaction. The hydroxymethylation experiment M3 was selected for coating the particles, based its higher hydroxymethyl groups content. Two formulations of hydroxymethylated lignin and phenol-formaldehyde resin (HML-PF) were prepared for phosphorus release experiments, its composition are shown in Table 4. For each formulation lignin/PF mass ratio was 2% and 10% respectively, and lignin/talc ratio was 50% for both formulation.

Table 4: Hydroxymethylated lignin coating formulatios (%wt)

Solution	NaOH (%wt)	Lignin (%wt)	Talc (%wt)	PF resin (%wt)
HML-PF_1	1.9	17.1%	8.6%	0.3%
HML-PF_2	1.9	16.9%	8.4%	1.7%



Figure 1: Pan Coater used with the hydroxymethylated lignin coatings

The coating solution was applied on superphosphate beads using a sprayer and a pan coater (Figure 1). The coater is an inclined rotating tray (diameter 30 cm, depth 6 cm, tilted 45 °) driven by an electric motor at 35 RPM. Inside the coater the granules are tumbled, thus exposing its surface area to the coating droplets. The temperature of the coater was controlled manually with a Bunsen burner and measured with an infrared camera. The coating procedure was as follows. First of all the pan coater was heated until it reached 150°C. Then 100 g of superphosphate beads were added. The granules were heated until 120°C, followed by a spray application of coating solution until it cooled to 80°C. The burner was turned off during this operation for safety reasons. The procedure was repeated until 100 ml of coating solution was used.

The coating content of the prepared fertilizers was determined by weighting the granules before and after the coating process to calculate the coating content.

The hydrolysis and hydroxymethylation experiments were performed as part of an Internship (*Di Pascua, 2015*), together with the coating of fertilizer particles by the method described above.

10.2 Acetylated Lignin Coatings

The acetylation reaction was carried out in a 500 ml three neck flask (Figure 2), where a condenser was connected to prevent solvent evaporation and a thermometer to control the temperature throughout the reaction. The temperature was adjusted using a laboratory heater with magnetic agitation.

The acetylation procedure was repeated for different reaction times to

study the acetylation efficiency. 25 g lignin and 125 ml acetic anhydride were added to the flask and gradually heated to 80°C with mild agitation. In order to stop the reaction and hydrolyze the remaining acetic anhydride 200 ml of water was added . The chemicals used and reaction conditions were taken from Musa (2016).

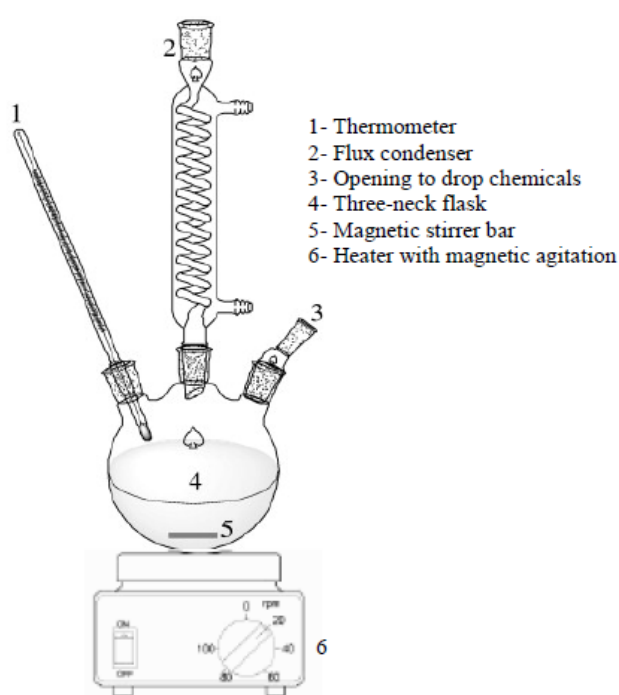


Figure 2: Diagram of equipment used for both lignin hydroxymethylation and lignin acetylation

The lignin acetate settled resulting in two phases, the aqueous phase was removed and 250 ml of water was mixed to wash the bottom phase. This decanting and washing step was repeated eight times to remove water soluble compounds. Afterwards 100 ml of methanol was added, mixed and decanted in the same manner. Acetylated lignin was washed to remove acetic acid and remaining salts (Jeong *et al.*, 2011). The resulting paste was dried at 50°C until constant weight and dissolved in 150 ml acetone.

The acetone was evaporated in an oven at 50°C for 24 hours leaving a thick film of lignin acetate at the bottom of the flask.

The acetylation efficiency was determined by ART-FTIR spectroscopy. The acetylated lignin samples were milled to a particle size appropriate for the Shimadzu IRAffinity-1S spectrophotometer. The spectrum was obtained within a range of 400– 4000 cm⁻¹ and 32 scans were accumulated. The acetylation efficiency (α) was calculated with Eq. 6 (Gordobil *et al.*, 2015).

$$\alpha = 1 - \left[\frac{\left(\frac{A_{3300 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}} \right)_t}{\left(\frac{A_{3300 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}} \right)_{t=0}} \right] \quad \text{Eq. 6}$$

Where the acetylation efficiency is the proportion of hydroxyl groups converted into acetyl groups. A_x are the peak intensities at their respective wave length. The height at 3300 cm⁻¹ is related to the presence of hydroxyl groups, while the height of the C-C of aromatic skeletal vibrations at 1510 cm⁻¹ was taken as reference.

The acetyl group content was calculated based on the acetylation efficiency and the total hydroxyl content of lignin. The later was calculated by comparing the FTIR absorbance for total hydroxyl and phenolic hydroxyl groups, given that the phenolic content was determined by an UV absorption method. These results were the average of seven different lignin samples.

The experiments to determine the influence of reaction time on the

acetylation efficiency were performed as part of an Undergraduate Project (Zeballos, 2017).

An acetylation time of 24 hours was selected for the fertilizer coating to ensure that the acetylation process was as complete as possible. A lignin acetate solution was prepared by dissolving 6.66 g of this sticky solid into 18.08 g acetone. 3.33 g cellulose acetate was dissolved in 16.37 g acetone and let alone for one hour before mixing it with the lignin acetate solution. Cellulose acetate is a complex polymer which takes time to unfold its molecular chains and completely dissolve. The resulting coating solution contained lignin acetate (15 %wt), cellulose acetate (7.5 %wt) and acetone (77.5 %wt). This proportions of cellulose acetate and lignin acetate resulted in a regular film. It was reported that higher proportions of lignin acetate left brittle films after the acetone dried (*Musa, 2016*).

This time eight granules were carefully coated one at a time with a brush and heated with a hair dryer (AL-CA coating). Each granule was weighed before and after being coated. The granules were selected in the 35 – 45 mg range, and the coating content fell in the 10–25 %wt range.

10.3 Fertilizer Performance Measurements

10.3.1 Hydroxymethylated lignin release measurements

5 g coated granules and 50 ml water were put into a 100 ml plastic container which was placed into a constant temperature incubator. The phosphorus release of the fertilizer coated with hydroxymethylated lignin was measured for 90 days. The experiment was done at 13°C and 25°C. The phosphorus content of the water was measured at days 1, 2, 3, 4, 8,

10, 14, and then weekly for 90 days. This particular sampling schedule was similar to an industrial criterion developed in China (Trenkel, 2010), and adapted to the resources available for this study.

On each sample occasion the water was removed, replaced with 50 ml distilled water into the container and returned to the incubator. This change of water rules out the possibility that a high phosphorus concentration may interfere with the release behaviour. Two duplicates were performed for each fertilizer and temperature.

The coated granules did not break easily, although the film itself was brittle when prepared on a petri dish. Since the fertilizer presented a light grey color and lignin is black, it was possible to appreciate any damage on the coating. It was observed that the coatings were strong enough to withstand the contact between granules and no damage was observed after the experiments performed with the three coatings.

10.3.2 Acetylated lignin coating release measurements

0.4 g coated granules were immersed in 25 ml water and its phosphorus concentration measured at defined intervals. This time the container was incubated at 25°C. The phosphorous release in the acetylated lignin coating was tested in a 48 hours experiment at 25°C. Samples were taken for phosphorus analysis at times 1, 2, 3, 4, 8, 12, 24, 36 and 48 h. The water was removed once at time 24 h and replaced with distilled water. Two duplicates were measured. This sampling schedule was different because it was defined after analysing the results from the hydroxymethylated lignin coating experiment described above.

10.3.3 Phosphorus measurement

The mass of phosphorus released in a day period was calculated by measuring the phosphorus concentration before a water change and multiplying it by the water volume. The total phosphorus released at a given time was calculated by adding the amount released during each day of measurement. The fractional release is the mass of phosphorus released divided by the phosphorus mass inside the particles at time zero.

The phosphorus concentration was measured by following a vanadomolybdophosphoric acid colorimetric method (*Standard Methods for the Examination of Water and Waste Water 4500-P C.*, 1998). The sample was diluted in such a way that the resulting concentration fell within the 4-20 mg/l range. A known volume of diluted sample and 5 ml vanadate-molybdate reagent were added to a 25 ml volumetric flask and completed with distilled water. The flask was given 10 minutes to allow for color development. The absorbance was measured at 420 nm. A stock solution was prepared with 4.6194 g sodium phosphate in a 1 L volumetric flask and completed with distilled water. A calibration curve was calculated daily with five calibration standards (0, 4, 8, 12, 16 and 20 mg L⁻¹ elemental P).

All the granules used in these experiments were visually inspected before and after the phosphorus release experiments. There were no visible cracks in the coatings.

The phosphorus analysis in the controlled release experiments were performed by the Group of Forest Process Engineering, School of Engineering, Universidad de la República.

10.3.4 Permeability calculations

The phosphorus permeability was calculated with Eq. 2. The saturation concentration was determined experimentally (23.2 g L⁻¹ elemental P). The coating thickness and surface area were calculated assuming the coating is evenly spread across the particle surface, knowing both the coating density and the coating content. Each particle is assumed to be a 2-mm diameter sphere. This calculation provides an approximation of the average coating thickness.

Coating density was determined by measuring the displacement of liquid in a graduated cylinder where a known mass of coating was introduced. An appropriate amount of coating solution was poured in a petri dish in order to obtain 5 g of solid coating. The solution was dried in an oven. Afterwards the solid was scraped from the petri dish and 3 g of it were introduced in a 20 ml graduated cylinder. The cylinder was filled up to 15 ml with distilled water. The coating density was calculated with Eq. 7.

$$\rho = \frac{M_{coating}}{V_{total} - M_{water}} \quad \text{Eq. 7}$$

Where ρ is the coating density (g cm⁻³), $M_{coating}$ is the solid mass (g), V_{total} is the filled cylinder volume (ml) and M_{water} (g). Three duplicates were performed for the AL-CA coating. The density of acetylated lignin was determined by the same method.

The release rate during the linear phase was calculated by a simple linear regression using the ordinary least squares method between the mass of phosphorus released and time. This method was applied only to the AL-CA

fertilizer because the other earlier experiment did not provide enough details on the linear phase period.

For this reason, the other permeabilities were estimated by comparing the behavior of the different fertilizers to that of the AL-CA coated fertilizer, which constant had already been calculated. The phosphorus permeabilities were estimated with Eq. 8.

$$P_{S_{HML-talc-PF}} = P_{S_{AL-CA}} \cdot \frac{g(24h)_{HML-talc-PF}}{g(24h)_{AL-CA}} \cdot \frac{l_{AL-CA}}{l_{HML-talc-PF}} \quad \text{Eq. 8}$$

Where $P_{S_{HML-talc-PF}}$ and $P_{S_{PAL-CA}}$ are the permeabilities of the hydroxymethylated lignin and acetylated lignin coatings respectively. $g(24h)$ are the fractional release at day 1 for the same fertilizers. l is the coating thickness of these fertilizers.

This equation is valid assuming that $g(24h)$ belongs to the linear release phase for all fertilizers and that the particles have the same dimensions (diameter). This equation can be deduced from Eq. 2 by substituting $\partial m(t)/\partial t$ by the fractional release and dividing the equations corresponding to the different fertilizers.

11 RESULTS AND DISCUSSION

11.1 Hydrolyzation of lignin

The results of the phenolic groups analysis of lignin hydrolysed at different temperatures and reaction times are represented in Figure 3.

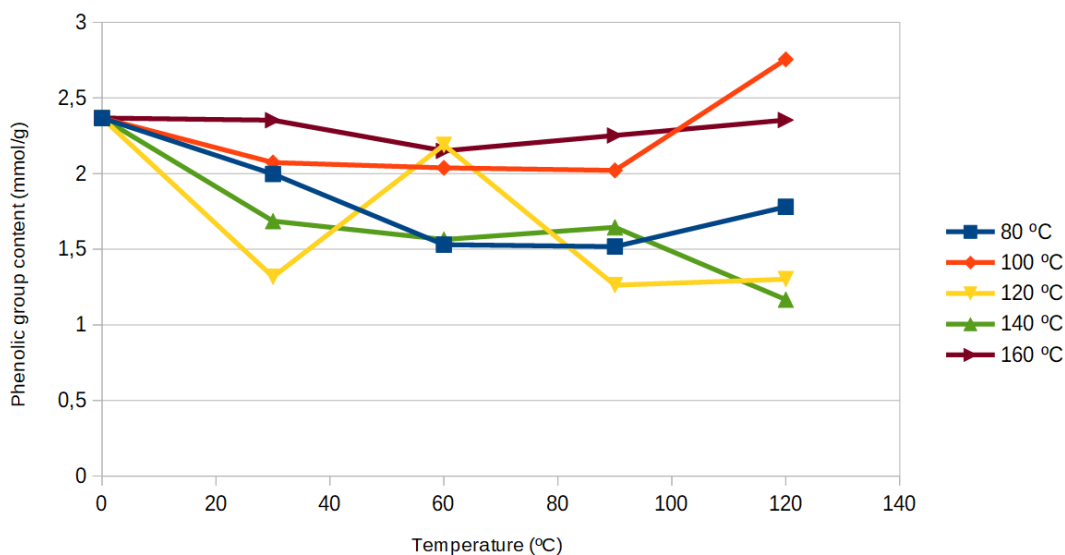


Figure 3: Phenolic group content for different hydrolysis temperatures

The results show no correlation between the amount of phenolic groups and the variables of this experiment. In general phenolic content of lignin decreased except for the experiments carried out at 160°C, which did not change significantly, and a single high value at 100°C- 120 min (2.76 mmol g⁻¹). This behaviour differs from bibliography (*El Mansouri., 2006*), where phenolic content increased continuously with both time and temperature.

The hydrolysis pre-treatment was performed in an attempt to increase the phenolic content of lignin. Since the results of this pre-treatment showed no consistent improvement, lignin was not hydrolysed before the following experiments.

11.2 Hydroxymethylation

The formaldehyde conversion in the blank samples increased with both time and sodium hydroxyde concentration, as was expected from the Cannizzaro reaction kinetics (Table 5).

Table 5: Results of the blanks corresponding to the hydroxymethylation reaction

	Blank 1 (6.8% NaOH)	Blank 2 (5.1% NaOH)	Blank 3 (2.6% NaOH)
Formaldehyde conversion at 150 min	66%	34%	26%
Formaldehyde conversion at 240 min	89%	72%	28%
Formaldehyde conversion at 300 min	92%	72%	30%

The results of the analysis done to the hydroxymethylated lignin solutions are shown in Table 6. The formaldehyde conversion increased in the same direction as the blank samples, proportionally to time and sodium hydroxyde concentration. The observed conversions in the reaction are lower than in the blank for all reaction conditions. Since the Cannizzaro reaction takes place in both the blank and the lignin reaction medium, the conversion was expected to be higher when lignin is present.

The hydroxymethyl group content increased in all experimental conditions, with a maximum in M3. The results show no clear relationship between the

hydroxymethyl group content and the sodium hydroxide concentration, but it suggests that these variables are inversely related. This suggests that the Cannizaro reaction rate increased more than the hydroxymethylation reaction rate when sodium hydroxide concentration increased, thus shifting the conversion towards the former reaction.

The phenolic group content showed a mild increase although these groups are consumed during the reaction. It has been suggested that lignin can be activated due to side reactions while being hydroxymethylated, but these effects were very small (*Malutan et al. 2008*).

M3 was selected to make the HML-PF coatings because of its higher hydroxymethyl group content. Two coating formulations were prepared with this modified lignin.

Table 6: Results of the hydroxymethylation experiment

	Unreacted Lignin	M1	M2	M3
Formaldehyde conversion at 150 min	-	49%	29%	19%
Formaldehyde conversion at 240 min	-	47%	38%	19%
Formaldehyde conversion at 300 min	-	59%	39%	22%
OCH ₃ group relative absorbance	0.69	0.84	0.8	0.91
Phenolic OH group relative absorbance	0.90	1.11	1.08	0.96

11.3 Acetylation

The acetylation of lignin was confirmed by the disappearance of hydroxyl groups, which is indicated by the 3300 cm⁻¹ absorbance band in Figure 4. A significant reduction in absorbance occurs at reaction times between 3 and 5 h.

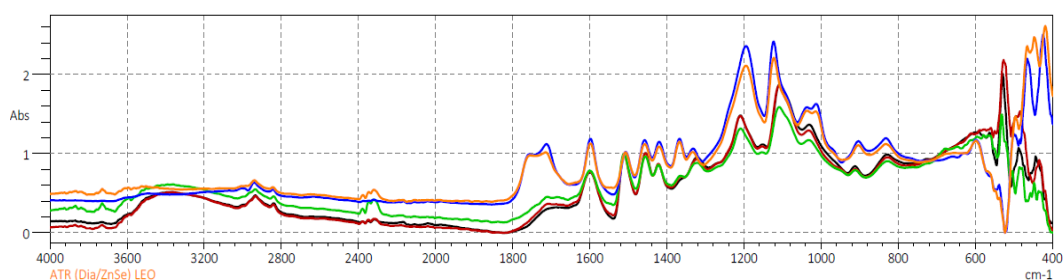


Figure 4: Fourier transform infrared spectra of acetylated Kraft lignin at different acetylation times (----: Reference, ----: 1 h acetylated lignin, ----: 3 h acetylated lignin, ----: 5 h acetylated lignin, ----: 20 h acetylated lignin)

The extent of the acetylation reaction is shown in Table 7. The results indicate no observable acetylation at times 1 and 3 hours and a sharp increase in efficiency at time 5 h. However, the acetylation achieved was always less than 50%, considerably lower than the value of 93% conversion reported by Gordobil et al. (2015). A possible explanation is that no catalyst was used in this experiment. Gordobil et al. dissolved lignin in formamide, then added pyridine as a catalyst before pouring acetic anhydride into the reaction vessel. Tertiary amine bases such as pyridine are catalyst to the acetylation reactions of alcohols and phenols (Lugemwa et al., 2013).

The ratios of FTIR absorbance for total hydroxyl and phenolic hydroxyl groups were 1.06 and 1.05 respectively. Considering this, the total hydroxyl group content was 2.4 mmol g⁻¹, hence the acetyl content of acetylated lignin was 1.01 mmol g⁻¹.

Table 7: Results of the acetylation experiment

Acetylation time (h)	1	3	5	20
Acetylation efficiency α (%)	0	0	49%	42%

A long reaction time (24 h) was selected to modify the lignin that was used for the AL-CA coating formulation.

11.4 Phosphorus Release

Figure 5 shows the fractional release of the three coatings over a 3 days period. The acetylated lignin coating was analyzed in more detail during the first two days, revealing a linear curve during the first 4 h (Figure 6). The slope is related to the phosphate permeability across the membrane because during the linear phase the aqueous solution inside the granule is saturated in calcium phosphate monobasic ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$). The linear release period starts at time zero when the granules are submerged in water, indicating that there is no lag time. According to Shaviv's model, the water vapor permeability is huge and the membrane hydrates immediately.

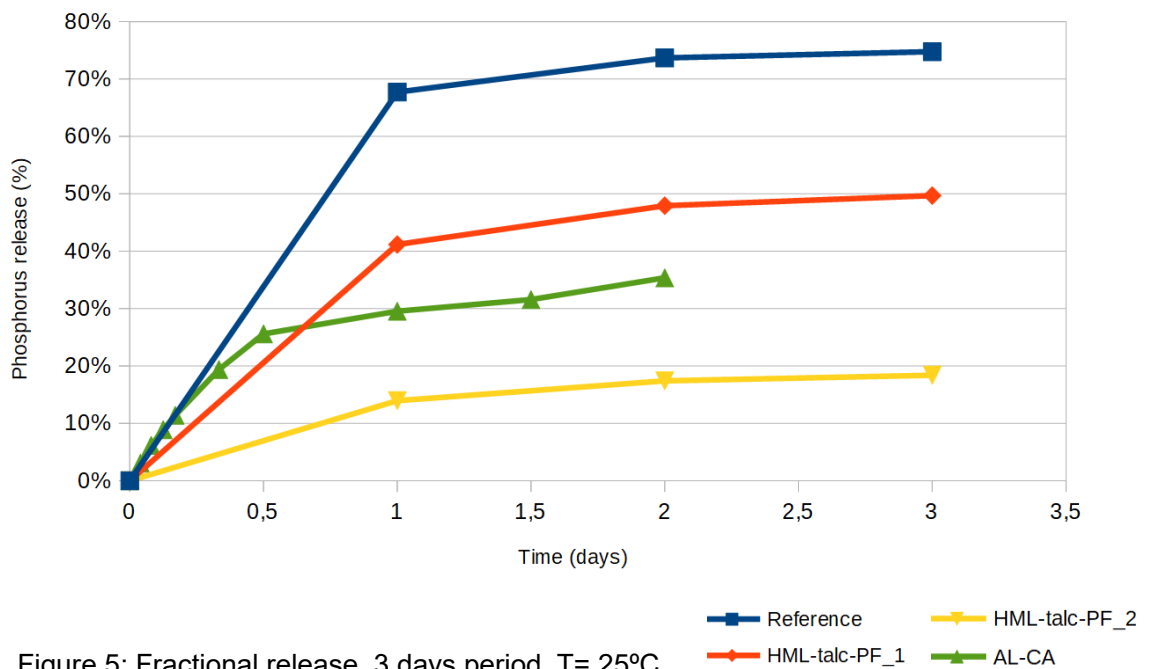


Figure 5: Fractional release, 3 days period, T= 25°C

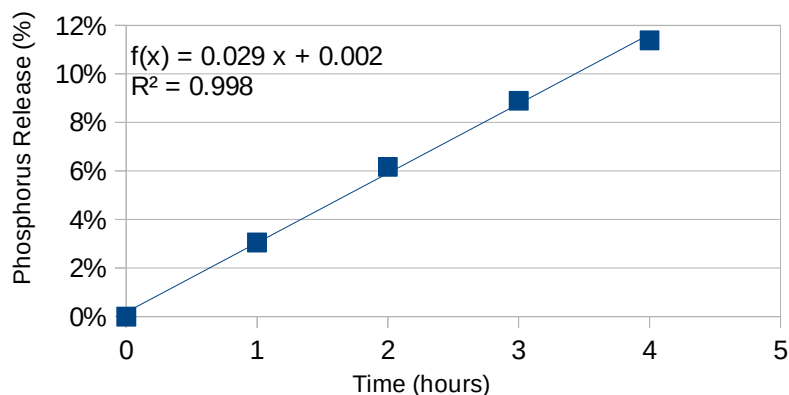


Figure 6: Fractional release from AL-CA coated fertilizer during its linear phase

The phosphate permeability was very similar for the three coatings, around $3.0 \times 10^{-2} \text{ cm}^2 \text{ day}^{-1}$. HML-PF-1 coating has the lowest phosphate permeability, although the results of the three coatings were in the same order of magnitude. These permeabilities are high compared with the results of Shaviv et al. (2003) for polyolefin and polyurethane coatings, around $1.0 \times 10^{-5} \text{ cm}^2 \text{ day}^{-1}$. Although phosphate permeability results were not reported in the work of Chang-wen Du et al. (2006), Multicote® fertilizer has lower release rates than the ones found in this work (40% fractional release at 60 days period, experiment carried out in water at 30°C). García et al. (1997) tested lignin coating bonded with rosin on triple superphosphate fertilizer, and found similar release rates to the ones reported in this work (between 10 and 40% fractional release at 4 days period, in an experiment carried out in water at 25°C).

Table 8: Coating parameters

	HML-PF-1	HML-PF-2	AL-CA coating
Coating Content (%wt)	8.50%	23.50%	13.53%
Coating Thickness (μm)	37	134	48
Coating Density (g cm^{-3})	0.74	0.74	0.72
Linear Release (mg h^{-1})	1.02	0.35	0.73
Solute Permeability ($\text{cm}^2 \text{d}^{-1}$)	2.6×10^{-2}	3.3×10^{-2}	3.4×10^{-2}

All the tested coated fertilizers presented curves which are remarkably similar. Considering this similarity, permeability values were estimated for the HML-PF coatings assuming its constant release rate is proportional to its fractional release at 24 h (Table 8).

It must be pointed out that the permeabilities calculated are approximate values because the coating thickness used in the calculations were estimated. In addition, the fertilizers coated with hydroxymethylated lignin are assumed to behave in the same manner as the AL-CA coated fertilizer, as those fertilizers were not tested in detail during the first hours of release.

The coating density of the three fertilizers were very similar, (Table 8). However, all density values were lower than expected. The density of acetylated lignin was 1.16 g cm^{-3} , which is consistent with literature values (1.05 g cm^{-3} ; *Jeong et al., 2011*). Considering that the density of cellulose acetate is 1.28 g cm^{-3} , it was expected to find coating densities higher than 1.1 g cm^{-3} .

It must be pointed out that the AL-CA coating that was scraped from the petri dish had visible bubbles and pores. In addition, during the drying of the AL-CA fertilizer it was observed that the coating swelled, as if bubbles

were growing beneath the surface. The particles seemed to have "blisters", which then imploded and the outer layer of coating attached to the inner surface. This explains the fact that the coating density was always lower than the density of its components.

It can be concluded that this process reduced the coating density. Since pores have a role in the diffusion process, the drying conditions may have affected the permeability of the membrane.

The superphosphate particles used in these experiments presented irregular shapes, a significant dispersion in particle weight and no evidence of regular film thickness. The dispersion in particle weight and coating content is known for the AL-CA experiment (Table 9).

Table 9: Mass and coating content variations in AL-CA fertilizer

	Fertilizer particles	Coating Content
Total mass (mg)	329 mg	67 mg
Average value	41 mg	17 %wt
Minimum value	36 mg	9 %wt
Maximum value	44 mg	25 %wt
Coefficient of variation (%)	7%	27%

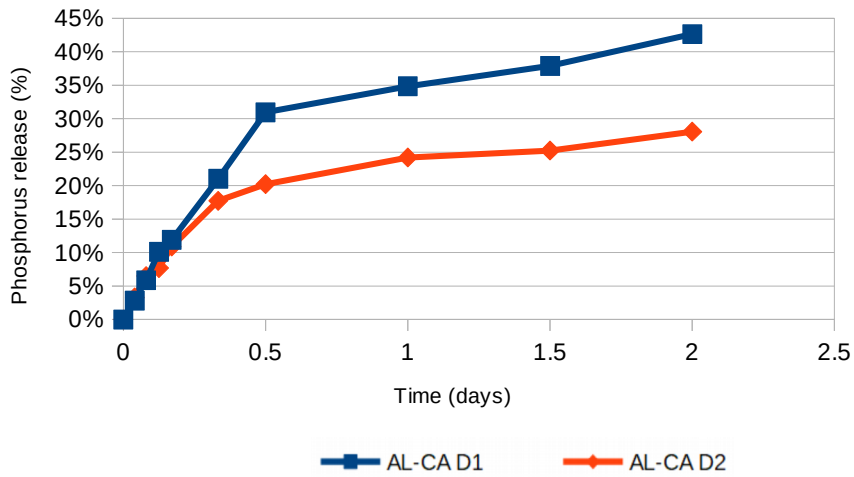


Figure 7: Duplicate phosphorus analysis for AL-CA coated fertilizer

It may be possible that the sample of particles studied in these experiments may behave differently from an ideal particle with average geometrical properties. It was reported that when the coefficient of variation is lower than 10-20%, then the population behave in the same way as if all particles had average properties (*Shaviv et al., 2003*).

In the case of the AL-CA particles, the coefficient of variation is acceptable for particle weight (7%) and rather high for the coating content (27%). The difference between the duplicate analysis was significant for this experiment (Figure 7). However, both curves are roughly equal during the linear release phase.

The duplicate analysis for all the HML-PF fertilizers show remarkably similar results (Figures 8 and 9). This convergence suggests that the average dimension of the particles was properly represented by the sample taken for analysis. The duplicate values were averaged to achieve the final result (Figure 10). It is noteworthy that the highest variations

between the duplicates was observed for the reference fertilizer.

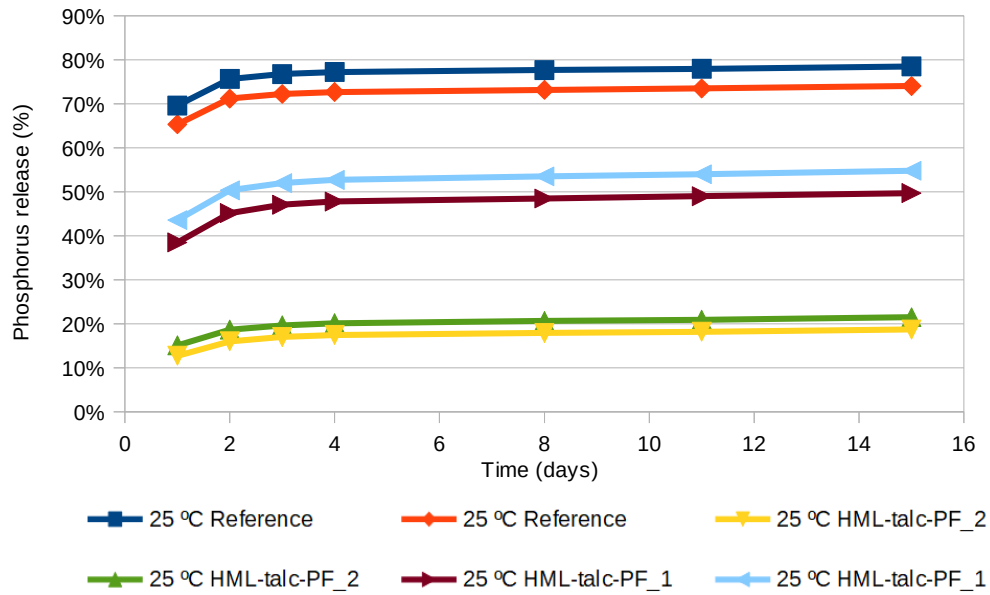


Figure 8: Duplicate analysis of the experiments with HML-PF particles at 25°C

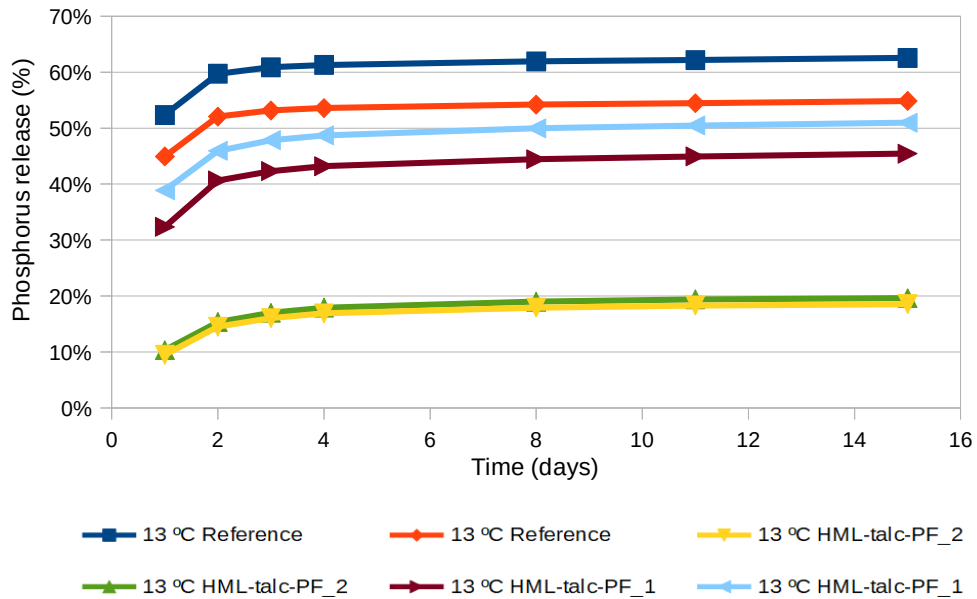


Figure 9: Duplicate analysis of the experiments with HML-PF particles at 13°C

11.5 Influence of Temperature on Release Rates

Surprisingly, the uncoated fertilizer was more sensible to the change in temperature than coated fertilizers (Figure 10). A 12°C reduction in temperature produced less than a 10% reduction in fractional release, contrary to the results obtained from Multicote® fertilizers (*Chang-wen Du et al., 2006*), where a 50% reduction was observed comparing the experiments at 30°C to those at 20°C. It is assumed that the difference between the control superphosphate curves at 25°C and 13°C is due to changes in solubility of both calcium phosphate monobasic and calcium phosphate.

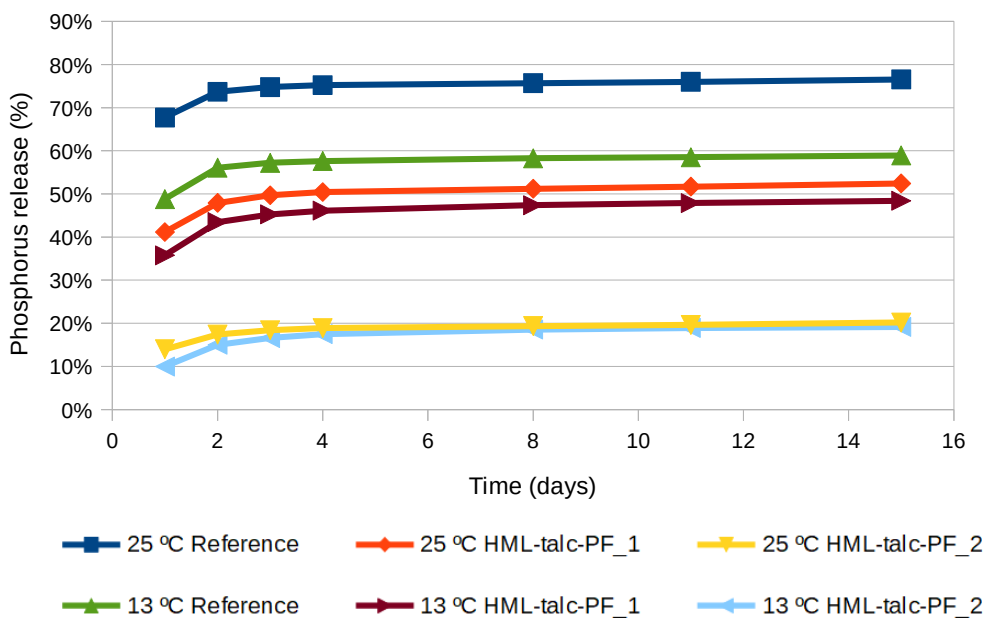


Figure 10: Effect of temperature on the hydroxymethylated lignin coating release

11.6 Maximum Fractional Release

From the linear stage curve it follows that a 80% fractional release would have been reached in less than 48 hours, however, this was not the case. The coatings could not control phosphorus diffusion effectively at the outset, but afterwards its release was prevented.

According to Shaviv's model, the constant rate release period ends when the solid fertilizer is dissolved and there is only saturated solution inside the granules. This always occur at the same fractional release, which depends only on the fertilizer. In addition, all nutrients should be released if given enough time (100% fractional release).

However, our experimental release curves show differences in both the end of the linear release period and the final fractional release. Each curve converges to a different maximum fractional release, which was confirmed in the 90 days experiments (results not included in Figure 10 for the sake of simplicity since it had already converged at day 16).

The fertilizer used, single superphosphate, contains calcium phosphate and calcium sulphate, the later one being slightly soluble at 18C°, 2,5 g L⁻¹ (Dean, 1992), relative to calcium phosphate monobasic, 327.6 g L⁻¹ (Sanyal and De Datta, 1991). The fact that it was necessary to mill the superphosphate fertilizer to reach a 100% fractional release suggests that phosphorus is entrapped inside an insoluble calcium sulphate matrix. One explanation is that the coatings may have offered a stronger barrier to calcium sulphate diffusion, thus indirectly reducing phosphorus release.

The experimental curves in the work of García et al. (1997) showed that the release rate decreased significantly long before all the fertilizer was

consumed. The difference between this work and García's is that the fertilizer used then, triple superphosphate, is completely soluble in water at 25°C. As a result there was no other salt present that may hinder phosphate dissolution. This suggests that the coating itself may play a role in explaining the observed limit in fractional release, in addition to calcium sulphate solubility.

12 CONCLUSIONS

The release behaviour of the coated fertilizers tested in this work can be explained by a diffusion mechanism. The shape of the fractional release curves were similar to the ones observed in bibliography (*García et al., 1997*). The release rate is constant when the fertilizer is submerged in water and then decreases until the phosphorus content inside the particles stabilizes. The immediate release of phosphorus indicates there was no lag phase present, so it can be concluded that the coatings are extremely permeable to water.

The permeability values of the fertilizers tested here fell in the same order of magnitude, around $3.0 \times 10^{-2} \text{ cm}^2 \text{ day}^{-1}$, which is significantly lower than the ones found in commercial fertilizers (*Shaviv et al., 2003; Chang-wen Du et al., 2006*). No conclusion could be drawn about which of the two lignin based materials is better for coating single superphosphate. The addition of more PF resin to hydroxymethylated lignin in HML-PF-2 did not decrease phosphorus permeability relative to the results of HML-PF-1. The temperature effect was relatively small compared to the consulted literature, and the behaviour of coated fertilizers were less affected by temperature than that of uncoated single superphosphate.

The transition from the linear release stage to a constant phase started at day 1, long before most of the fertilizer had been released. The maximum fractional release varied among the different fertilizers, but was always lower than 60%. The diffusion models state all phosphorus should be released if given enough time. This suggest that phosphorus release is hindered by some phenomena other than the diffusion resistance.

The most probable cause of the premature ending of the linear release stage is that part of the initial calcium phosphate monobasic is entrapped inside a slightly soluble calcium sulphate matrix. Then, the membrane was an effective barrier to calcium sulfate release, indirectly holding phosphorus inside the granule. Future research should confirm this explanation, and new ways of controlling phosphorus release with a lignin-based coating may be developed based on this idea.

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