KINETIC MODEL OF PECTIN DEMETHYLATION

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***Abstract*— Pectins are polysaccharides that act as a cellular binder in the peel of many different fruits and vegetables. An important feature of pectins is the esterification of the galacturonic acid residues with methanol. The degree of methylation is defined as the number of moles of methanol per 100 moles of galacturonic acid. The objective of the present work was to study the acid demethylation of apple pectin at different temperatures, by following changes in the degree of methylation. A solution of high methoxyl apple pectin was demethylated with concentrated HCl (pH = 0.5). The processes were carried out for 120 min at T = 80°C and 400 min at T = 65°C and T = 50°C. Anhydrogalacturonic acid content, degree of methylation and intrinsic viscosity as a function of reaction time were determined. Results showed pectin demethylation followed a second order kinetics and demethylation rate increased exponentially with temperature. Results also showed pectin "purity", as anhydrogalacturonic acid content, increased with demethylation. However, intrinsic viscosity reduced with reaction time. This behavior was associated with the hydrolysis of non-polyuronic material during the acid treatment, lowering in that way the average molecular weight.**

***Keywords*— Pectin, Demethylation, Kinetic model, Bio-polymer, Low methoxyl.**

I. INTRODUCTION

Pectic substances are glycosidic macromolecules exclusively present in plants. They are industrially extracted to be used as a food additive. The pectic substances act as lubricating or cementing agents in the cell walls of plants, also they are nutritional fibers and have many interesting medical properties (Kravtchenko *et al.*, 1992).

Pectins are complex polysaccharides, basically polymers of α-D-(1-4)- linked galacturonic acid, but they also contain neutral sugars such as L-rhamnose, D-galactose, L-arabinose, D-xylose, etc. (Schols and Voragen, 1996). As they occur naturally, the galacturonic acid sugars are usually highly esterified and are interrupted by L-rhamnose residues.

Occasionally, at points along the backbone there are sites of extensive branching involving neutral sugars, these structural features giving rise to terminology "smooth" and "hairy" regions when referring to regions of the pectin backbone (Morris *et al*., 2000). Depending upon sources, galacturonic acid residues of the pectin are esterified to various degrees, and the size and composition of neutral sugar side chains vary.

Pectins have been divided into two groups in the market: those containing more than 50% esterification (high methoxyl pectin, HMP) and those containing less than 50% esterification (low-methoxyl pectin, LMP). The main sources of HMP are **c**itrus peel and apple pomace. Commercial LMP are obtained from HMP by chemical demethylation.

Pectins provide beverage viscosity, LMP may be used as a gelling agent in low-sugar products, such as low-calorie jams and jellies, confectionery jelly products, and other food applications. The heat reversibility of LMP gels can be utilized in bakery jams and jellies for glazing, microwaving, baking, sterilizing or pasteurizing, and freezing/thawing (Kertesz, 1951).

The anhydrogalacturonic acid content (AGA), degree of methylation (DM), molecular size, distribution of carboxyl groups, and therefore the charge on a pectin molecule are important to the functional properties of pectin solutions and can affect structural and textural properties of pectin gels. Pectin viscosity is also affected by extrinsic factors such as temperature, concentration of solute, pH, and the presence of salts and co-solutes.

Although some LMP occurs in plants, they are usually manufactured from HMP. There are four methods of demethylation according to the agents used: acids, alkalis, enzymes and ammonia in alcohol. Acid demethylation is commonly used to manufacture LMP. Depolymerization is the main disadvantage of the acid treatment which hydrolyzes glycosidic bonds (Kertesz, 1951). Kim *et al.* (1978) showed that using higher concentration of acid at low temperatures gave less depolymerization during demethylation than when lower concentration and higher temperatures were used.

Padival *et al.* (1979) stated that demethylation of pectin extract at 80 and 90 °C yielded LMP of poor gelling characteristic and molecular weight decreased with increased temperature of demethylation.

The objectives of this study were (i) to prepare LMP by acid demethylation of apple HMP; (ii) to determine kinetics of demethylation at different temperatures; and finally (iii) to characterize the obtained product.