Direct determination of cationic starches in paper samples using analytical pyrolysis

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ABSTRACT

The current work presents a method for direct detection and quantification of cationic starch in paper samples. Based on analytical pyrolysis gas chromatography–mass spectrometry (Py-GC/MS), the method allows for simplified sample preparation. Furthermore, the proposed method assesses the amount of cationic starch in the presence of other starches. The cationic starch concentration in paper is calculated using a pyrolysis product from the cationic group. Therefore, the results of the described method are unbiased in the presence of other starch modifications. Validation characteristics of the method, such as standard error of calibration, limit of determination, linearity and accuracy, are reported. To demonstrate the accuracy of the novel method, a comparison against the existing reference quantification method, SCAN-P 91:09, from the Scandinavian Pulp, Paper and Board Testing Committee was performed.

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1. Introduction

Chemical additives in papermaking processes are of utmost importance. They are introduced to improve quality of the final product and production efficiency, as well as reduce costs [1].

Starch is an important additive in papermaking [2]. After lignocellulosic fibers and mineral pigments, starch is the third main component in paper [3]. Addition of starch can be done at different steps in process to adjust production parameters or achieve certain properties in end product. During the wet end process of paper production, starch is used to improve paper strength, as well as keeping fines particles in the paper and improving drainage of water [4]. During the surface-sizing of the paper, starch is used to adjust porosity, roughness and internal strength of the paper [5]. Also during coating, starch can be used as a thickener or adhesive [6,7]. Furthermore, during water treatment in the paper mill, starch can be used as a flocculating agent [8].

The various applications of starch in papermaking can be attributed to the fact that starch properties can essentially be tailored for multiple purposes using chemical modification. In the paper industry, unmodified native starch is rarely used because its functional characteristics are limited. Instead, the starch is modified in order to change the pasting temperature, viscosity, gelatinization and retrogradation behaviour, as well as its ionic and hydrophilic characteristics [9].

Typical starch modifications include etherification or esterification in the presence of an alkaline catalyst. Specially, ethers or esters linked to a functional group substitute the hydroxyl groups of the glucose unit. During the modification of starch, non-ionic, anionic or cationic functional groups can be introduced into the starch molecules [9].

The most important products from the etherification of starch are cationic starches. The cationic group enhances the molecule's polyelectrolyte properties and strengthens the attractive forces between anionic charged particles, making cationic starches important additives in the wet end process, where electrostatic repulsive forces dominate since several components are negatively charged. The negative charges in fibers are due to carboxylate groups and possible traces of sulfonic acids. This repulsion between the anionic groups hinders fibre-to-fibre, fibre-to-native starch and fibre-to-anionic pigment interactions [10]. The cationic groups in starch facilitate electrostatic [11] and ionic interactions [12] with the negatively charged fibres or pigments, which also reduces the repulsion between the anionic compounds. In addition, the affinity of the cationic starch for the anionic compounds strengthens inter-fibre and fibre-pigment bonding and improves the retention of fine particles such as cellulose fibres, pigment and filler during sheet formation.

Although cationic groups enhance the affinity of the starches for fibres and pigments, adsorption of the cationic starches is not always complete [13,14]. The unretained starch is drained from the pulp during sheet formation with the process water. Reduced adsorption of cationic starches results in lower mechanical

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strength, lower retention of fine particles and pigments and higher wastewater pollution.

According to available data [15–17] various factors may influence the adsorption of cationic starch by cellulosic fibres, such as starch concentration, charge density of the starch, water quality [17] and morphology of the cellulosic fibres [15,18].

The absorption of cationic starch by fibres is a frequently investigated topic [17,19]. Starch quantification is often done indirectly by collecting filtrates from sheet formation or extraction of the starch from the paper sample [20]. For accurate starch quantification in paper samples, complete extraction of the starch must be performed. Due to the affinity of cationic groups to the fibres, cationic starch may not be easily extracted from the paper as an unmodified or anionic modified starch [20].

In suspensions starch can be quantified by measuring the absorbance of a complex formed by starch and iodine-potassium iodide [20]. A disadvantage of this approach is that the wavelength of the absorption maximum of the starch-iodine complex depends on several factors including pH, temperature and degree of starch polymerisation and concentration of iodine-potassium iodide. Furthermore, the amylose fraction of the starch, the actual derivatization process and the degree of substitution in the starch can also influence the wavelength of the absorption maximum [21,22]. As process water becomes turbid, this method of starch quantification becomes less reliable [23].

Ulbrich et al. [24] described a method for starch determination in its polymeric form using size-exclusion chromatography with multi-angle laser light scattering (SEC-MALLS). However, the SEC-MALLS method is used for quantifying cationic starch during sheet formation at a laboratory-scale. The cationic starch concentration in paper is calculated from the depletion of starch polymers in the starch-fibre suspension during sheet formation. The amount of starch in samples from paper machine or commercial samples cannot be calculated with this method.

Another potential technique to quantify starch is the SCAN test method [25]. Extracted starches are first reduced to their monomeric form (i.e. glucose) using acid hydrolyses or enzymatic procedures [25]. Acid hydrolysis pretreatment has certain limitations since it cannot be applied to all kinds of starches [25] and cellulosic fibres can be inadvertently hydrolysed to glucose well. Using an enzymatic method permits selectivity of starch hydrolysis. However, enzymatic hydrolysis is suboptimal if the starches are modified, leading to incomplete hydolysis of cationic starches [25,26].

In order to quantify the amount of free glucose after hydrolysis or enzymatic degradation, polarimetry, high-performance liquid chromatography (HPLC); ion exchange chromatography (IC), or spectrophotometery techniques can be used.

Analytical methods consisting of several steps have been established to quantify starch in paper samples [20,24,25]. Each step may be a source of error. In order to quantify cationic starches with minimal error, a direct analysis method is described in the current study. The proposed method combines analytical pyrolysis gas chromatographic separation and mass spectrometric detection (Py-GC/MS). This technique is commonly used for quantification of additives in solid samples, avoiding laborious sample preparation. Furthermore, use of a direct analytical method reduces source of potential error sources, the use of solvents and hence, overall energy consumption. The described method was developed and validated in the current study.

2. Materials and methods

2.1. Materials and reagents

Cationic potato starches with different degrees of substitution were kindly supplied by SOLAM. Pulps, including fully bleached, spruce acid, sulfite pulp and eucalyptus sulfate pulp, were collected from industrial sources. Ten industrial paper samples with only cationic starch and diverse additives and 6 laboratory paper samples were used for testing and validation.

Hand sheets were prepared on a Rapid-Köthen hand sheet forming system according to the norm DIN 54358, where 16 g of pulp were allowed to swell overnight in 267 g of water. The pulp solution was then beaten for 10 min using a Jokro mill at 150 rpm^{-1}. The mixture was then diluted to 6.67 L to a final pulp concentration of 2.5 g L^{-1}.

For laboratory validation samples, cationic starch was added into the pulp suspension before sheet formation. Four grams of starch were suspended in 100 mL water and heated for 30 min at 95 °C to ensure complete dissolution. The starch solution was then added to the pulp suspension and stirred for 5 min. Validation hand sheets were produced using 1 L of the suspension.

For the calibration samples, the hand sheets were prepared without addition of the starch. Different amounts of starch were applied onto dry paper sheets. Various solutions of cationic starch with different concentrations were prepared with water as a solvent after complete dissolution of the starch. Approximately 250 µL of starch solution was applied to approximately 100 mg of paper. Paper sheets were dried overnight with silica gel in a vacuum oven.

2.2. Equipment

Approximately 80 ± 3 µg of the sample was weighed into a crucible. The crucible was then placed into the autosampler for the direct introduction into the pyrolysis oven.

Py-GC/MS analyses were performed using a Frontier Lab Micro furnace multiple-shot pyrolyzer (EGA/Py-3030D) equipped an autosampler (AS-1020 E). The temperature for pyrolysis was set to 500 °C. The temperature at the interface was set to 300 °C with a pyrolysis time of 0.5 s. Helium was used as a carrier gas for pyrolysis and gas chromatographic separation. After pyrolysis, the pyrolysate was directly transferred into the GC-Column with a split ratio of 30:1. A DB-WAX fused silica capillary column (30 m × 0.25 mm (i.d.), 0.25 µm film thickness) was used in the current study.

The flow rate for gas chromatographic separation was 1 mL/min. The oven of the gas chromatograph started at 37 °C for 4 min, thereafter the temperature increased incrementally by 25 °C per min up to 250 °C. This temperature was maintained for 5 min. For mass spectrometric detection, a 5973 Agilent Inert MSD with electron impact ionisation energy of 70 eV was used. The transfer line temperature from the GC to the MS as set to 280 °C. The ionisation source and quadrupole temperature were set to 230 and 150 °C, respectively. The range of the scan for the measurement in total ion count (TIC) was 35–400 m/z with a threshold of 100 and scan rate of 2.76 scans/s. The mass resolution was R (m/z 69) = 117.

If not stated otherwise samples were measured in triplicate. For tables and illustrations, averaged values are displayed. Selective ion mode (SIM) of the mass spectrometer was used to quantify of cationic starch with two mass fragments (m/z 58 and 59).

3. Results

3.1. Pyrolytic degradation of cationic starch

Pyrolysis of cellulosic materials (D-glucose linked with β-1-4 glycosidic bonds) and starches (D-glucose linked with α-1-4 glycosidic bonds) give rise to several similar pyrolysis products [27]. The pulp and starch pyrograms do not include obvious differences that allow clear distinction between them. In order to discriminate between glucose-based polysaccharides, it is necessary to treat the samples prior to pyrolysis to minimise changes that may bias