Understanding Sizing Conditions with Alkenyl Succinic Anhydride: Experimental Analysis of pH and Anionic Trash Catcher Effects on Softwood Kraft Pulp

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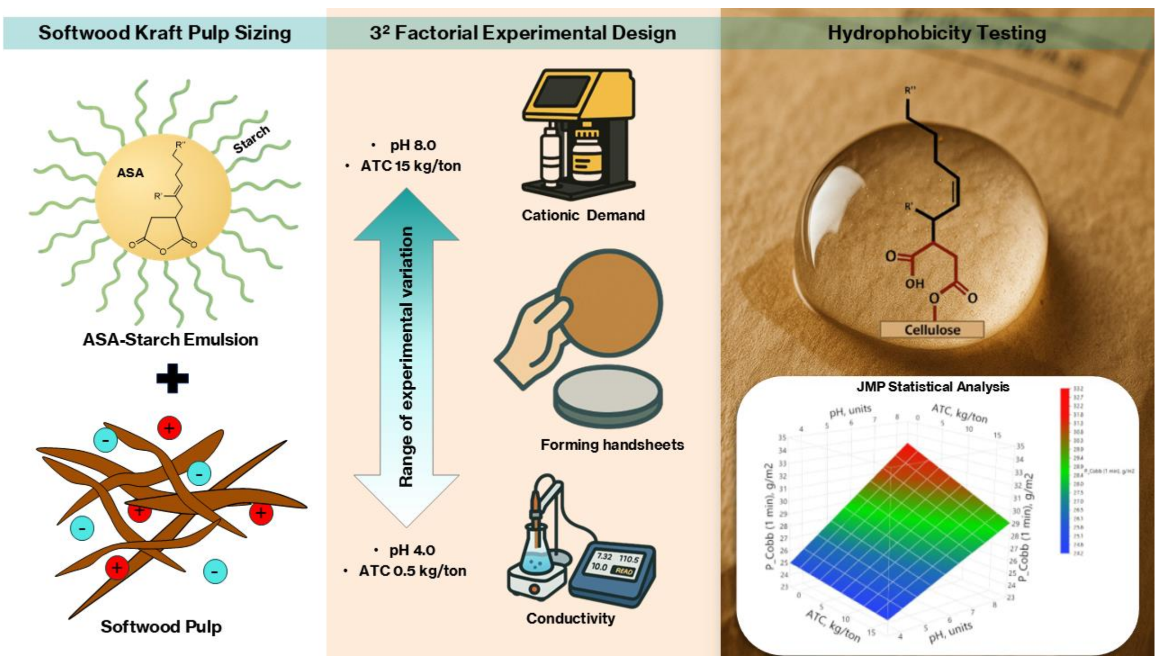
GRAPHICAL ABSTRACT



Understanding Sizing Conditions with Alkenyl Succinic Anhydride: Experimental Analysis of pH and Anionic Trash Catcher Effects on Softwood Kraft Pulp

Jorge Franco,[a] Juan Carlos Bastidas,[b] Hasan Jameel,[a] and Ronalds Gonzalez [a,]*

A 3^2 factorial experimental design was conducted to evaluate the effects of pH and anionic trash catcher (ATC) dosage on Cobb number (1 min), cationic demand, and conductivity in softwood kraft pulp sizing with Alkenyl Succinic Anhydride (ASA). Results indicated that acidic conditions tended to enhance ASA's reaction with cellulose, leading to superior hydrophobicity (Cobb number, 1 min = 23 g/m² at pH 4.0 and 121 µeq/L cationic demand). Statistical analysis confirmed that pH exerted a stronger influence on ASA performance (p-value 2.0×10^{-7}) compared to ATC dosage (p-value 0.0297), while conductivity had minimal effect. The findings suggest that optimizing ASA application in acid conditions improves water resistance, reducing reliance on high ATC dosages. This study provides valuable insights into ASA application strategies for papermaking, particularly in furnishes that do not require alkaline conditions to retain fillers, by optimizing wet-end chemistry control for enhanced sizing efficiency.

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Keywords: Alkenyl Succinic Anhydride (ASA); Anionic Trash Catcher (ATC); Experimental design; Sizing agents; Papermaking; Polyelectrolyte; Hydrophobicity

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INTRODUCTION

In papermaking, chemical additives play a crucial role in enhancing paper properties and improving process efficiency. Most chemical treatments in kraft paper production are applied at the wet end of the paper machine, where complex interactions occur between fibers, fines, dissolved ions, and process additives. These interactions involve electrostatic forces, Van der Waals interactions, hydrogen bonding, and covalent bonds, all of which affect the final paper properties (Hubbe 2006; Ntifafa *et al.* 2023). For kraft paper production, including kraft paper bags or cement sacks, achieving high mechanical strength and water penetration resistance is critical. However, since lignin-containing fibers alone naturally are hydrophilic, chemical sizing agents must be added to impart the necessary hydrophobicity (Jin *et al.* 2022). Among various sizing agents, alkenyl succinic anhydride (ASA) is widely used due to its ability to enhance water repellency in neutral and alkaline conditions (Hubbe *et al.* 2015; Kumar *et al.* 2018).

The use of ASA in papermaking has grown since the 1960s, primarily due to its compatibility with calcium carbonate fillers, unlike acid-based sizing agents such as rosin products (Ntifafa *et al.* 2023). It is commonly accepted that ASA reacts with cellulose through esterification (Fig. 1), forming strong covalent bonds that enhance hydrophobicity (Hubbe 2006; Bajpai 2010). This reaction is optimal within a pH range of 7.5 to 8.5, ensuring minimal interference with calcium carbonate fillers, which could otherwise dissolve fillers under acidic conditions (Savolainen 1996). However, despite its advantages, ASA's high reactivity and instability make its application challenging. Poor control of ASA hydrolysis and retention can result in sizing inefficiencies, deposit formation, and increased downtime due to cleaning process in the paper machine.

One of the main challenges in ASA sizing is understanding the chemical conditions that optimize its retention and reactivity. In industrial papermaking, sizing performance is typically assessed at the end of the process by using the Cobb test, making it difficult to predict issues in advance. This lack of real-time chemical control leads to quality defects, reprocessing costs, and equipment fouling. Although common laboratory measurements, such as pH, conductivity, cationic demand, and zeta potential, provide insights into wet-end chemistry, they do not reliably correlate with ASA retention and sizing efficiency. Therefore, understanding the interactions between pH, anionic trash, and ASA reactivity is essential for improving process efficiency and reducing material losses (Martorana *et al.* 2010). To address these challenges, this study applied a 3^2 factorial design to evaluate the influence of pH and ATC dosage on ASA sizing in softwood kraft pulp "kappa 56" used in kraft paper production. This approach aims to isolate key factors affecting ASA-cellulose interactions and support the development of more effective sizing control strategies.

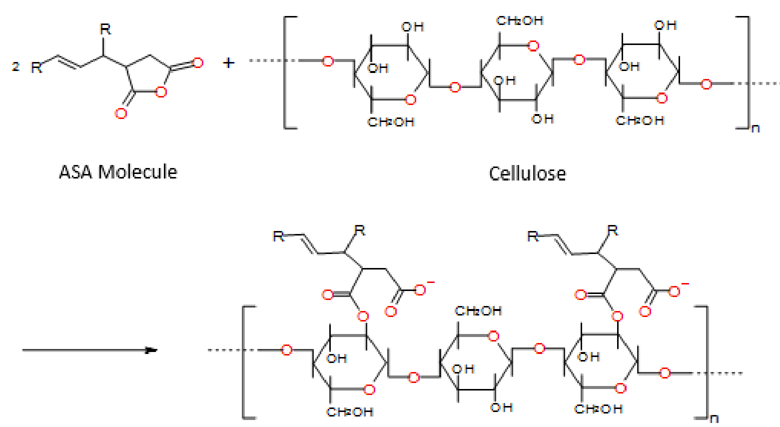

Fig. 1. ASA-cellulose esterification reaction. Adapted from (Nishiyama *et al.* 1995)

EXPERIMENTAL

Experimental Design

A randomized 3^2 factorial experiment was designed to investigate three objective variables that influence the kraft paper manufacturing process. The controlled factors were pH (4.0, 6.0, and 8.0) and Anionic Trash Catcher (ATC) dosage at three levels: low (0.50 kg/ton), medium (7.75 kg/ton), and high (15.0 kg/ton). The response variables included cationic demand, conductivity, and Cobb number (1 min) value. The experimental design was generated using JMP Statistical Discovery Software, ensuring a randomized execution of trials to minimize systematic errors. Figure 2 illustrates the interaction between the test factors and the corresponding response variables, forming the foundation of the experimental approach.

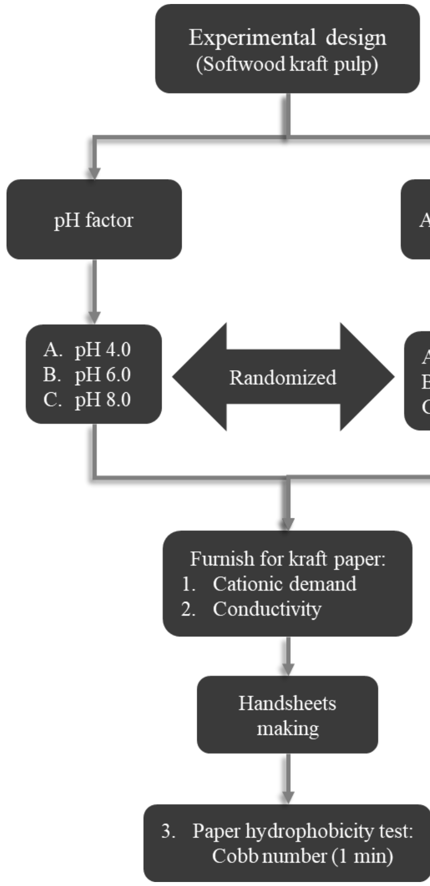

Fig. 2. Experimental design for paper hydrophobicity (Cobb number), cationic demand and conductivity testing

Materials

Table 1 lists the chemical additives used in handsheets preparation. The formulation corresponds to typical kraft paper manufacturing chemicals, except for sulfuric acid and sodium hydroxide, which were utilized as pH regulators.

Table 1. Chemicals Additives for Handsheet Making

Chemical	Dosage (kg/ton)
Anionic Trash Catcher (ATC)	0.5 – 7.75 - 15.0
Polyaluminum chloride	2.6
Alum	10
Alkenyl Succinic Anhydride (ASA)	1.0
Starch	6.0
Silica	2.0
Sulfuric acid	*pH adjusted to 4.0 and 6.0*
Sodium hydroxide	*pH adjusted to 8.0*

The Anionic Trash Catcher (ATC) used in this study is a high-charge-density, low-molecular-weight quaternary polyamine, which is commonly employed to neutralize negative charges during stock preparation. The softwood kraft pulp (kappa number 56) was obtained directly from the machine chest tank after refining, with a Canadian Standard Freeness (CSF) between 600 to 550 mL and consistency of approximately 3.6% . The pulp was then diluted to 0.4% consistency using industrial-grade water to prepare the working furnish. For each combination of the experiment was prepared a fresh softwood furnish and ASA-starch emulsion. Table 2 outlines the laboratory equipment used for the experiments.

Table 2. Laboratory Equipment

Equipment	Manufacturer
Handsheet former	Lancaster, OHIO
Handsheet press	Lancaster, OHIO
Stirrer	IKA – RW20
pH-meter	Schot - Handylab pH12
Conductimeter	Schot - Handylab FL 12
Charge analyzer (Titrant: PolyDadmac 0.001N)	AFG – CAS
Speed dryer	Labtech
Analytical balance ±0.0001g	Mettler Toledo - AG204
Scale ±0.01 g	Mettler Toledo - PB1502-S
Blender, 1 Speed, Stainless Steel	Waring - 33BL79

Alkenyl Succinic Anhydride (ASA) Emulsion Preparation

The ASA-starch emulsion was prepared using a 1:4 (oven-dry basis) ASA-to-starch ratio. Commercial cationic starch was first cooked at a 4% solids concentration, consistent with typical conditions used in paper machine, followed by the addition of ASA at the specified ratio. The mixture was then emulsified using a high-speed blender.

To ensure proper emulsion quality, the particle size distribution was monitored using an ultrasonic particle size analyzer, maintaining an average particle size of ~1 µm. Each emulsion batch was freshly prepared and stored in an ice bath for no longer than one hour after its use to prevent the formation of hydrolyzed ASA.

Handsheets Forming

The handsheets were prepared according to TAPPI T205 sp-24, “Forming handsheets for physical tests of pulp,” at a basis weight of 86 g/m² (air-dried). After pressing, the sheets were subjected to brief thermal treatment at 120 °C for 1 min using a Labtech dryer, in accordance with previous studies indicating that synthetic sizing performance improves with heat curing (Blanchard 1984). Subsequently, the handsheets were then conditioned at 23 °C and 50% relative humidity for 24 hours prior to testing. A total of ten handsheets were prepared for each experimental condition.

Furnish Measurements

After adjusting the ATC dosage and pH levels in each furnish batch, conductivity and cationic demand were measured using a 300-mesh filtrate. For cationic demand, a 10 mL sample was taken from the filtrate, and the anionic charge was titrated using a charge analyzer (AFG - CAS) with polyDADMAC 0.001N as the titrant. Another portion of the filtrate was used for conductivity measurement, performed with a Schott Handylab FL12 conductimeter. The experiments were randomized and conducted on different days to account for variability. Pulp samples were collected during stable machine operation to ensure consistency in production conditions.

Paper Hydrophobicity Testing

The Cobb number tests were conducted following TAPPI T441 om-24, "Water absorbability of sized (non-bibulous) paper, paperboard, and corrugated fiberboard (Cobb Test)." This method quantifies the water absorption of the treated handsheets, providing insights into their hydrophobicity and sizing performance.

A test duration of 1 min was selected to maintain consistency with product specifications at the paper machine. Finally, a total of five determinations were performed for each evaluated condition to ensure a statistically significant dataset, in accordance with the defined experimental design.

RESULTS AND DISCUSSION

This study employed a 3^2 factorial design to systematically evaluate the effects of pH and anionic trash catcher (ATC) dosage on the response variables: Cobb number, cationic demand, and conductivity. The factorial approach allowed for the independent assessment of each variable while ensuring a randomized experimental structure to minimize bias and enhance reproducibility. Statistical analysis plays a critical role in experimental design, particularly in complex chemical interactions where multiple factors influence the outcome (Montgomery 2017). Surface plots and interaction analyses further enabled visualization of trends, highlighting key regions where pH and ATC concentrations optimize the system's performance. The results were analyzed using JMP Statistical Discovery Software, ensuring robust statistical and graphical representation of the effects. The findings allow the understanding of chemical interactions in the system but also provide a data-driven foundation for optimizing operational conditions in kraft paper sizing applications.

Analysis of Cobb Number (1 min)

The Cobb number (1 min) test measures the water absorbency of paper and board, with lower values indicating higher resistance to water penetration. This property is crucial for applications requiring moisture resistance, such as required for packaging grades (Todorova *et al.* 2022). In this study, the lowest Cobb number (23 g/m^2) was obtained under experimental conditions at pH 4.0 and ATC doses of 15 kg/ton. Statistical results suggest that pH plays a significant role in fiber chemistry, as illustrated is Fig. 3, where the predicted model of the pH versus Cobb number clearly shows its impact on Cobb number response, improving the retention of hydrophobic sizing agent at lower pH and cationic demand. Studies have shown that acidic conditions can enhance the deposition of certain sizing agents, such as rosin, alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), which in turn reduces water absorbency (Gess and Render 2005).

Similarly, ATC dosage influences the Cobb number by reducing anionic trash in the furnish, which can interfere with the retention and effectiveness of hydrophobic additives. However, an excess of ATC could lead to over-flocculation, affecting paper formation and subsequently its water absorption properties. The surface response plot also indicates a minimal interaction effect between pH and ATC, suggesting an optimal range for minimizing the Cobb number in the acid region, thereby improving hydrophobicity of the paper. However, their interaction was not significant, as the standardized effect analysis suggests, with a p-value above 0.05 for the pH*ATC interaction (Fig. 4).

On the other hand, alkaline conditions may favor the use of fillers such calcium carbonate or clay for printing and writing or specialized grades (Bajpai *et al.* 2008). Nevertheless, it is also well known that alkaline environments can promote hydrolysis on the ASA-starch emulsion, leading to deposit formation in the paper machine and a lower sizing effect due to side reactions.

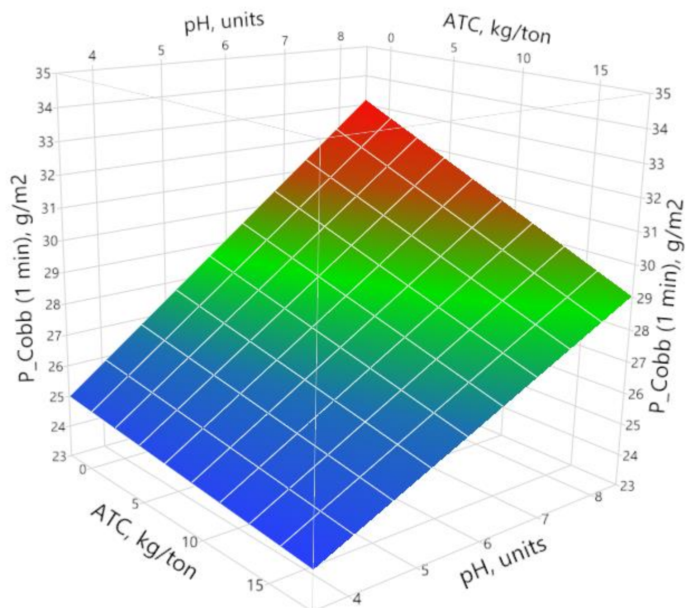

Fig. 3. Response surface plot of the predicted Cobb number (1 min)

These findings align with previous research demonstrating that surface chemistry modifications, particularly through charge demand control and sizing optimization, are crucial for enhancing water resistance in paper products (Seppanen 2007).

The standardized effect diagram of the Cobb number response (Fig. 5) indicates that pH had the most significant influence on the Cobb number test within the studied range of 4 to 8. The LogWorth value of 6.779 (p-value = 2×10^{-7}) provides strong statistical evidence that pH directly affected the Cobb number values, making it the most critical variable to control, followed by ATC doses, having a LogWorth value of 1.527 (p-value = 0.0297). Both factors were statistically significant at the 95% confidence level.

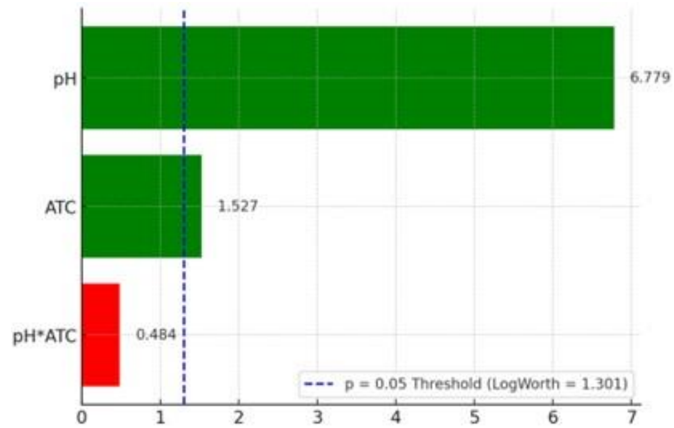

Fig. 4. Standardized effect diagram for the Cobb number test (1 min)

The improved hydrophobicity observed at lower pH levels may be attributed to esterification reactions and the availability of exposed carboxyl groups in the acidic range, which enhance fiber surface sizing conditions. However, this does not fully explain why pH had a significantly greater impact on water resistance than the polyelectrolyte effect, as suggested by the statistical analysis.

Analysis of Cationic Demand

The pulp used for kraft paper manufacturing contains a high concentration of dissolved materials, either from the pulping process or due to the intense refining of fibers (Wang *et al.* 2014). This leads to an increase in "anionic trash," which ultimately interacts with ASA, reducing its effectiveness in paper sizing (Lindström 2012). The addition of selected polyelectrolytes and charge-neutralizing agents helps condition the fibers, creating more bonding points between the fiber and ASA (Bung and Chemie 2004). As a result, greater hydrophobicity is achieved in the paper sheet. Introducing substances with opposite charges to the anionic trash enhances attraction or repulsion interactions, while the stability of suspended substances depends on the forces acting within the pulp stock, as shown in Fig. 5. Increasing the concentration of cationic agents reduces the repulsion energy between fibers, optimizing their preparation so that other additives, including ASA, can function more effectively.

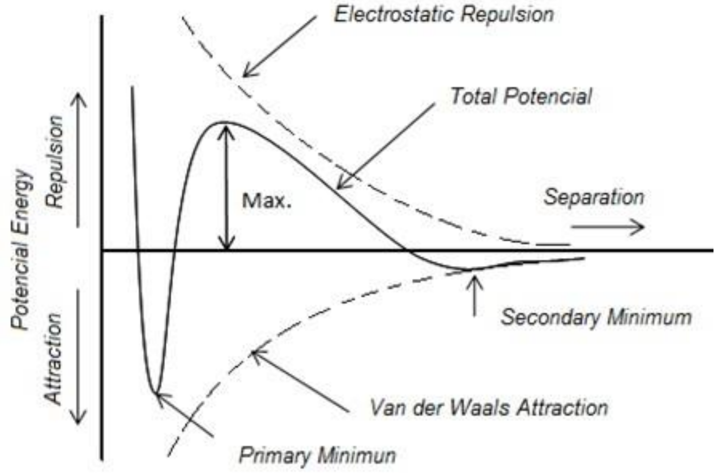

Fig. 5. Representation of the interaction energy between particles as a function of the separation distance between two particles. Adapted from Adair *et al.* (2001)

As shown in Fig. 6, the greatest reduction in cationic demand occurred at high polyelectrolyte doses (15 kg/ton) and pH 4.0. This supports the hypothesis that a "cleaner" system is achieved under these conditions, which enhances paper sizing.

The drastic changes in cationic demand can be attributed to the polyelectrolyte agent used in the tests (ATC), which consisted of a high-charge-density, low-molecular-weight polyamine. Such polyamines interact with oppositely charged colloidal substances, neutralizing them through electrostatic interactions. The polyamine is synthesized from a series of dimethylamine and epichlorohydrin copolymers, which, after isomerization (Fig. 7), convert their secondary amino groups into quaternary amines. This transformation maintains a high cationic charge across a wide pH range, making them highly effective in the papermaking process.

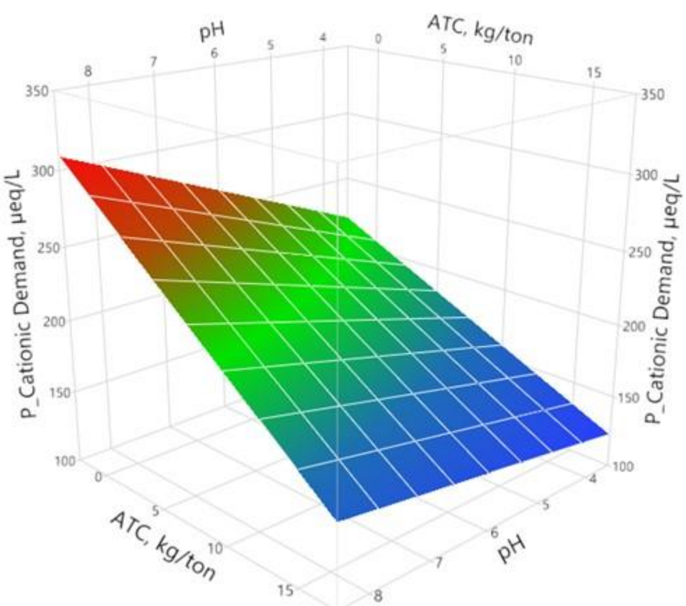

Fig. 6. Response surface plot of the predicted cationic demand

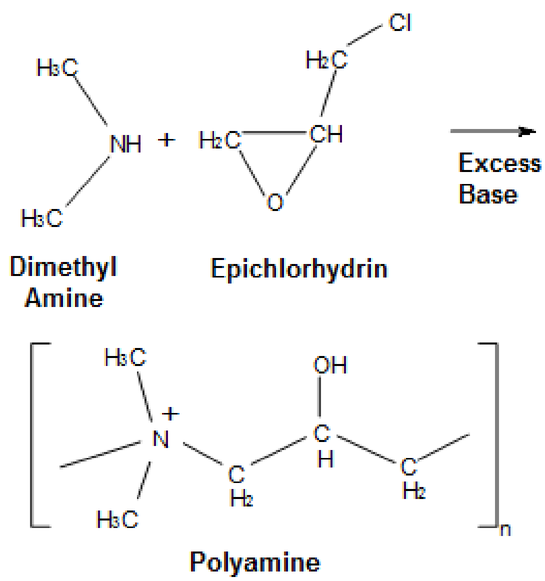

Fig. 7. Polyamines synthesis

However, the addition of sulfuric acid to the furnish also contributes to reducing the cationic demand. The increase in H^+ ion concentration in the pulp suspension suggests a significant counterion effect on the inherent anionic particles present in the kraft process (anionic trash). This ultimately conditions the medium, allowing ASA-starch emulsion to react more efficiently with the fibers.

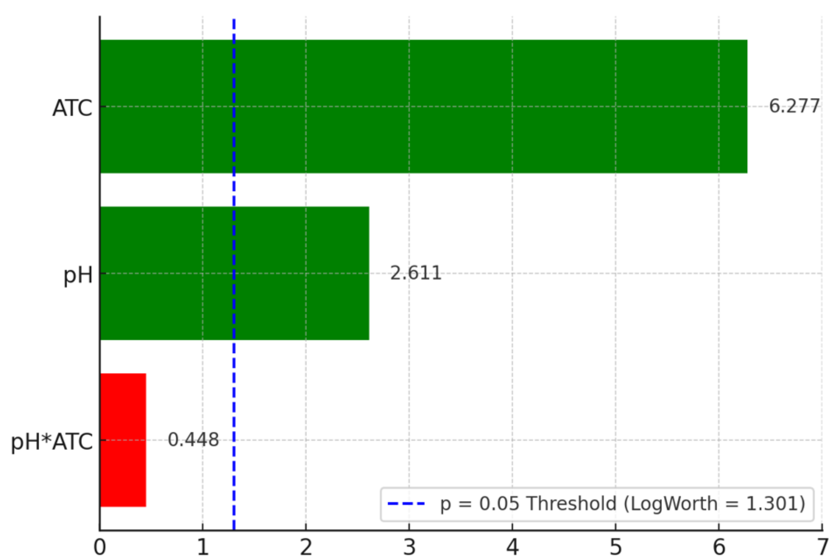

Fig. 8. Standardized effect diagram for the cationic demand

The standardized effect diagram for cationic demand (Fig. 8) provides strong evidence that both polyelectrolyte dosage and pH significantly influenced cationic demand, as indicated by p-values below 0.05 for both factors. Their impact is largely dependent on the initial cationic demand of the furnish. However, the interaction between these factors was not statistically significant at the 95% confidence level.

Analysis of Conductivity

Figure 9 presents the surface response plot for the predicted conductivity model, demonstrating that pH variations had a significantly greater impact on conductivity than the amount of polyelectrolyte added. This reinforces that conductivity changes primarily arise from pH modifications rather than from the presence of polyelectrolytes.

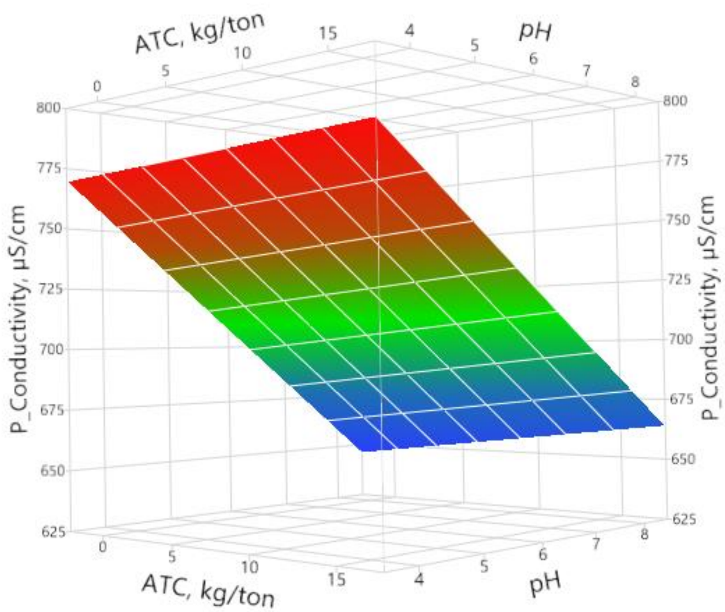

Fig. 9. Response surface plot of the predicted conductivity

Despite the observed conductivity variations, sizing performance was not negatively affected by high conductivity. In fact, the lowest Cobb number results were obtained in conditions with the highest conductivities, suggesting that conductivity alone does not hinder ASA retention. The increase in H^+ ion concentration at lower pH levels likely contributes to higher conductivity values due to increased ionic strength. In fact, lower pH suppresses the dissociation of acidic groups (*i.e.*, carboxyl groups) on the fiber surface, decreasing their negative charge. However, this environment may still enhance the neutralization of anionic trash, improving ASA accessibility to fiber surfaces (Hubbe *et al.* 2024). However, the complexity of the papermaking system introduces additional variables, such as dissolved salts, fiber charge, and residual process chemicals, which influence conductivity measurements without directly correlating to optimal sizing conditions.

Unlike the trends observed for the Cobb number and cationic demand, the standardized effect diagram in Fig. 10 confirms that pH variations significantly influenced conductivity, whereas ATC dosage and its interaction with pH had no measurable effect.

The effect of pH was statistically significant (LogWorth = 4.265, p-value = 0.00005), while ATC dosage and the pH*ATC interaction were not significant (p-values = 0.67677 and 0.88445, respectively). This result is expected, as conductivity in pulp suspensions is predominantly governed by the concentration of free ions, which are sensitive to pH changes. In contrast, low-molecular-weight quaternary polyamines used as anionic trash catchers act primarily through electrostatic complexation with dissolved anionic substances and do not release significant amounts of free ions into the solution. As such, their impact on conductivity is minimal (Miao *et al.* 2013; Zhang *et al.* 2013).

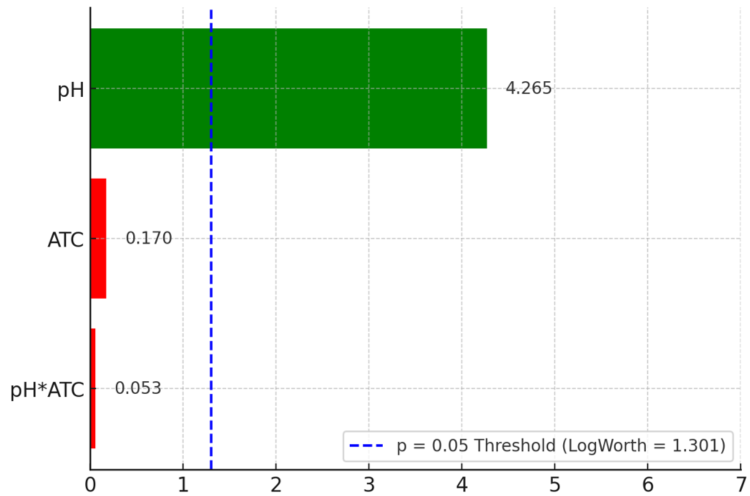

Fig. 10. Standardized effect diagram for the conductivity variable

Further Analysis: The Role of pH Control in ASA Sizing

As observed in the Cobb number (1 min) analysis, lower pH levels result in improved hydrophobicity (lower Cobb number) and reduced cationic demand. This finding contrasts with the conventional understanding that ASA performs optimally under neutral-alkaline conditions. However, given the limited literature on ASA interaction in filler-free systems, alternative explanations may account for the observed behavior. Two primary mechanisms may explain this trend:

pH-driven esterification enhancement

Sulfuric acid, which was used as the pH-modifying agent in this study, may enhance ASA-cellulose esterification by creating an acidic environment that promotes the protonation of hydroxyl groups on the fiber surface. This protonation increases the reactivity of hydroxyl sites, facilitating the nucleophilic attack on ASA through ring opening and subsequent covalent bond formation, which contributes to improved water resistance (Mobley *et al.* 2018). Although carboxylic groups in hemicellulose exhibit acidic character (pKa ~3.8), the enhanced reactivity under acidic conditions is primarily associated with the behavior of hydroxyl groups, while protonated carboxyl groups may influence surface chemistry and accessibility. Furthermore, previous studies have shown that ASA hydrolysis is minimized under acidic conditions, allowing a greater proportion of ASA to react with fiber hydroxyl groups rather than undergoing premature degradation. (Ntifafa *et al.* 2023; Sun *et al.* 2014).

Reduction of Anionic Trash Interferences

Acidic conditions protonate negatively charged species (anionic trash) in the pulp furnish, thus reducing their electrostatic repulsion with ASA emulsions and enhancing retention (Lindström and Larsson 2008). Anionic trash consists of dissolved and colloidal substances (*e.g.* lignin, and extractives), which compete with ASA for fiber surfaces (Kumar *et al.* 2020). At lower pH, the protonation of these species reduces their negative charge, allowing ASA droplets to adsorb onto fibers more efficiently (Ashish *et al.* 2019).

Although these hypotheses cannot be directly confirmed by the current experimental design, the statistical analysis strongly supports the conclusion that pH control is a critical factor in promoting ASA retention and improving paper hydrophobicity when using softwood kraft pulp.

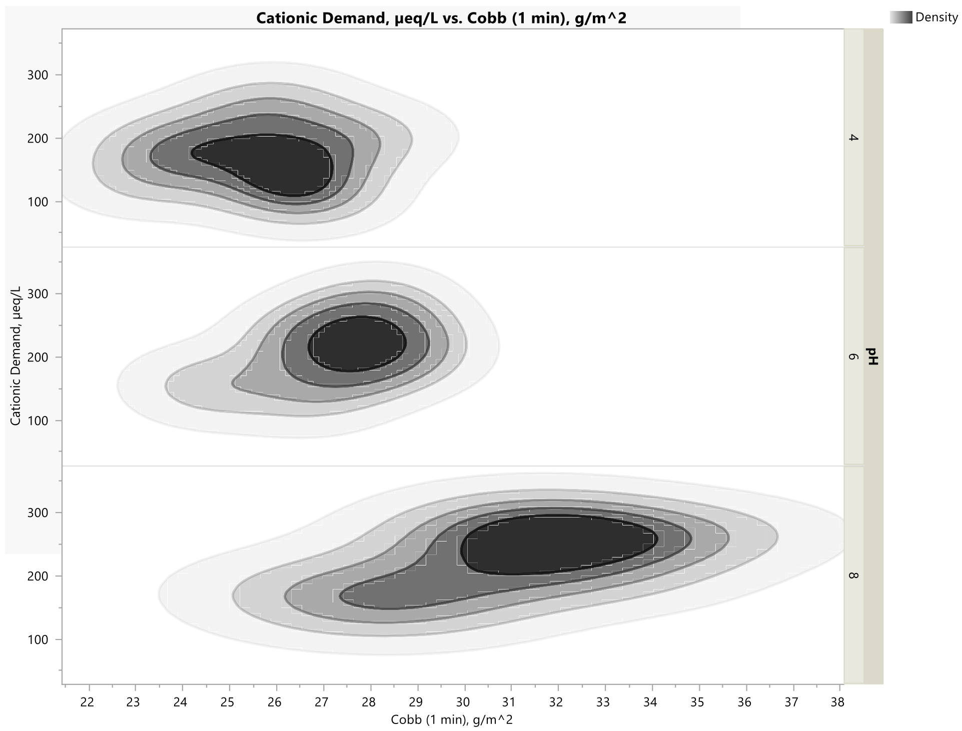

Fig. 11. Influence of pH on Cobb number and cationic demand

Dominance of pH over ATC dosage in ASA performance

Figure 11 illustrates the statistical distribution of Cobb number responses mapped separately against cationic demand and pH, confirming that pH 4.0 provided optimal conditions for ASA retention. This finding supports previous studies showing that acidic environments enhance ASA efficiency by minimizing hydrolysis and improving fiber-ASA interactions (Martorana *et al.* 2010).

Additionally, the results indicate that furnish pH and cationic demand exerted a greater influence on ASA sizing than ATC dosage. While ATC is designed to neutralize anionic trash, the data suggest that its effect on ASA retention is secondary to pH-driven interactions. This effect has been studied in the context of ionic strength, which challenges the common assumption that ATC is the primary factor governing ASA efficiency in papermaking (Iselau *et al.* 2018). Instead, the results align with studies suggest that ATC primarily acts as a stabilizer rather than a direct sizing enhancer, meaning that its role is supportive rather than definitive.

CONCLUSIONS

1. This study demonstrated that pH played a critical role in optimizing alkenylsuccinic anhydride (ASA) sizing efficiency in paper formed from softwood kraft pulp. The results indicated that lower pH levels significantly enhanced ASA retention and

hydrophobicity, as evidenced by the lowest Cobb number (23 g/m²) achieved at pH 4.0. Statistical analysis confirmed that pH exerted a dominant influence over ATC dosage, with a highly significant effect (p-value = 2.0×10^{-7}), whereas ATC dosage, though relevant for anionic trash reduction, had a secondary impact on sizing performance. Excessive addition of quaternary polyamine (ATC) did not further improve Cobb number reduction and may lead to over-flocculation, potentially affecting sheet formation.

2. The improved hydrophobicity observed under acidic conditions can be attributed to enhanced ASA emulsion reactivity. At lower pH, partial protonation of carboxyl and hydroxyl groups on the fiber surface may facilitate esterification between ASA and cellulose, thereby promoting covalent bond formation and improving sizing efficiency. Additionally, the reduced pH neutralizes anionic substances and decreases the overall anionic charge in the system. This reduction minimizes electrostatic repulsion between the cationic starch-stabilized ASA emulsion and fiber surfaces. A cleaner environment under acidic conditions also lowers the likelihood of ASA being consumed through side interactions with anionic trash, thereby improving ASA availability and retention.
3. These findings provide valuable insights into wet-end chemistry control, particularly for kraft paper production in furnishes that do not require calcium carbonate fillers. Effective pH management enables precise ASA dosing, reducing reliance on high ATC dosages while improving paper hydrophobicity.

ACKNOWLEDGMENTS

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APPENDIX

Table A1. Experimental Design Pattern for the Evaluated Conditions and Results of their Combinations

Experiment #	Pattern	pH	ATC (kg/ton)	Cobb number (g/m^2)	Cationic demand (µeq/L)	Conductivity (µS/cm)
1	33	8.0	15	29.0	175.5	647
2	21	6.0	0.5	28.2	297.8	653
3	22	6.0	7.5	27.0	240.0	667
4	12	4.0	7.5	25.6	238.6	743
5	31	8.0	0.5	31.4	303.3	636
6	31	8.0	0.5	31.6	275.6	739
7	22	6.0	7.5	24.2	161.3	754
8	11	4.0	0.5	26.0	267.5	734
9	31	8.0	0.5	34.0	256.9	615
10	22	6.0	7.5	27.0	170.3	648
11	23	6.0	15	27.6	197.5	679
12	12	4.0	7.5	23.6	160.8	812
13	23	6.0	15	24.6	143.7	761
14	32	8.0	7.5	30.0	248.0	641
15	13	4.0	15	24.6	197.7	733
16	23	6.0	15	26.8	123.9	651
17	21	6.0	0.5	26.6	230.5	741
18	32	8.0	7.5	26.6	190.9	761
19	22	6.0	7.5	28.0	241.7	701
20	32	8.0	7.5	35.5	269.8	686
21	11	4.0	0.5	28.3	206.0	808
22	11	4.0	0.5	23.4	195.0	820
23	13	4.0	15	23.0	121.1	838
24	21	6.0	0.5	29.0	208.4	645
25	33	8.0	15	31.5	201.0	694
26	13	4.0	15	26.8	100.3	724
27	31	8.0	0.5	31.8	266.1	693
28	21	6.0	0.5	28.3	254.6	706
29	11	4.0	0.5	27.3	197.4	725
30	23	6.0	15	28.3	191.0	693
31	12	4.0	7.5	26.5	155.9	796
32	33	8.0	15	29.0	133.6	641
33	13	4.0	15	26.0	133.9	809
34	12	4.0	7.5	26.5	110.4	715
35	33	8.0	15	27.0	145.0	747
36	32	8.0	7.5	33.3	194.8	629