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Comparison of the Efficacy of Sodium Acid Sulfate and Citric Acid Treatments in Reducing Acrylamide Formation in French Fries

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ABSTRACT

Two acidulant food additives, sodium acid sulfate (SAS) and citric acid, were investigated for their effectiveness in reducing acrylamide formation in french fries. Acrylamide concentration was determined by gas chromatography-mass spectrometry (GC-MS) after cleanup of french fry extracts by passage through a C-18 column and derivitization by bromination. At a frying temperature of 180°C, both acidulants appeared ineffective, possibly due to the rapid rate of acrylamide formation, which surpassed the capacity of the acidulants to protonate acrylamide intermediates. At the lowest frying temperature tested (160°C), 3% SAS and 3% citric acid significantly ($P < 0.05$) inhibited acrylamide formation as compared to the control. However, 3% SAS appeared to inhibit acrylamide formation more effectively than citric acid at 160°C, as well as at frying temperatures of 170 and 180°C. Our results indicate that acrylamide formation during frying can be reduced by treatment of potatoes with 3% SAS or citric acid, but SAS, a stronger acid with a lower pKa, is the more effective acidulant.

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INTRODUCTION

Acrylamide is a neurotoxic chemical compound and a probable human carcinogen (Friedman 2003; U.S. EPA 1990). In April 2002, Swedish researchers found high levels of acrylamide in various fried and oven baked foods (Tareke et al. 2002). Currently, there are several ways to reduce acrylamide formation in foods, including removing asparagine and reducing sugars (which are precursors for acrylamide formation), adding free amino acids (other than asparagine), or decreasing pH. When the pH is lowered, the Schiff base, a crucial intermediate required for acrylamide formation, will attract protons from the acidic environment. This protonated Schiff base will regenerate asparagine and reducing sugars (Yaylayan and Stadler 2005), rather than being converted to acrylamide. The inhibitory effect of pH on acrylamide formation has previously been demonstrated in a model system using citric acid (Vleeschouwer et al. 2006; Jung et al. 2003).

Citric acid has long been used as an acidulant in food processing and is known as an effective treatment for inhibiting acrylamide formation. However, citric acid imparts a sour taste and tougher texture on dip-treated french fries when applied in concentrations greater than or equal to 2%. Sodium acid sulfate (SAS) is a relatively new acidulant approved by the FDA in 1998 for use in the food industry. With a lower pKa than citric acid (1.99 vs 3.14, respectively), SAS dip treatments have a lower pH and may be used to reduce production of acrylamide in fried potatoes. According to a flavor profile prepared by Sensory Spectrum, Inc. (Chatham, NJ), SAS may reduce the sour taste produced by low concentration citric acid treatments.

The inhibitory effects of SAS on acrylamide formation in carbohydrate-rich foods have not been investigated to date. A comparison of the effects of SAS and current citric acid treatments could facilitate development of a novel food safety product and improved potato treatment and processing protocols. The objective of this research was to measure the comparative reduction of acrylamide formation in potatoes treated with SAS and citric acid and subsequently cooked at various frying temperatures. Acidulant concentrations were investigated to determine optimum treatment conditions. Acrylamide was quantified using a GC-MS analytical method developed by Tareke et al. (2002) and modified in our laboratory.

MATERIALS AND METHODS

All the chemicals used in this experiment were purchased from Fisher Scientific (Pittsburgh, PA). Potatoes (Russet Norkotah) were peeled and cut into french fry strips using a french fry cutter (3/8 inch, Vollrath Co., Sheboygan, WI). The fries were treated with distilled water, citric acid (1 and 3%; w/v), or sodium acid sulfate (1 and 3%; w/v) solutions by dipping for 5 min. After freezing the potato strips for 1 hr at −20°C, they were fried in a fryer (Hotpoint Co., Peterborough, UK) using vegetable oil obtained from a local supermarket for 5 min at a temperature of 160, 170, or 180°C. After cooling for 10 min, french fries were frozen at −20°C and blended using a kitchen blender (Handy Chopper Plus, Black & Decker, Towson, MD).

The analytical method used to quantify acrylamide by GC-MS was as described by Tareke et al. (2002), with slight modifications. The homogenized sample (5 g) was diluted into 35 mL of water, and mixed for 2 min using a polytron (CH-6010, Kinematica Inc., Bohemia, NY). After centrifugation for 20 min at 5,000 rpm, the supernatant was filtered using a Whatman #50 filter with suction. For final purification, filtered extract (15 mL) was loaded on a graphitized carbon black column (1,000 mg, 15 mL, Alltech, Deerfield, IL), or a C18-U or C18-E column (500 mg, 6 mL, Strata, Phenomenex, Torrance, CA). C18-U and C18-E columns were conditioned with 5 mL of methanol followed by 5 mL of water before loading the extract. The graphitized carbon black column did not require pre-conditioning.

The acrylamide in the purified extract (25 mL) was derivatized through bromination by adding potassium bromide (3.75 g), hydrobromic acid (acidification to pH 1–3), and saturated bromine water (1.25 mL). The sample was kept at 4°C for 24 hours. Excess bromine was decomposed by adding sodium thiosulfate (1 M), in single drops until the yellow color disappeared. Sodium sulfate (7.5 g) was added and the solution stirred vigorously for 10 min, transferred to a separatory funnel and extracted by shaking with 5 mL of ethyl acetate for 2 min. The ethyl acetate extraction was repeated and the two organic fractions combined in a 25-mL volumetric flask.

The acrylamide in french fry samples was quantified using an Agilent 6890 gas chromatograph (GC) coupled to an Agilent 5973 quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA). The GC column was a DB-5 fused silica capillary column (30 m X 0.25 mm i.d., 0.25 µm film thickness; Varian Inc., Walnut Creek, CA). Two microliters of sample were injected with a splitless mode, facilitating injection of the entire sample volume (2 µL) for analysis.

The temperature program was as follows: isothermal for 1 min at 65°C, increased to 250°C at a rate of 15°C/min, and isothermal at 250°C for 10 min. The analysis was performed using electron ionization (70 eV) and selected ion monitoring. The ions used to facilitate identification of the target analyte (2,3-difromopropionamide) were $[C_3H_5{}^{81}BrNO]^+$ = 152 (100%), $[C_3H_5{}^{79}BrNO]^+$ = 150 (100%), and $[C_2H_3{}^{79}BrNO]^+$ = 106 (65% to 70%) using 150 (m/z; mass-to-charge ratio) for quantification. Quantification was performed by comparison of peak areas on a chromatogram with a five point standard curve prepared with acrylamide solutions in water at concentrations of 0, 10, 50, 100, and 1000 µg/L.

STATISTICAL ANALYSIS

Significant differences ($P > 0.05$) between the mean value of each treatment at the same frying temperature and mean value of each cartridge column were calculated using Duncan's multiple range tests with SAS software 9.1 (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

Three different columns (graphitized carbon, C18-U, and C18-E) were compared for acrylamide purification efficiency (data not shown). The graphitized carbon column efficiently removed all interfering co-extractants and resulted in the highest acrylamide recovery. The lowest acrylamide content was measured when no clean-up column was used. These results indicate that compounds in the french fry extract interfere with acrylamide derivatization and can affect acrylamide detection by GC-MS. There were no significant differences in acrylamide content quantified by the graphitized carbon and C18-U columns ($P > 0.05$). C18-U would be the most accurate column for acrylamide clean-up based on standard deviations calculated for each column.

The inhibitory effects of SAS and citric acid on acrylamide formation are shown in Figure 1. GC-MS analysis detected the greatest acrylamide content in the control samples (A) and dramatically reduced acrylamide peaks with the citric acid and SAS treatments (Figure 1, B and C).

Figure 2 shows the effect of acidulants on acrylamide formation at various frying temperatures (160, 170, and 180°C) and at different concentrations. Results show acrylamide formation increased with increasing frying temperatures. No significant inhibitory effect ($P > 0.05$) from treatment with acidulants was noted at the two highest

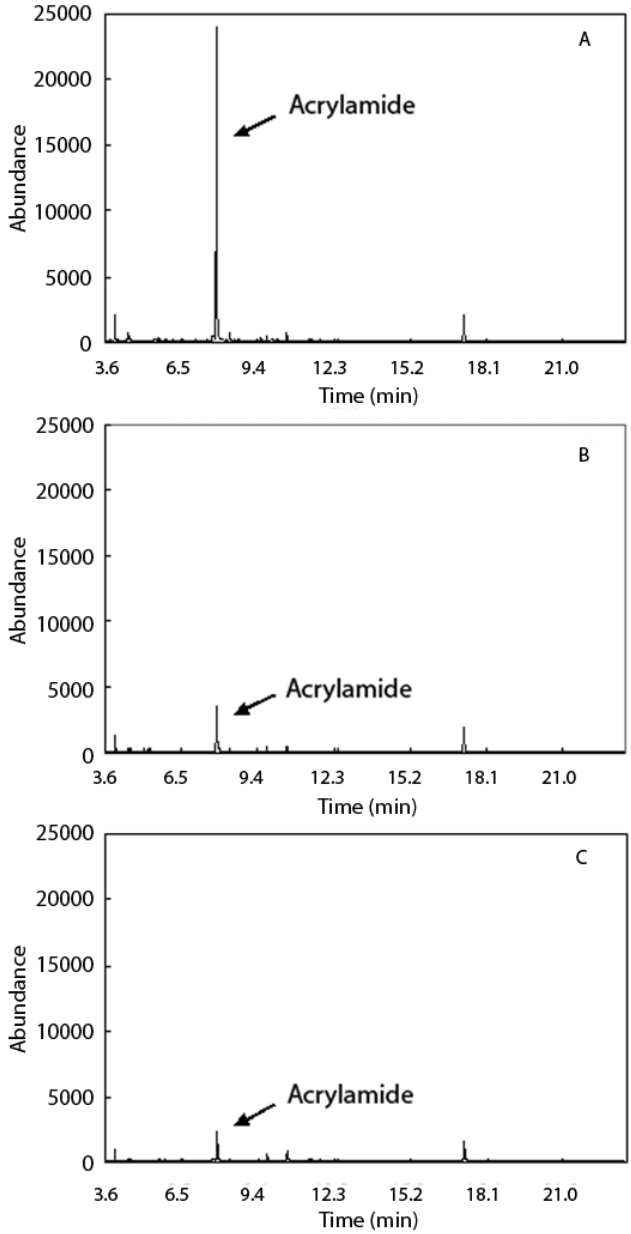

Figure 1. GC-MS chromatogram of acrylamide in french fries dip-treated with distilled water or acidulants before frying. (A) Distilled water; (B) 3% citric acid; (C) 3% SAS treatment. Potatoes were dipped for 5 min, and then fried at 160°C for 5 min.

frying temperatures (170 and 180°C), although both decreased acrylamide formation at 170°C, as compared to the control. Acrylamide levels were similar for all treatments at 180°C, suggesting that there are no inhibitory effects at higher temperatures. The rate of acrylamide formation may have accelerated beyond the acidulants' capacity to effectively protonate the intermediate Schiff base at the higher frying temperature rendering the acidulants less effective in inhibiting acrylamide formation. When potatoes were fried at 160°C, 3% citric acid and 3% SAS significantly decreased acrylamide formation ($P > 0.05$) as compared to the acrylamide levels measured in the extract of potatoes fried at the higher temperatures. Three percent SAS had a greater inhibitory effect on acrylamide formation than citric acid and control samples at frying temperature of 160 and 170°C.

As expected, the SAS solutions had a lower pH than citric acid solutions of the same concentration due to lower pKa values. One percent solutions of SAS and citric acid had pH values of 1.61 and 2.21, respectively. The pH of 3% SAS was 1.33, and the pH of 3% citric acid was 1.98. Based on the lower pH and confirmed by GC-MS analysis, a SAS dip treatment is more effective for inhibiting acrylamide formation in french fries than citric acid.

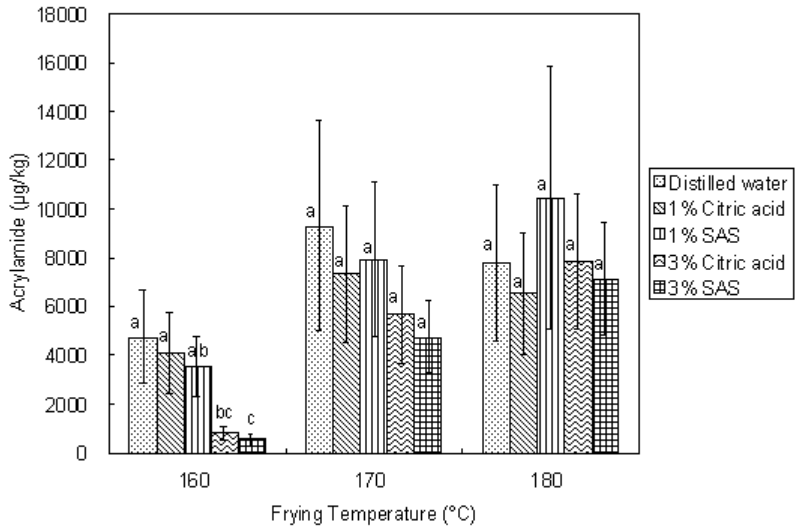

Figure 2. Effect of acidulants on acrylamide formation in french fries at various frying temperatures and treatment concentrations. Within each frying temperature, different letters indicate significant differences. Means were calculated from triplicate analysis for each column.

SUMMARY

The inhibitory effect of SAS and citric acid on acrylamide formation in french fries was investigated in this work. Initial comparison of three cleanup columns indicated a C18-U column was the most effective for separating acrylamide based on analytical results, least variance and the lower cost for this column. At the highest frying temperature (180 °C), the tested acidulants were less effective, possibly due to the rapid rate of acrylamide formation which surpassed the acidulants' capacity to protonate acrylamide intermediates. However, at the lowest frying temperature (160°C), 3% SAS and 3% citric acid significantly ($P > 0.05$) inhibited acrylamide formation. Frying temperature strongly influenced the effectiveness of these acidulants. Currently, high temperature (around 190°C) is used to make french fries for favorable texture. Temperature control from initial high temperature (170°C) to low temperature (140–150 °C) during frying could be another way to reduce acrylamide formation (Palazoglu and Gokmen 2008; Fiselier et al. 2006). Overall, SAS was more effective than citric acid in reducing acrylamide formation in french fries. However, further study is needed to confirm these results and sensory testing is required to determine flavor acceptability of SAS-treated potatoes.

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