

Novel Corrosion Inhibitors Derived from Agricultural Byproducts

In an effort to prepare corrosion inhibitors using renewable, nonhazardous and biodegradable materials, a number of agriculture byproducts have been evaluated for protection in vapor phase, in acidic solutions, and in salt solutions.

Molasses and raffinate (de-sugared molasses) have been reported to be multimetal corrosion inhibitors in water-based electrolytes,¹ but their vapor phase protection has not been reported. This article investigates the ability of molasses and raffinate to provide vapor phase protection. Distillation, cation exchange, ultra-filtration, and reactions with common volatile nitrogen-containing components were evaluated as means to concentrate and enhance molasses for use as a volatile corrosion inhibitor (VCI).

A variety of corn-derived byproducts from ethanol production were also studied (Figure 1). They included thin stillage, thick stillage, and distillers dried grains with solubles (DDGS). Stillage is the material left behind in still bottoms after fermentation and ethanol removal. DDGS are dried residue remaining after the starch fraction of grain is fermented. Containing proteins, fibers, and oils, DDGS represent one-third of the weight of the starting material in ethanol production.² Each of these corn ethanol byproducts is solid or semi-solid. Liquid extracts of these materials were prepared for inhibitor evaluation. DDGS were chosen as the main focus as they contain all the basic components in stillage.

A solvent extract of DDGS demonstrated up to 97% protection for steel in acidic environments and in salt water. A variety of plant extracts have been shown to inhibit corrosion of steel in acidic conditions,³⁻⁹ but such activity has not previously been reported with corn extracts. Aqueous corn extracts provided corrosion protection as an inhibitor in de-icing compounds.

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Agriculture byproducts were evaluated to determine their potentials as nonhazardous corrosion inhibitors. Sugar beet molasses showed vapor phase protection. A solvent extract of distillers dried grains with solubles (DDGS), a byproduct from corn ethanol, demonstrated protection for steel in acidic and salt solutions. Aqueous extracts of corn ethanol byproducts provided inhibition in de-icers. Tests, enhancements, and applications are presented.

TABLE 1

VAPOR-INHIBITING TEST RESULTS ON MOLASSES AND VARIOUS TYPES OF TREATED MOLASSES

Component	Sample	Sample	Sample
Molasses/raffinate as received	Plug #1	Plug #2	Plug #3
5 g sugar beet raffinate	Grade 2	Grade 3	Grade 3
5 g sugar beet molasses	Grade 1/0	Grade 3	Grade 3
5 g (Sample 1 food grade molasses)	Grade 1/0	Grade 2	Grade 2
5 g (Sample 2 food grade molasses)	Grade 2	Grade 0	Grade 0
2.5 g sugar beet raffinate	Grade 2	Grade 2	Grade 3
2.5 g sugar beet molasses	Grade 2	Grade 2	Grade 3
Control	Grade 0	—	—
Raffinate after distillation	Plug #1	Plug #2	Plug #3
2.5 g of distillate	Grade 3	Grade 3	Grade 3
2.5 g of pot residue	Grade 3	Grade 3	Grade 3
Raffinate treated with cation ex resin	Plug #1	Plug #2	Plug #3
Equivalent 0.3 g raffinate (pH 1.94 adjusted to 9.8)	Grade 2	Grade 2	Grade 2
Molasses after ultrafiltration			
MW range of fraction (equivalent to 0.5 g solids)	Plug #1	Plug #2	Plug #3
<1,000	Grade 0	Grade 0	Grade 0
1,000–3,000	Grade 3	Grade 2	Grade 2
3,000–10,000	Grade 0	Grade 0	Grade 0
10,000–30,000	Grade 0	Grade 0	Grade 1
>30,000	Grade 2	Grade 2	Grade 2
Control	Grade 0	—	—
Molasses after ammonium blending	Plug #1	Plug #2	Plug #3
1 g of sugar beet molasses with 1.5% NH_4OH	Grade 3	Grade 3	Grade 3
1 g of Sample 1 food grade molasses with 1.5 NH_4OH	Grade 3	Grade 3	Grade 3
0.25 g of aqueous NH_4OH	Grade 0	Grade 0	Grade 0

FIGURE 1



A variety of corn-derived byproducts were analyzed for use as corrosion inhibitors.

Experimental Procedures

Molasses as a Vapor Phase Corrosion Inhibitor

Sugar beet molasses and raffinate (feedstock grade) and sugar cane molasses (food grade) were evaluated for their VCI ability. Efforts were made to concentrate and enhance the vapor-inhibiting ability (VIA) of the sugar beet molasses. The data showed no discernable difference between molasses and raffinate in terms of their VIA capability so the terms are used interchangeably for the discussion of VCI in this article.

Distillation

Distillation was carried out on sugar beet raffinate. Typically, up to 30% of the

starting material was collected as distillate with an apparent boiling point of 100 °C. The temperature of the pot residue (70% of starting material) was about 127 °C when distillation was terminated.

Cation Exchange

Cation exchange was performed using Dowex® HCR-W2 H⁺ cation exchange resin (J.T. Baker). The resin was first washed with de-ionized water, and added to a 50% raffinate solution. After decanting the resin, the pH of the solutions was adjusted to 9.8 with aqueous ammonia (NH₃).

Ultrafiltration

Ultrafiltration was performed with a Stirred Ultrafiltration Cell Model 8400[†] (Millipore). Fifty percent of the diluted raffinate was subjected to sequential size fractionation using cellulose membranes with cutoffs in nominal molecular weight of 30,000, 10,000, 3,000, and 1,000.

Chemical Treatment with Ammonia

Combinations of molasses or raffinate with 5% of ammonium hydroxide (NH₄OH) solution were obtained.

Evaluation of Vapor-Inhibiting Ability

A VIA test evaluates a product's ability to protect metal from corrosion without being in direct contact. A sample of vapor inhibitor was placed in a capped quart jar with a freshly polished and cleaned carbon steel (CS) (SAE 1010 [UNS G10100]) plug for 20 h at ambient temperature. A relative humidity of nearly 100% was then created in the jar by the addition of 3% glycerol in water for 2 h at ambient temperature, followed by another 2 h at 40 °C. After that the plugs were inspected and rated on a scale of 0 to 3, where 0 is heavily corroded (no corrosion inhibition), and 3 means no visible corrosion and good inhibiting effects.

Chemical Identification by Solid Phase Micro Extraction

A solid phase micro extraction (SPME) fiber (polydimethylsiloxane/divinylben-

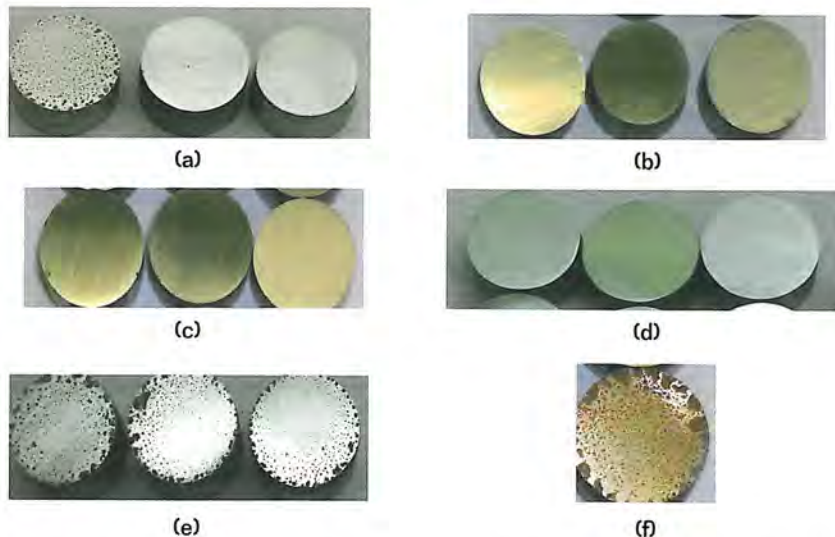
[†]Trade name.

TABLE 2

PROTECTION OF STEEL FROM ACID CORROSION BY 2% DDGS SOLVENT EXTRACT

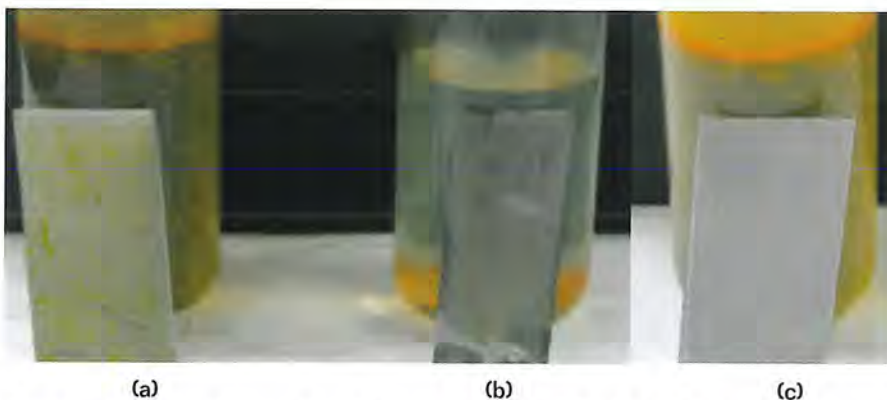
Acid	Acid Concentration	Z (% Corrosion Protection)
Hydrochloric	10%	97%
Sulfuric	10%	95%
Phosphoric	10%	90.9%
Citric	20%	87.7%

FIGURE 2



VIA test results of 5 g of sugar beet molasses: (a) as received, (b) raffinate distillate, (c) raffinate pot residue, (d) NH₃-treated molasses, (e) NH₃ only, and (f) control.

FIGURE 3



Steel coupons after removal from saltwater immersion test: (a) 0.5% DDGS extract, (b) control, and (c) cleaned coupon from (a).

zene) was inserted into the headspace of a jar containing molasses for 30 min at ambient temperature, then placed into the injection port of a gas chromatography column (Hewlett Packard 6890 GC with 5975 MSD[†]); column DB5MS[†] 30 m

x 0.25 mm x 1.0 µm; carrier: Helium Gas[†]. The injection temperature was 250 °C, the interface temperature was 290 °C, and the temperature ramp was 10 °C/3 min, 10 °C/min to 200 °C/0 min, and 40 °C/min to 280 °C/5 min.

TABLE 3
DE-ICER TEST RESULTS (3% FORMULA IN 3% NaCl SOLUTION)

Sample No.	Formula Composition	Pass/Fail (PNS Test)	Corrosion Rate (mpy) (PNS Test)	% NaCl Corrosion Rate	Freezing Point (°C)
1	50% propylene glycol + 25% aqueous extract of DDGS + 25% water	Pass	1.73	3.3	-35
2	50% propylene glycol + 25% extract of thick stillage + 25% water	Pass	0.07	0.13	-35
3	24% calcium chloride (CaCl ₂) + 20% aqueous extract of DDGS + 56% water	Pass	18.56	29.6	-35
4	3% NaCl (control 1)		62.62		
5	De-ionized water (control 2)		0.42		

Solvent Extract and Aqueous Extract of DDGS as Corrosion Inhibitors

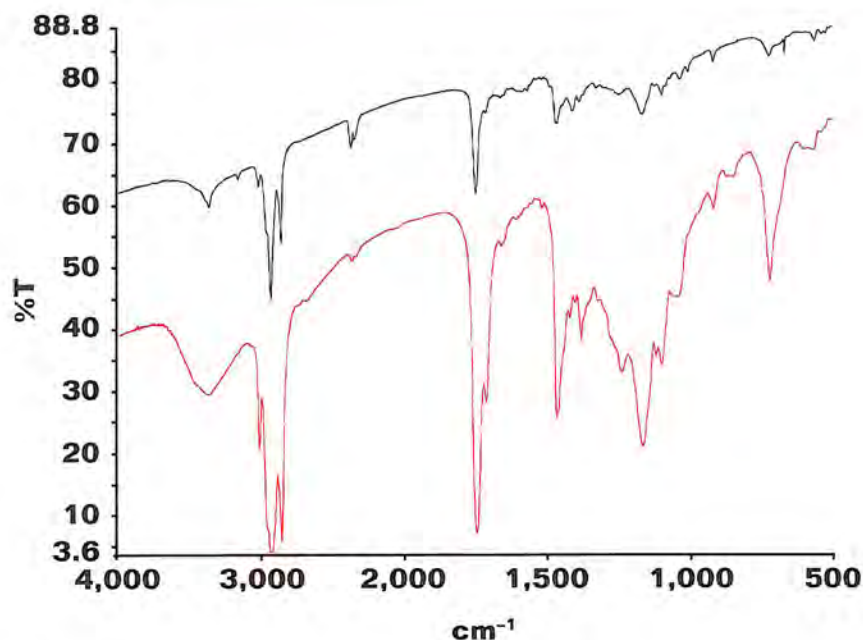
Solvent Extraction

DDGS were extracted with ethyl acetate at 4 g/25 mL ratio overnight. Removal of the solvent yielded an amber-colored viscous oil in low yield (20%). Being immiscible, the extract/test solutions were agitated throughout the following tests to achieve an even distribution. The extracted oil was evaluated in acidic solutions according to a modified ASTM G31¹⁰ immersion test. Two percent of the amber oil was added to 10% solution of hydrochloric acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and 20% citric acid (C₆H₈O₇), respectively. Steel coupons (SAE 1010) were immersed in the above acidic solutions at room temperature for 24 h. After cleaning, the mass loss of each coupon was determined and the corrosion rate was calculated. The extracted oil, at 0.5% w/w, was also evaluated in synthetic seawater. Synthetic seawater by itself was a control. CS coupons (SAE 1010) were immersed in the two test solutions for 48 h, cleaned, and visually inspected for corrosion.

Aqueous Extraction

For aqueous extractions, a ratio of one part DDGS, four parts water, and one part NH₄OH (30%) or 40 h at 80 °C, and a ratio of two parts thick stillage, two parts water, and one part NH₄OH were used. The nonvolatile content of the aqueous extract was 11%. To determine the effectiveness of the aqueous extracts as

FIGURE 4



FTIR spectrum of solvent extract (red) and aqueous extract (black).

de-icers, freezing point and corrosion inhibition through Pacific Northwest Snowfighter (PNS)¹¹⁻¹⁴ testing were performed. Formulas of freezing points below -35 °C were subjected to PNS testing. Test solutions were 3% formula in a 3% sodium chloride (NaCl) solution. Two controls, 3% NaCl and de-ionized water, were used. Metal coupons, hung from an automatic PNS testing apparatus, were dipped into the test solutions at a rate of 10 min/h for 72 h. The coupons were cleaned according ASTM G1¹⁵ after the test, and their mass losses and corrosion

rates were calculated according to PNS protocol. The effectiveness of the de-icer was reported as a percentage of the corrosion rate in a 3% NaCl solution. PNS requires that a de-icer must be at least 70% less corrosive than the 3% NaCl control solution.

Compound Identification

The extracts were analyzed using gas chromatography mass spectroscopy (GCMS), liquid chromatography mass spectroscopy (LCMS), and Fourier transform infrared (FTIR) spectroscopy.

Results

Molasses as a Vapor Phase Corrosion Inhibitor

Molasses and raffinate from sugar beet and sugar cane showed significant VCI ability (VIA grades 2-3) in as-received forms (Figure 2[a] and Table 1). Interestingly, less processed molasses showed better VCI property than the more processed molasses. For instance, feedstock sugar beet molasses showed better VCI than the Sample 1 food grade molasses; less processed Sample 1 food grade molasses showed better VCI property than the more processed Sample 2 food grade molasses.

Effect of Distillation

Surprisingly, both distillate and pot residue from the distillation of raffinate showed strong VCI property (Figures 2[b] and [c], Table 1). Also, 2.5 g of either distillate or pot residue showed better VCI property than 5g of as-received raffinate.

Effect of Ion Exchanging

Ion exchange using a strong cation exchange resin showed that when potassium ions were removed and replaced with ammonium, the resulting organic salts demonstrated VCI property. It is likely that VCI components in molasses and raffinate existed as potassium salts of a number of organic acids.

Ultrafiltration

Ultrafiltration showed that those raffinate fractions of molecular weight (MW) between 1,000 to 3,000 and of MW above 30,000 demonstrated VCI properties (Table 1).

Chemical Treatment with Ammonia

The addition of 5% NH_4OH solution (~1.5% NH_4OH) enhanced the vapor corrosion inhibiting ability of the molasses. It was noted that 1 g of enhanced molasses (blended with NH_4OH) (Figure 2[d]) showed better VCI protection than 5 g of as-received molasses (Figure 2[a]). NH_4OH by itself showed almost no VCI effect (Figure 2[e]).

Chemical Identification

SPME GCMS of the volatile portion of molasses showed a number of organic acids, ketones, aldehydes, pyrazines, alcohols, alkenes, pyrrolidinones, lactones, and furanones. Some of the identified components match those found in the aroma analysis of molasses.¹⁶ Due to the complexity of molasses, no inhibiting compound was identified.

Solvent Extract and Aqueous Extract of DDGS as Corrosion Inhibitors

Acid Immersion Test

Two percent DDGS solvent extract showed significant protection of steel from acid corrosion (Table 2).

Saltwater Immersion Test

The solvent extract, 0.5 wt%, provided excellent protection for steel in synthetic seawater. Figure 3(a) displays the film-forming properties of the solvent extract. This viscous yellow film acts as an air, moisture, and salt barrier protecting the coupon from saltwater attack. This film, however, was easily removed using conventional detergent. Figure 3(c) illustrates the coupon that has been cleaned, showing no corrosion on the surface. The control (Figure 3[b]) was found to have a lot of corrosion on the surface.

De-icer Testing

Aqueous extracts of both DDGS and thick stillage showed good potential as a de-icer component (Table 3).

Gas and Liquid Chromatography

Gas and liquid chromatography results showed that the chemical makeup of the solvent and aqueous extracts are similar. Due to the complexity in the GCMS and LCMS data, the specific molecular basis of corrosion inhibition could not be established for the DDGS extracts. Some of the major components detected were long chain fatty acids, C-16 and C-18 specifically; ethyl esters; butanediol; tocopherol; ergost-5-en-ol; sig-

mast-5-en-3-ol; methoxy propanol; and ethoxy ethanol, among a large number of minor peaks.

FTIR Spectroscopy

Figure 3 shows the FTIR spectra. The spectra are dominated by peaks characteristic of corn oil. However, the peak at $1,711\text{ cm}^{-1}$ is indicative of a carboxylic acid, possibly fatty acid. The broad peak at $3,359\text{ cm}^{-1}$ is indicative of a small amount of hydrogen-bonded water or possibly polyols (e.g., glycerol or butanediol).

Conclusions

Feedstock sugar beet molasses and raffinate are compelling raw materials as VCIs. It is known that vapor corrosion inhibition is mostly provided by the salts of weak volatile acids and weak volatile bases.¹⁷⁻¹⁸ Molasses and raffinate appear to be good sources of such materials. The easy addition of a small amount of NH_4OH greatly enhanced the VCI property of molasses and raffinate.

A solvent extract of DDGS demonstrated good corrosion prevention in acidic and/or saltwater solutions. The extract forms a tenacious film on metal surfaces and lends itself very well as a float coat with applications in holding tanks, ballast tanks, and offshore structures. This float coat has the advantage of not drying out and not cracking after prolonged use. It can be easily removed using conventional detergents and is very economical. Being bio-based and biodegradable, it doesn't pose a problem when discharging into ground or surface water; however, the maximum discharge amount should be verified through testing by the EPA laboratory.

Aqueous extracts of DDGS and thick corn stillage revealed several de-icer formulations that met the freezing point requirements. Moreover, the extracts yielded increased corrosion protection. Commercially available propylene-glycol-based deicing fluids report corrosion rates of 2 to 20 mpy on CS,⁶ whereas the aqueous extracts of DDGS and thick corn stillage offer protection rates as low as 0.07 mpy.

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