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In collaboration with

Cornell CALS College of Agriculture and Life Sciences

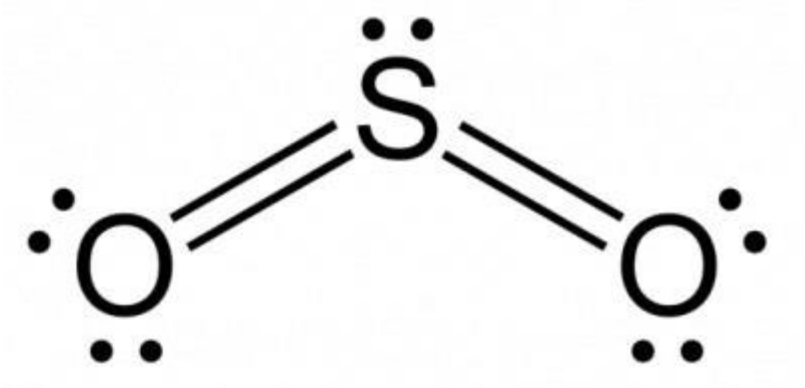
Canned Wine Part 2: New Information on the Impact of SO_2 for Canned Beverages

Moderator: Rachel Allison

Presenters: Dr. Gavin Sacks & Jasha Karasek

DATE 6/18/20

SO_2



H_2S

Survey Questions

SO_2 and Canned Wine

Gavin L. Sacks (Professor)
Rachel Allison (PhD Candidate)

Department of Food Science
Cornell University

June 18, 2020

The questions you probably care about.

"What can liner / manufacturer should I use?"
"What wine components are most important?"
"What shelf-life can I get?"

I'll be explaining how we hope to get to these answers

The fastest growing wine packaging sector
Wine in aluminum cans

Sep 1, 2018

FOOD & BEVERAGE

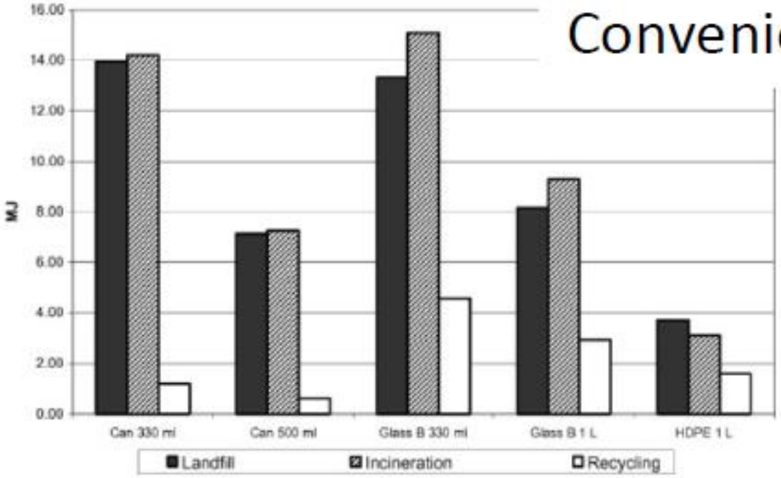
RETAIL | AUTOS | FOOD AND BEVERAGE | RESTAURANTS | FASHION | GOODS | RETAIL REPORT

Canned wine is no longer a fad, it's a $45 million business

- Sales of canned wine grew 43 percent in the U.S. from June 2017 to June 2018.
- While canned wine is still a tiny portion of the wider industry, it is one of the fastest growing categories thanks to millennial drinker.
- These cans can be brought to places that glasses cannot, like the beach, the park and campsites and are also easier to recycle than glass bottles. Some casual drinkers also see canned wine as less pretentious.

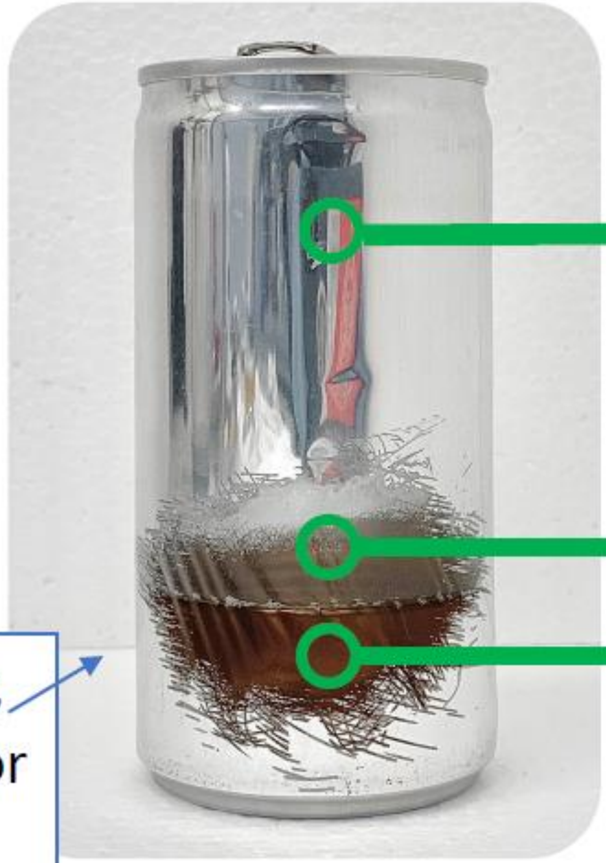
Nielsen.
Jan 16, 2018

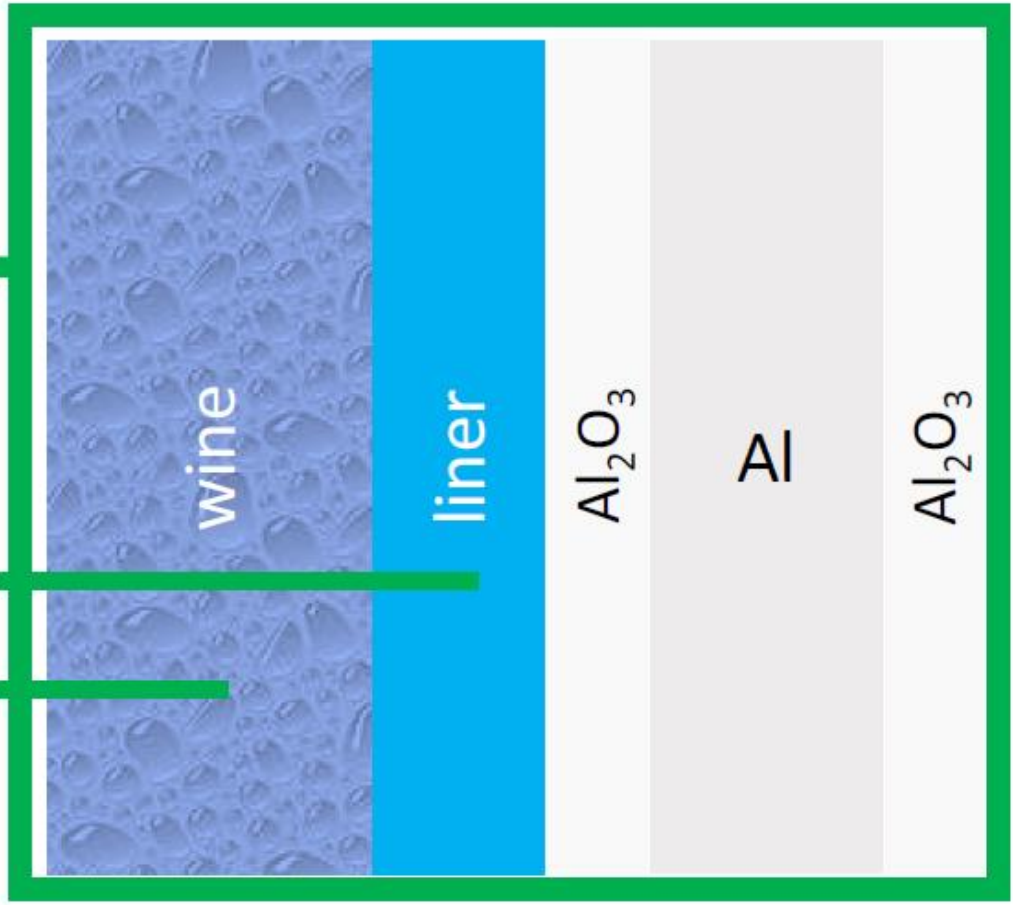
High recycling rates
Good barrier properties
Lightweight, strong
Less emissions impact
Convenient



Pasqualino, et al 2011

Anatomy of a can: Really, it's a plastic bottle (with super thin walls, and a hermetic seal)





Can liner (BPA epoxy, other epoxy, acrylic, or polyester)

Effects of packaging on flavor – the big “textbook” categories

1. **DEGRADATION – Flavor changes due to ordinary processes, e.g. oxidation**
   For cans: Oxidation not a big deal *unless* there is high total package oxygen (especially headspace)

2. **SCALPING - Loss of desirable compounds by absorption**
   For cans: Will affect highly non-polar compounds, e.g. TCA. Probably minor concern

3. **TAINTING – Flavor changes due to sorption from or reaction with packaging**
   For cans: a potential issue . . . Next slides!

Tainting of canned wines (and ciders)
Hydrogen sulfide, H_2S: "rotten egg" odor

(19) Europäisches Patentamt / European Patent Office / Office européen des brevets

(12) EUROPEAN

(45) Date of publication and mention of the grant of the patent: **14.11.2018 Bulletin 2018/46**

(21) Application number: **14167862.3**

(22) Date of filing: **26.03.2012**

(54) **WINE PACKAGED IN ALUMINIUM CONTAINERS**

*"This invention is in part based on the discovery that excess levels of Free SO_2 .... will also affect the nose (**odour-sulphidic characters**)"*

Foul odor spurs Oliver Winery hard-cider lawsuit

KEYWORDS LEGAL ISSUES / LAWSUITS / MANUFACTURERS / FOOD MANUFACTURERS / REGIONAL NEWS / LAW / MANUFACTURING

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An agreement Oliver Wine Co. Inc. made with a container manufacturer to purchase cans for the winery's hard apple cider has gone sour.

Bloomington-based Oliver filed suit against the Broomfield, Colo.-based Ball Metal Beverage Container Corp., once headquartered in Muncie, in Monroe Circuit Court in December. The case was transferred to federal court in Indianapolis last week.

Oliver claims the metal cans Ball supplied for the cider produced a chemical reaction when coming into contact with the beverage, causing a foul odor and spurring customer complaints.

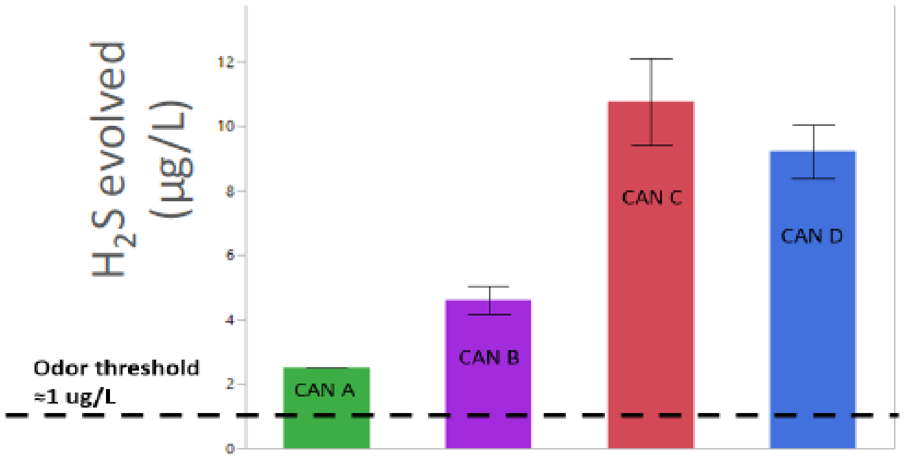
The winery issued a voluntary recall of the cider and since has suffered "significant damages," according to its complaint.

Oliver does not specify the amount of damages it is seeking. The price Oliver paid to buy a total of 1.3 million cans from Ball has been redacted from a purchase order included in the complaint.

The winery is claiming breach of warranties and contract, negligence and product liability.

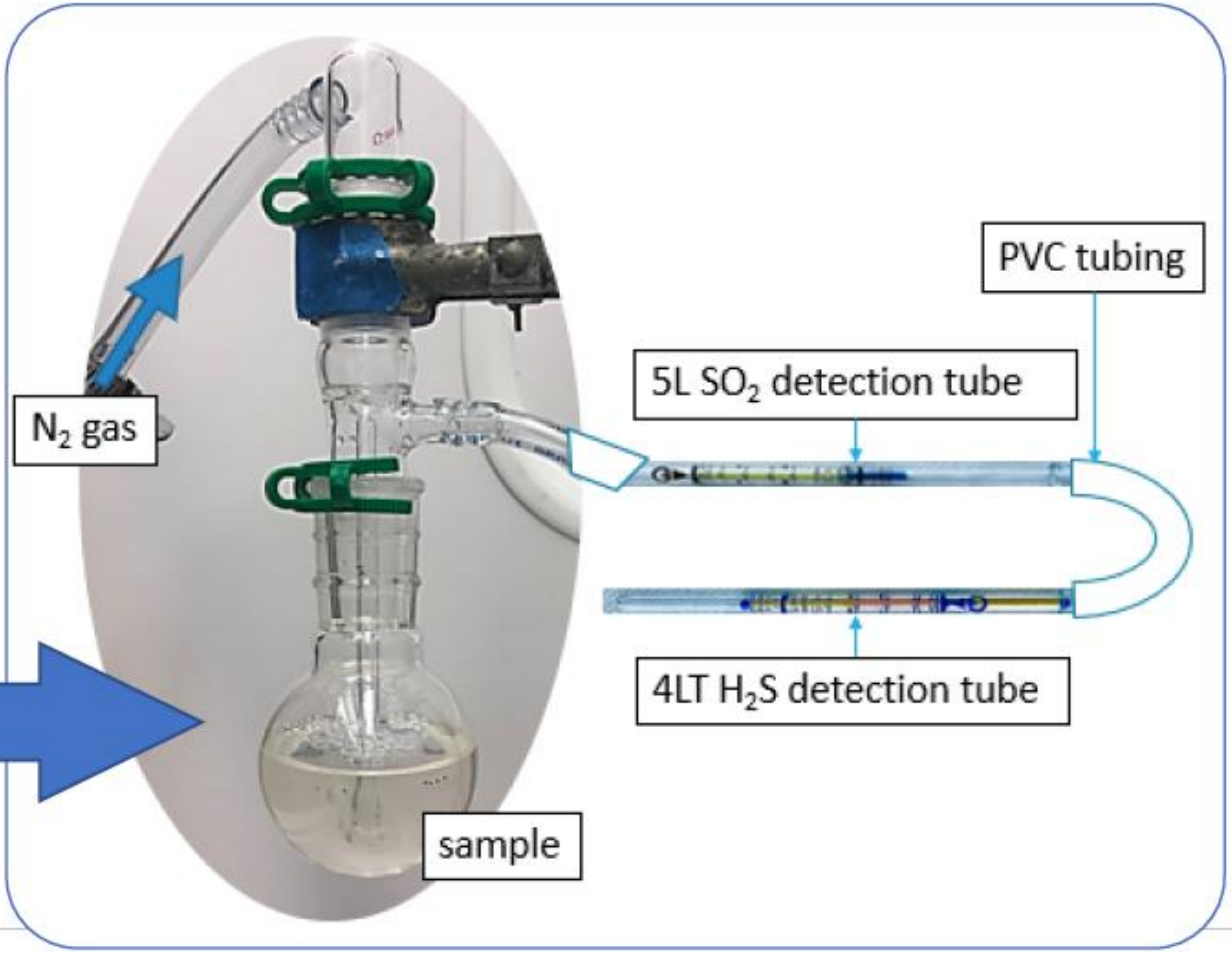
Citing company policy, a Ball spokesman declined to comment on the pending litigation.

Model wine (50 mg/L SO_2, pH=3.5) in commercial cans (10 days @ 30°C)



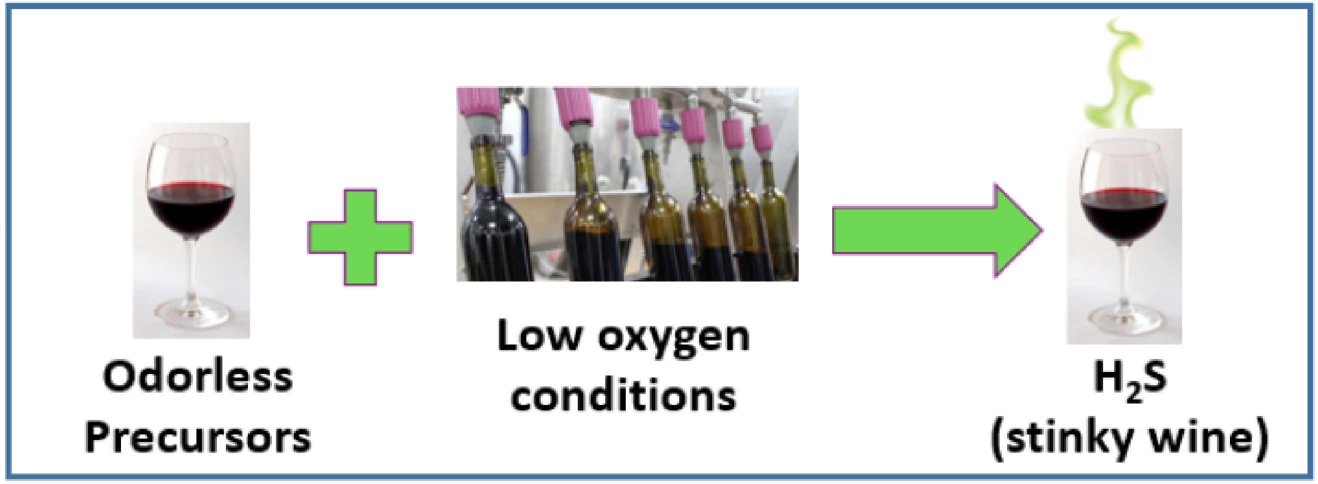
Aside: Our approach to measuring H_2S

- Modified A-O unit, with H_2S gas detection tubes
- <15 min/analysis
- ~0.2 ppb detection limit



(Allison and Sacks; *unpublished*)

Sources of H_2S during anoxic storage in cans



1) **Release from odorless precursors**
   a) **Copper-sulfide complexes**
   (see presentations from Wilkes and Scrimgeour in earlier Enartis webinar)
   b) Polysulfides (from wine oxidation or S-pesticide degradation)

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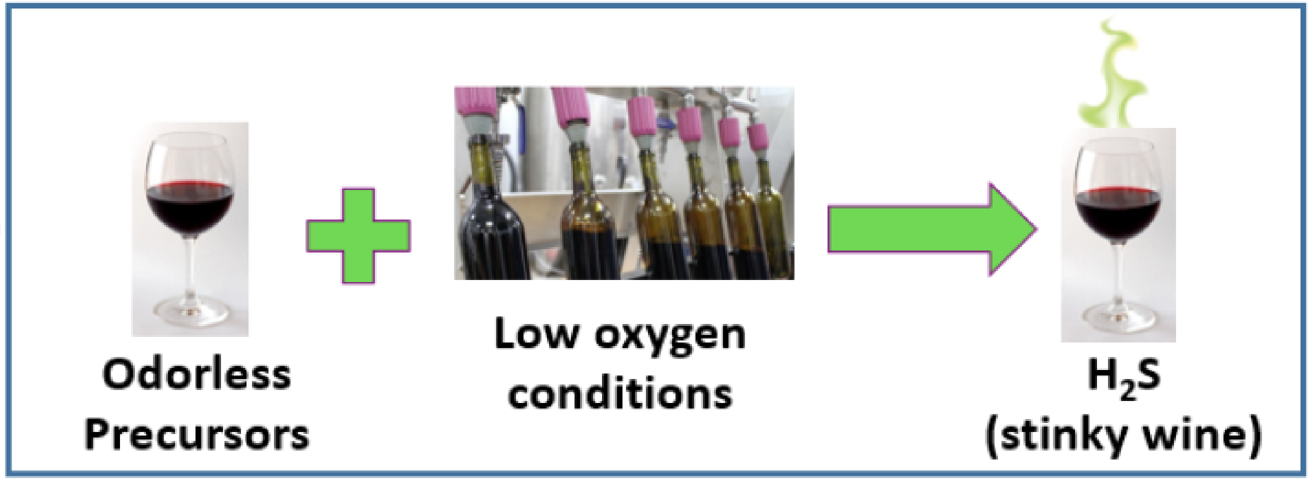

1) Release from odorless precursors
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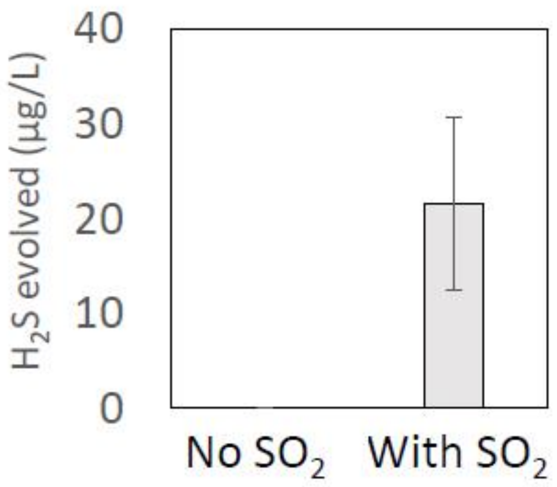
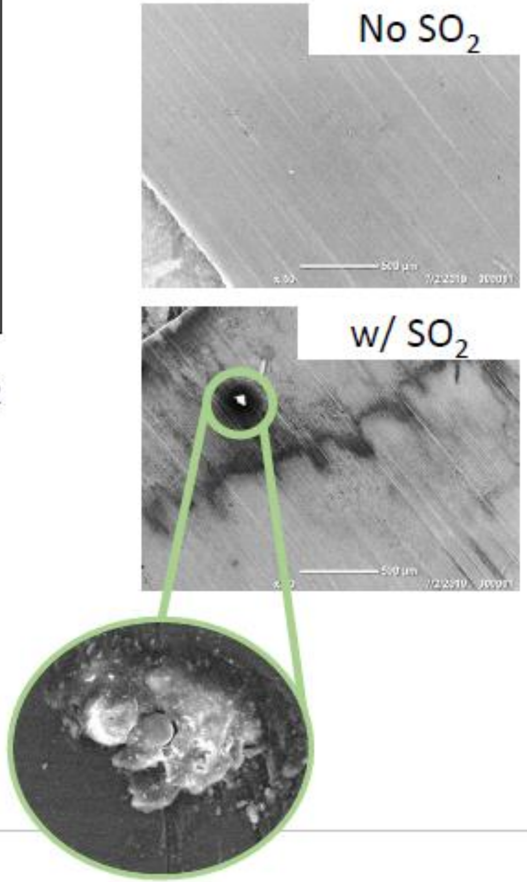
2) New formation of H_2S by reaction of aluminum with SO_2

Aluminum will corrode under aqueous conditions
Will also react with SO_2 to yield H_2S

50 mg/L SO_2, Al foil, neutral pH, 24 h





A "blister" formed on aluminum surface at neutral pH

(dissolves at wine pH)

Corrosive reactions involving Al metal in wine

$$3Al_{(s)} + SO_{2\,(aq)} + 6H^+ \rightarrow 3Al^{3+}_{(aq)} + H_2S_{(aq)} + 2H_2O$$

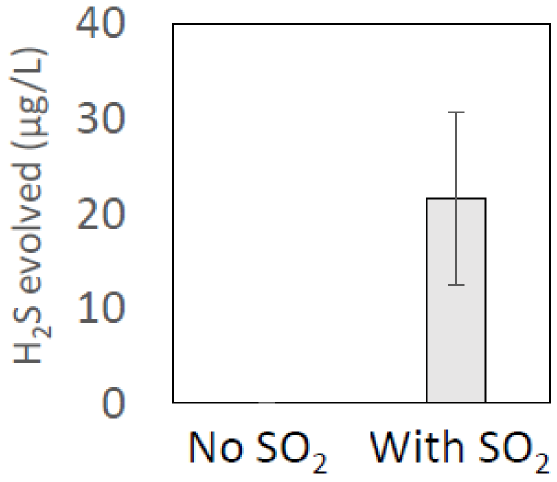
$$2Al_{(s)} + 3H_2O \rightarrow 2Al(OH)_{3\,(aq)} + 3H_{2\,(g)}$$

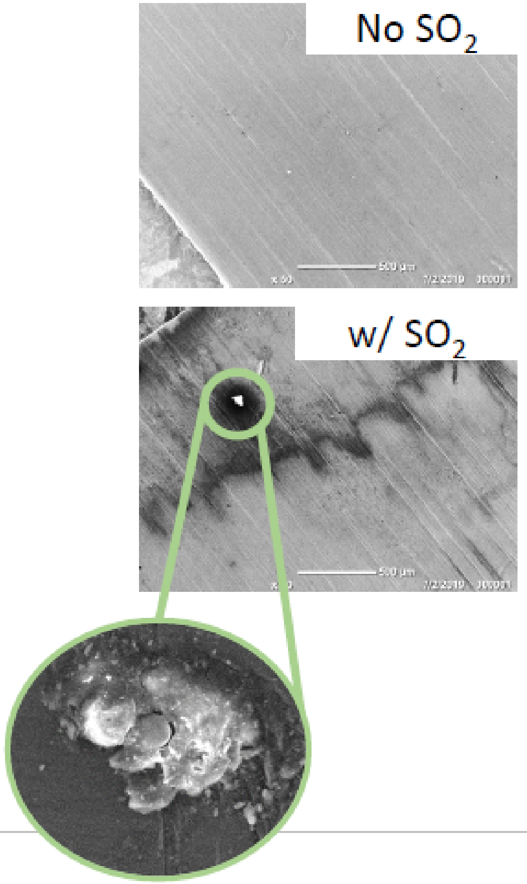
$$2Al_{(s)} + 3H^+ \rightarrow 2Al^{3+}_{(aq)} + 3H_{2\,(g)}$$

Formation of dissolved Al is typically much higher than H_2S formation

Aluminum and its alloys react with SO_2 to yield H_2S

50 mg/L SO_2, Al foil, neutral pH, 24 h





A "blister" formed on aluminum surface at neutral pH

(dissolves at wine pH)

The reaction has been known for some time in the wine world

EFFECTS OF CERTAIN METALS AND ALLOYS ON CLARET- AND SAUTERNE-TYPE WINES MADE FROM VINIFERA GRAPES

E. M. MRAK, L. CASH,[1] AND D. C. CAUDRON [2]
University of California, Berkeley, California

1937

TABLE 4
Effect of Metal Turnings on Appearance and Bouquet of Wines

Metal	Sauterne wine		Claret wine	
	Appearance	Bouquet	Appearance	Bouquet
Aluminum pure	T[1]	N	Pale	N
Aluminum 76	V. T.	H_2S	V. T.	H_2S
Aluminum 12	V. T.	H_2S	....	....
Aluminum-bronze	N	N	N	N
Acid-bronze	N	N	Sl.T.	N
Everdur	N	N	Sl.T.	N
Manganese-bronze	Sl.T.	....	Pale	N
Phosphorous-bronze	Sl.T.	N	N	N
Machine-brass	Sl.T.	N	N	N
Waukesha-alloy	Sl.T.	N	Sl.T.	N
Cupro-nickel	Sl.T.	N	Sl.T.	N

Review of SO_2 in wine *(sorry, we need to do this)*: free vs. molecular vs. bound vs. total

"Free SO_2" = molecular + bisulfite

molecular SO_2 $\rightleftharpoons$ ***Bisulfite***

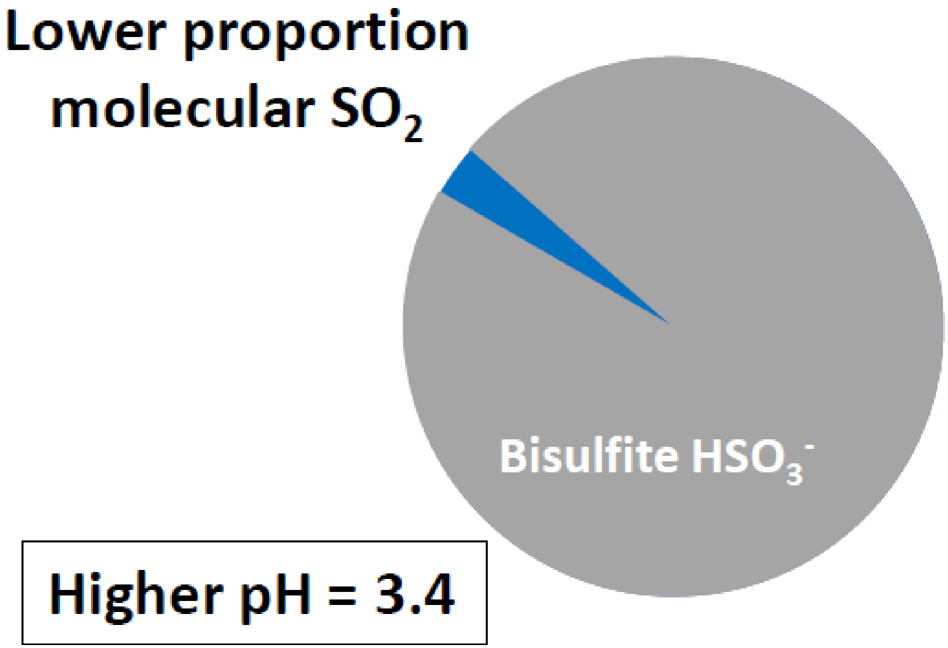
SO_2 $\rightleftharpoons$ HSO_3^-

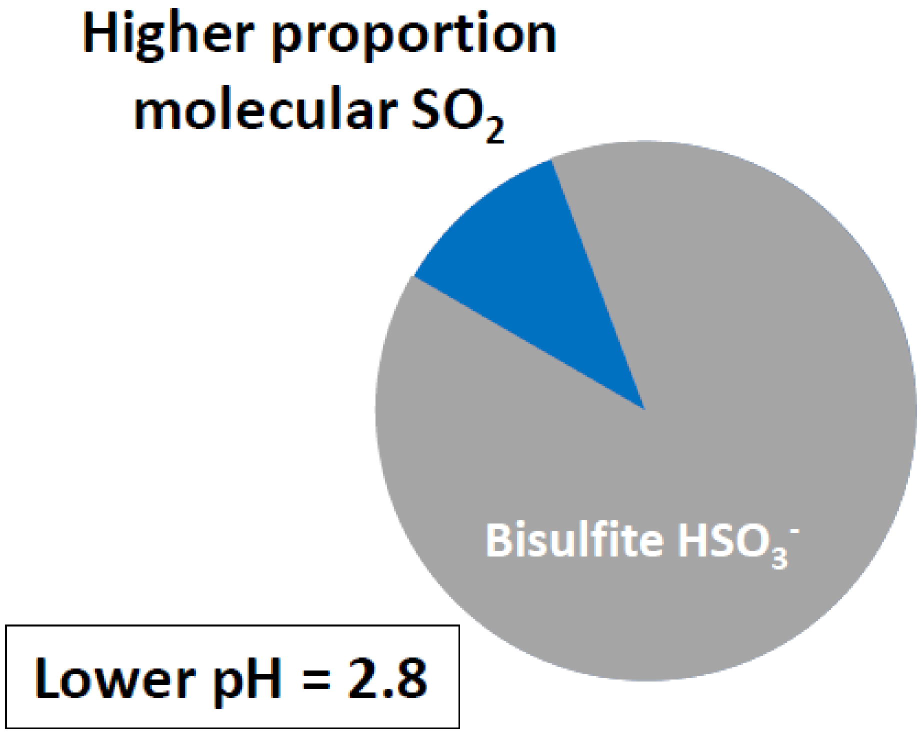
HSO_3^- $\xrightleftharpoons{\text{+ binder}}$ ***Bound SO_2***

Ratio depends on pH

"Total SO_2" = Free + Bound

Molecular SO_2 is a minor component of free SO_2, typically ~1-2%
Higher molecular SO_2 proportions at lower pH

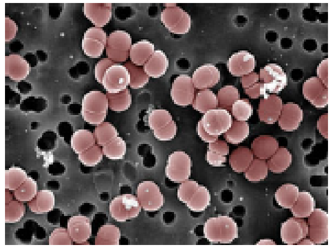




These different forms of sulfur dioxide (SO_2) have different, complementary roles in a packaged wine

1) Molecular SO_2 is an **antimicrobial**

Typically, **0.5-0.8 mg/L molecular** SO_2 recommended to prevent spoilage



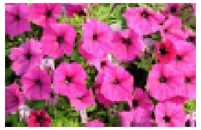
2) Free SO_2 (as bisulfite) is an **antioxidant**

~30 mg/L **free** SO_2 common recommendation for glass packaging
Reacts with oxidation products (e.g. hydrogen peroxide, quinones)
Typically, at **<10 mg/L free** SO_2, oxidized aromas appear

“Bound” SO_2 – What’s doing the binding? A partial list of binder

Weaker binder

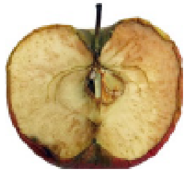
Glucose
(sweet wines)



Anthocyanins
(red-purple color)

Methional
(“potato” odor)

Stronger binder



Acetaldehyde
(“old apple” odor)

Free SO_2

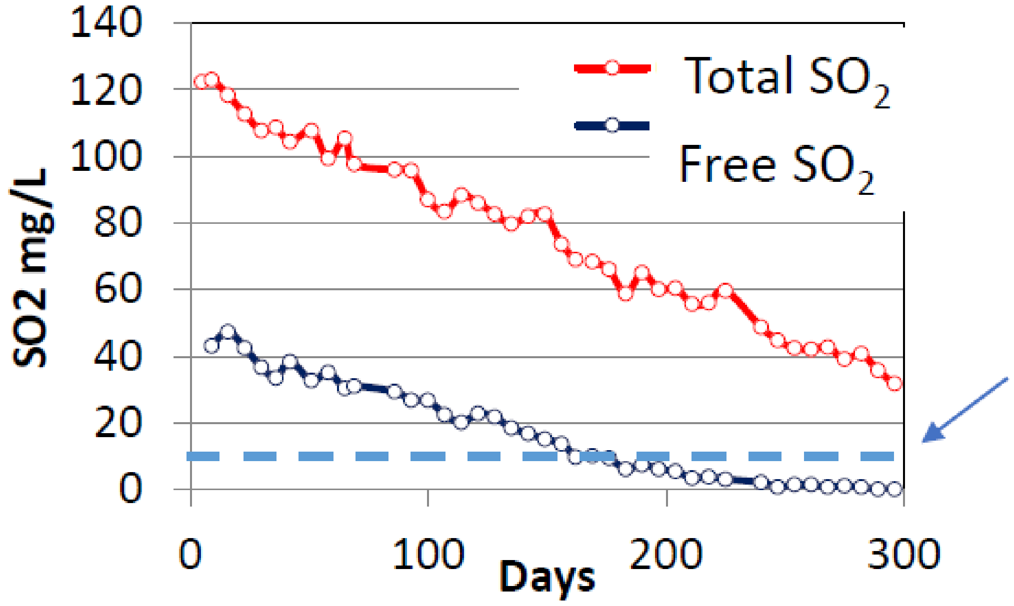
Glucose — Bound SO_2

Anthocyanins — Bound SO_2

Methional — Bound SO_2

Acetaldehyde — Bound SO_2

As Free SO_2 decreases, release of SO_2 from bound forms is favored, and wines take on oxidized character



At ~10 mg/L free SO_2, oxidized aromas appear

Godden, et al; *AJWGR* **2001**)

And this is where we expect to see release of "bound" aldehydes as free SO_2 is depleted

(Sacks, Howe, Standing, and Danilewicz; *AJEV* **2020**)

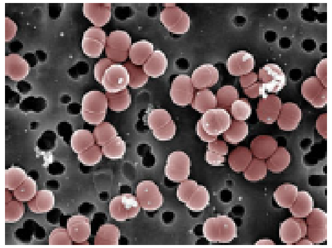
Methional — Bound SO_2

Loss of Free SO_2 →

Methional ("baked potato") — Free SO_2

Limiting SO_2 in canned wine makes sense, but the unique role of SO_2 as an antioxidant makes elimination challenging

1) Molecular SO_2 as an antimicrobial



There are other options! You don't need SO_2 to prevent spoilage!

DMDC, sterile filter, pasteurization (yikes?), and more

2) Free SO_2 (as bisulfite) as an antioxidant

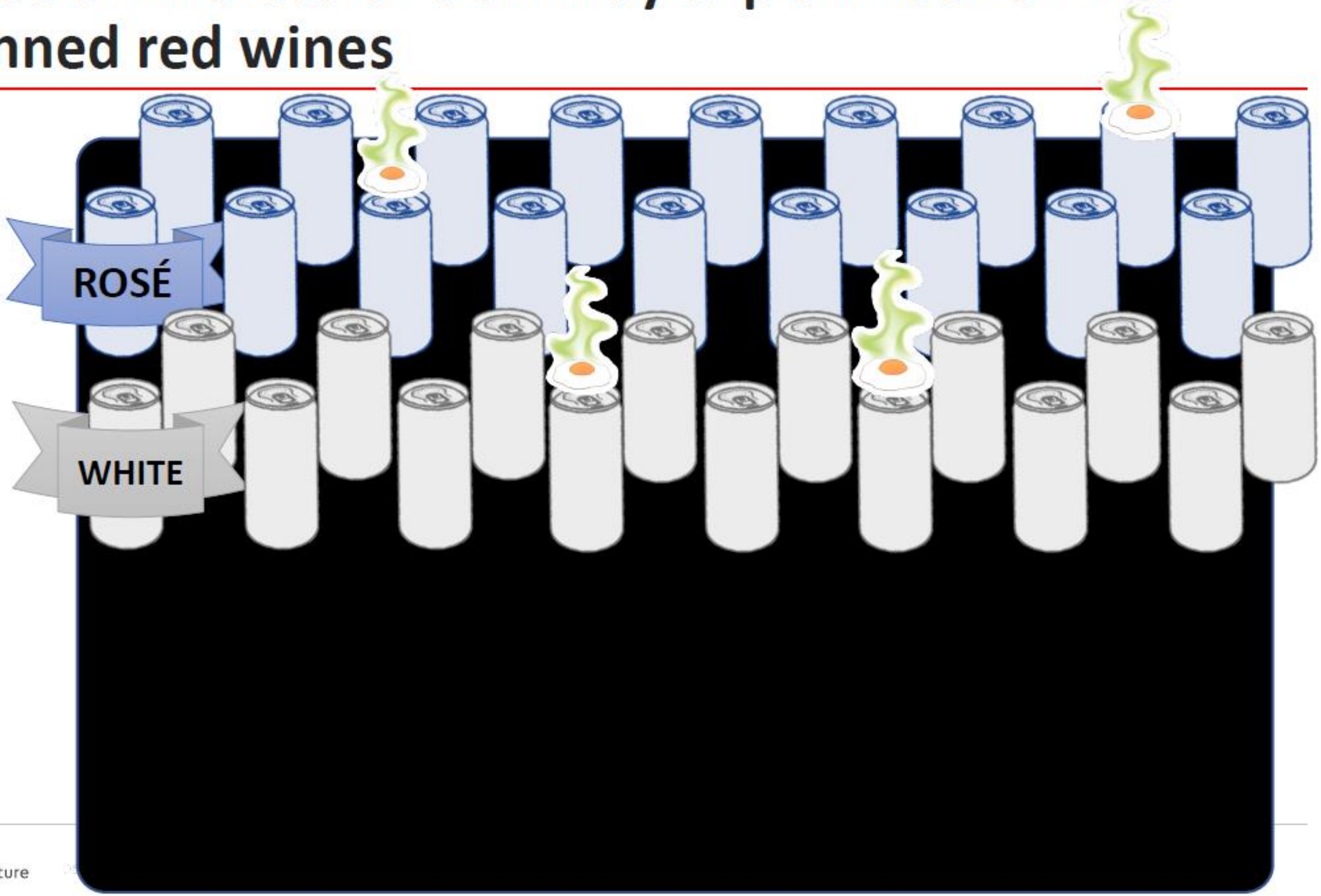
There are a lack of options for eliminating SO_2's role as an antioxidant

We do not (yet) have an alternative rapid scavenger for hydrogen peroxide

We do not (yet) have an alternative strategy for binding aldehydic off-aromas

The dependence on molecular SO2 may explain lack of H2S reported in canned red wines

H_2S *sometimes* found in canned white and rosé wines



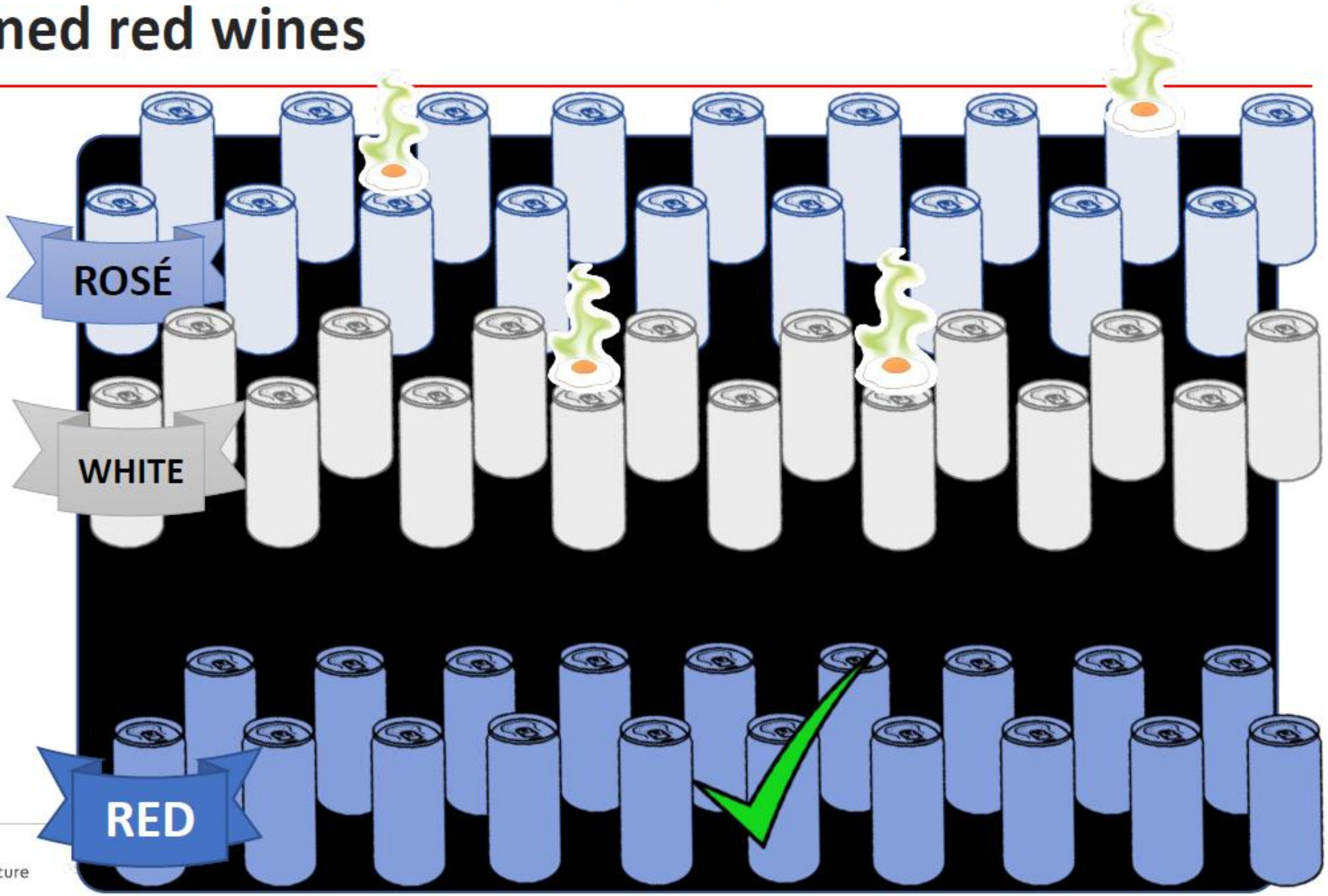
The dependence on molecular SO2 may explain lack of H2S reported in canned red wines

H_2S *sometimes* found in canned white and rosé wines

H_2S is **rare** in canned reds

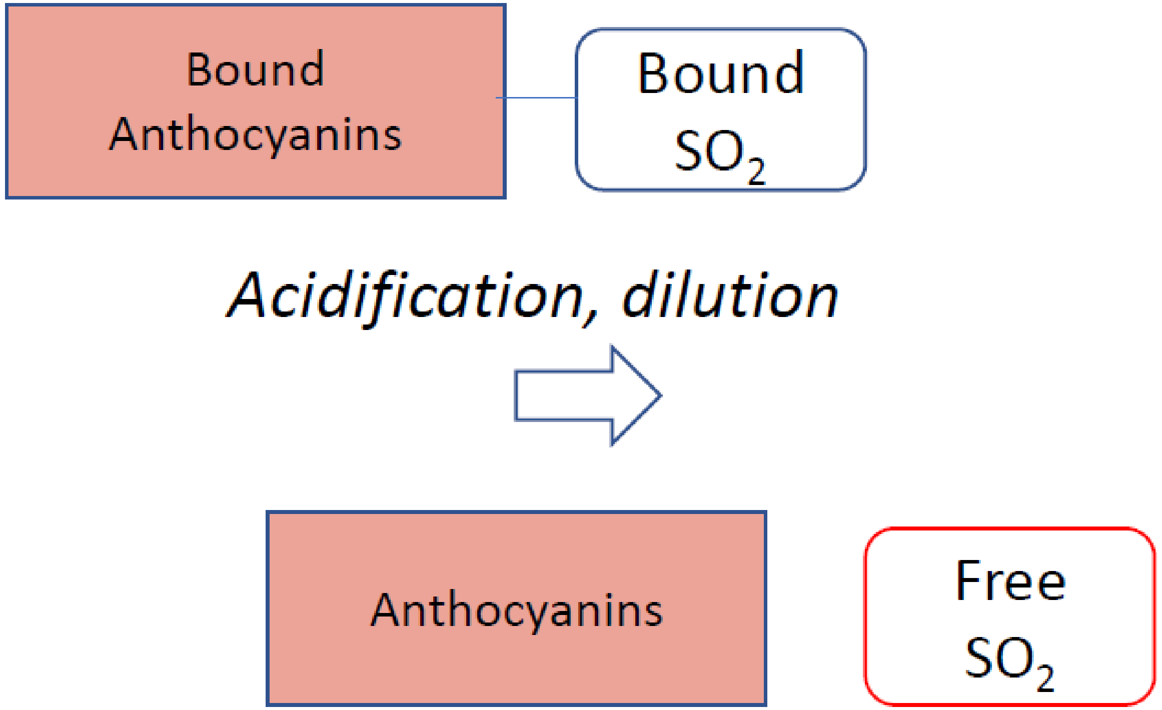
Lower molecular due to higher pH?

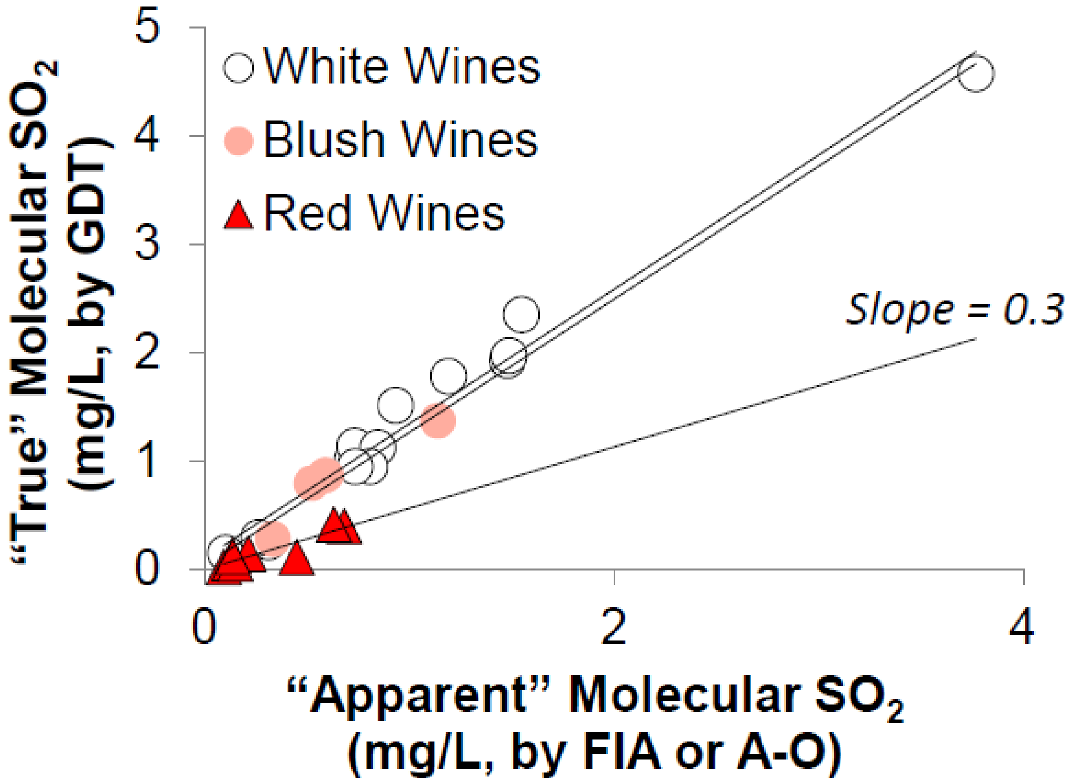
But there's more!



Conventional SO_2 methods (A-O, Ripper, FIA) overestimate free and molecular SO_2 in reds

Why? Dilution and acidification steps of these methods release anthocyanins



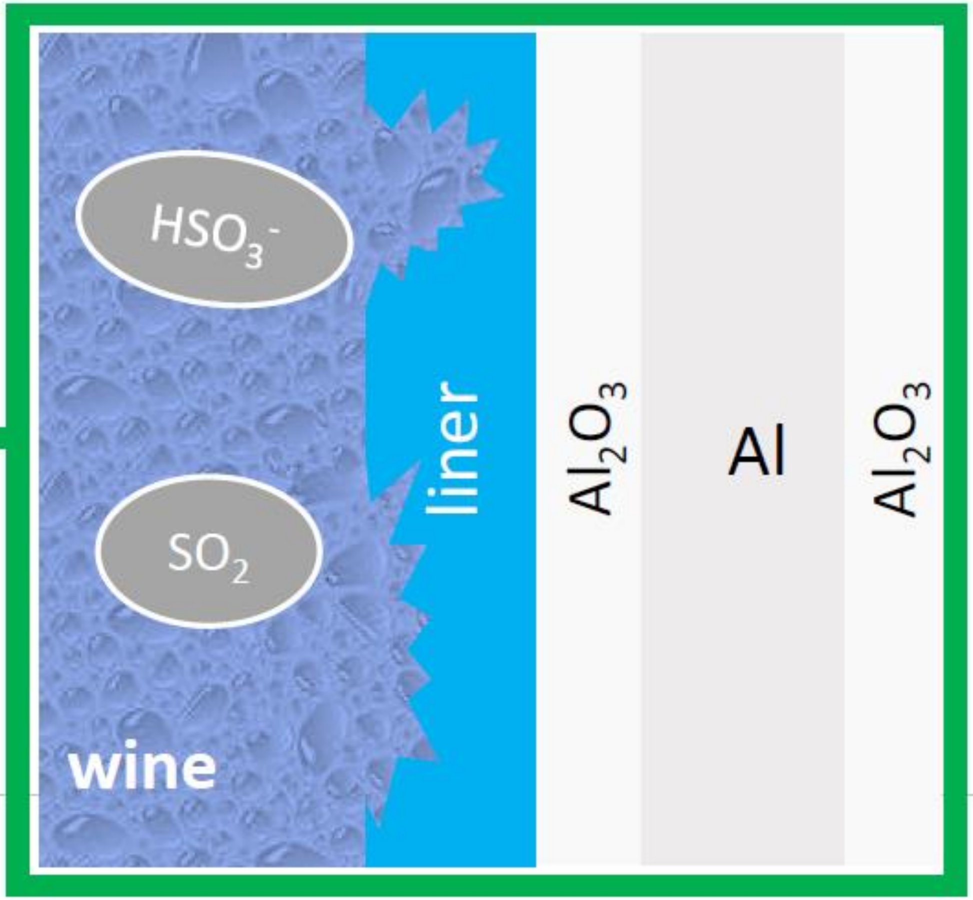


Coelho, Howe, and Sacks, *AJEV* **2015**

The "true" molecular SO_2 of your red wine is ~70% lower than what your data sheet says!

Which form of SO_2 (Bisulfite? Molecular?) is involved?

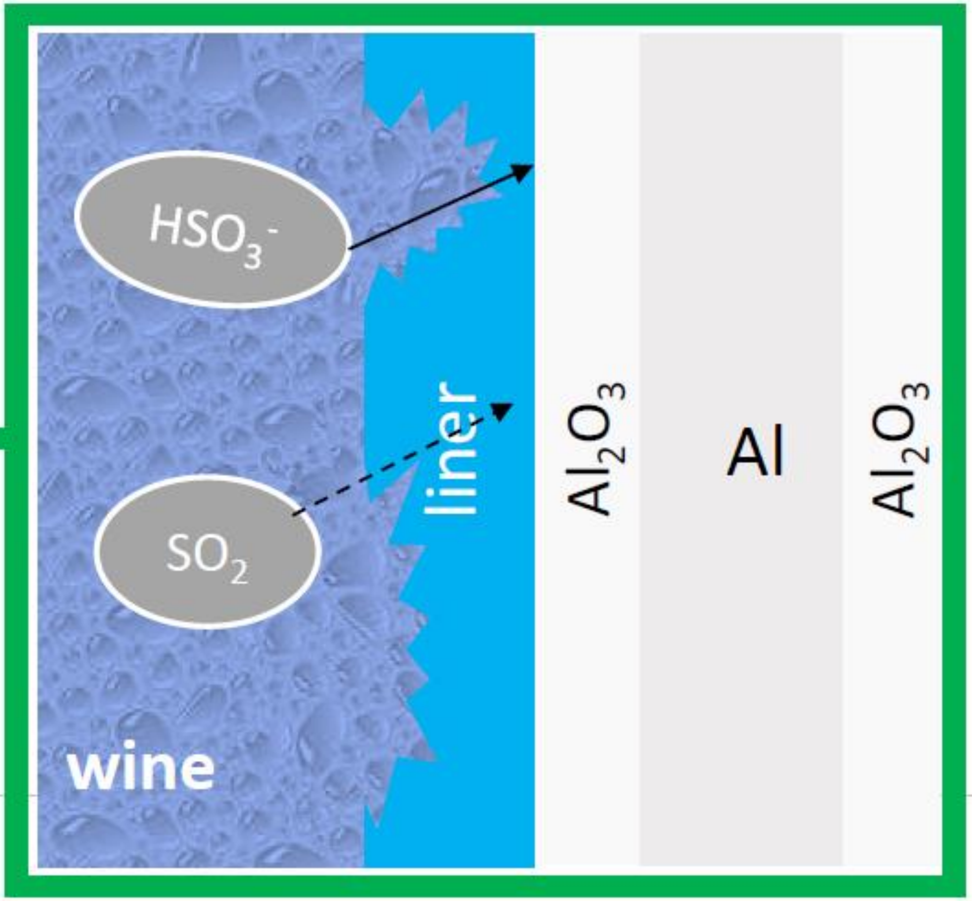
And how do they get through the can liner and passive alumina layer?



And the form of SO_2 likely matters

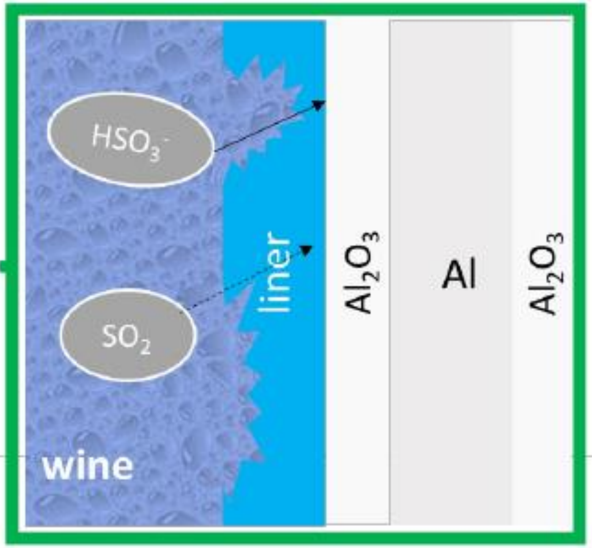
- Does it pass through imperfections/holes (more likely bisulfite)?
- Does it diffuse directly through the liner or (more likely molecular SO_2)

Preliminary work: molecular SO_2 (and diffusion) is probably more important



This is one of several questions our group is investigating

1) How does SO_2 get through the liner and alumina (Al_2O_3) layers? What form of SO_2 is involved



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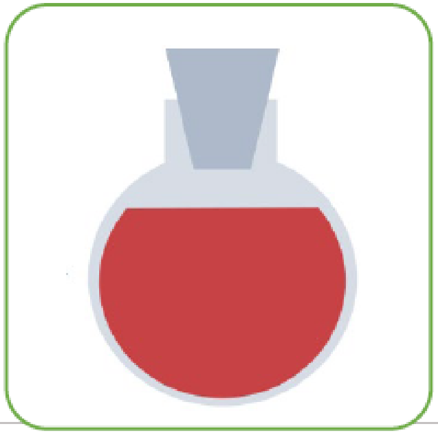
1) How does SO_2 get through the liner and alumina (Al_2O_3) layers?

2) Do other wine components exacerbate or mitigate H_2S production?

- pH, ethanol, Cu, Cl, polyphenols, acetate, and others
- There are recommendations . . . But based on what? How was this validated

Examples:
Cl- is well known to corrode bare aluminum
Cu can facilitate electrochemical reactions . . . But may also bind up H_2S ("labile" Cu, see Wilkes talk)



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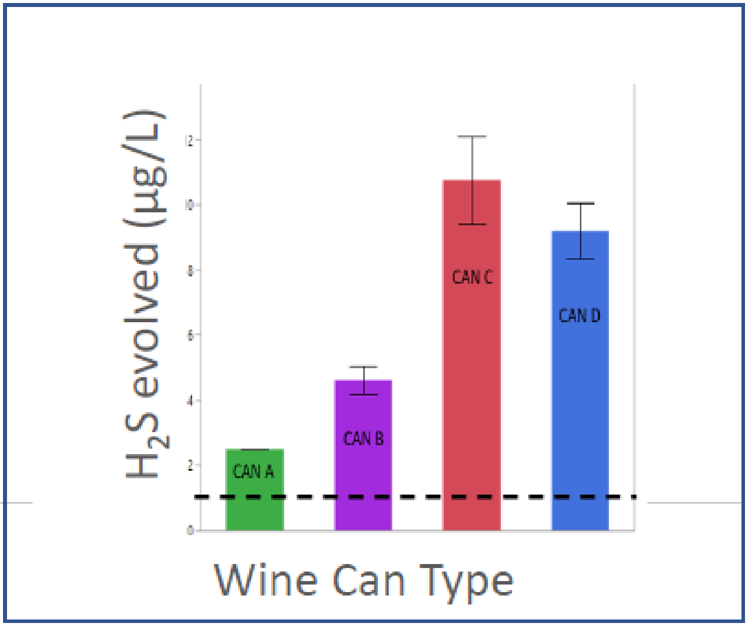
1) How does SO_2 get through the liner and alumina (Al_2O_3) layers?

2) Do other wine components exacerbate or mitigate H_2S production?
- pH, ethanol, Cu, Cl, polyphenols, acetate, and others
- There are recommendations . . . But based on what?

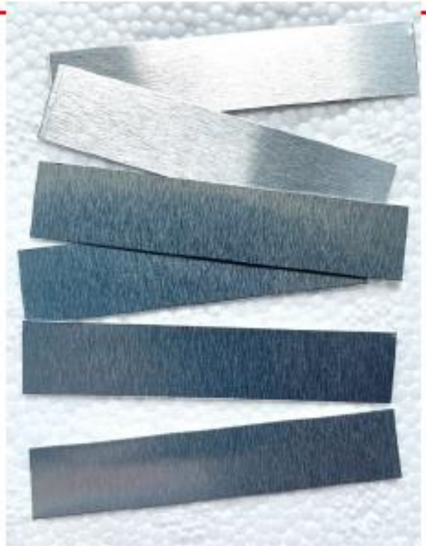
3) *Will <u>this</u> wine work with <u>this</u> liner?*
- Current tests are validated for corrosivity
- They are not validated for H_2S production
- What we want is a valid bench test



Ongoing work in the Sacks lab

Accelerated aging tests

- Al pieces ("coupons") coated with commercial liners
- Small volume containers
- Elevated temps



Evaluate model and real wines with a range of compositions

pH, Molecular SO_2, HSO_3^-, Cl^-, Cu, etc to determine key factors

Validate against canned wines

Take-home messages

SO_2 is used in packaged wines as an antimicrobial and antioxidant, The antioxidant role is hard to completely replace

SO_2 can bypass or diffuse through liner to react w/ Al and form H_2S

What to do?

- Reconsider your free SO_2 target. For example, (10 + (4 × TPO)) mg/L at packaging instead of 30 mg/L
- Molecular may matter more
- Role of other components still murky

Current tests for wine+can interactions are either tedious, or based on overall corrosivity, or have not been validated

- Ongoing work: appropriate small scale accelerated tests

Acknowledgements

Dr. Luna Maslov Bandić

Austin Montgomery

Industry cooperators

Funding Sources:

NSERC CRSNG

NSERC Canada

Saltonstall Wine Endowment

New York Wine and Grape Foundation

Survey Question

Analysis and Treatments for Canned Wine

Jasha Karasek
Winemaking Specialist, Enartis USA

DATE 6/18/20

Overview

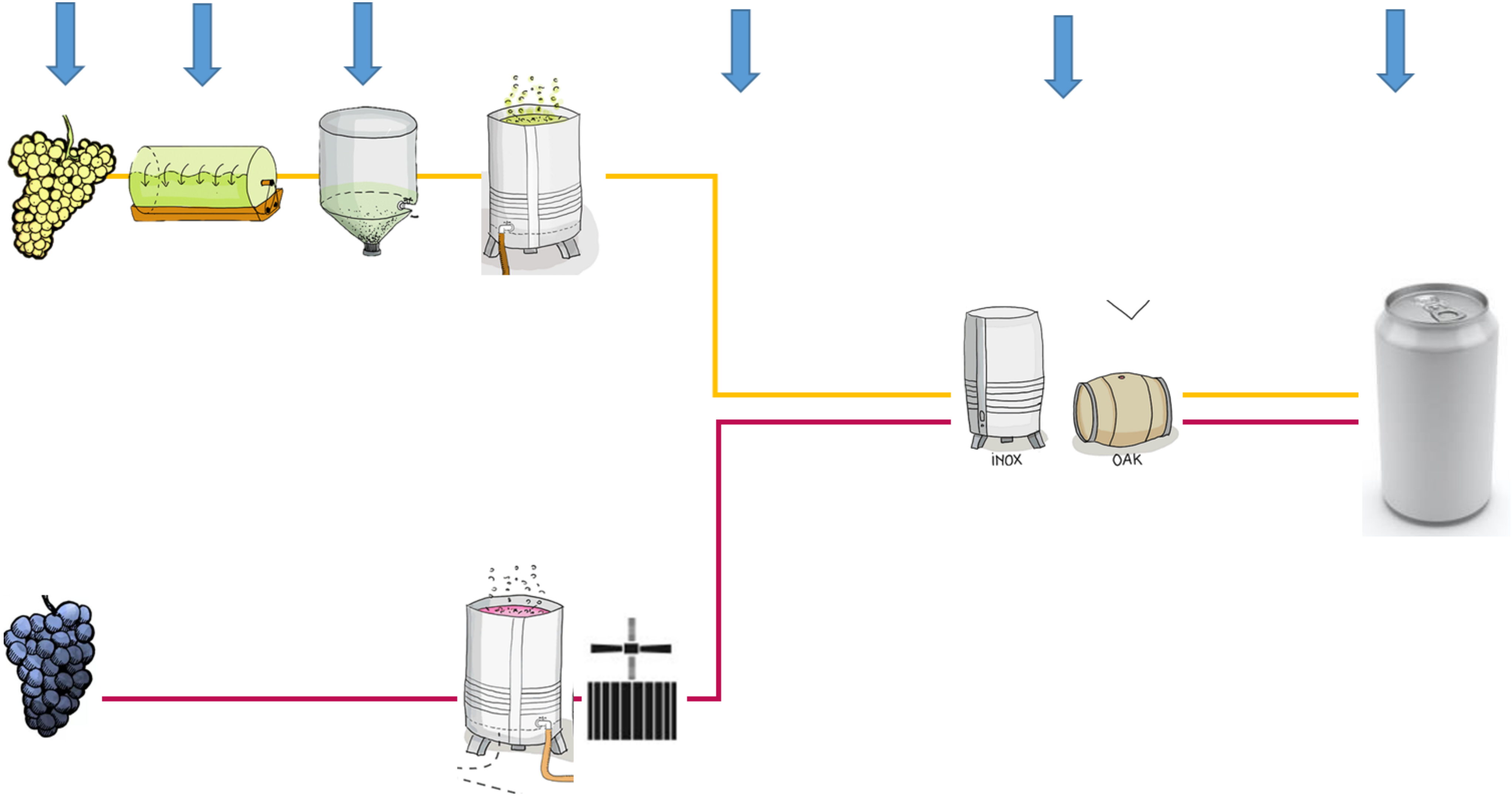
- Lowering SO_2 levels
- Antioxidant
- Antimicrobial
- Trials and results

enartis

How do we make wines with low(er) SO_2?

- Understand SO_2 activities
- Reduce SO_2 losses
- Replace SO_2 activities
- Reduce SO_2 additions at packaging

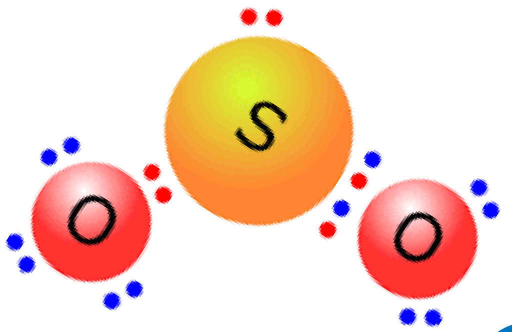
LOWERING SO_2 LEVELS STARTS AT HARVEST



SO_2 ACTIVITIES

ANTIMICROBIAL

(microbial control)



ANTIOXIDANT
(chemical oxidation)

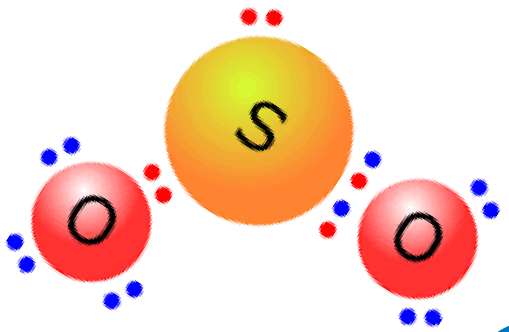
ANTIOXIDASIC

(enzymatic oxidation)

SO_2 PROTECTION

ANTIMICROBIAL

(microbial control)



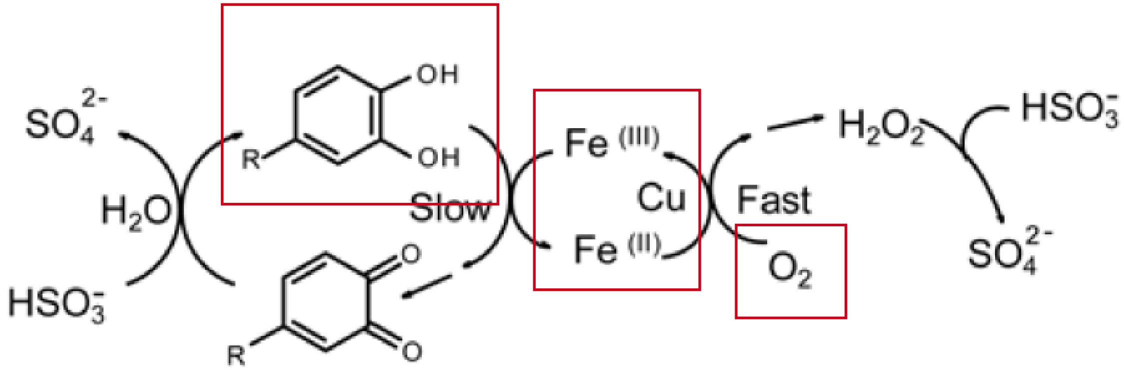
ANTIOXIDANT

(chemical oxidation)

ANTIOXIDASIC

(enzymatic oxidation)

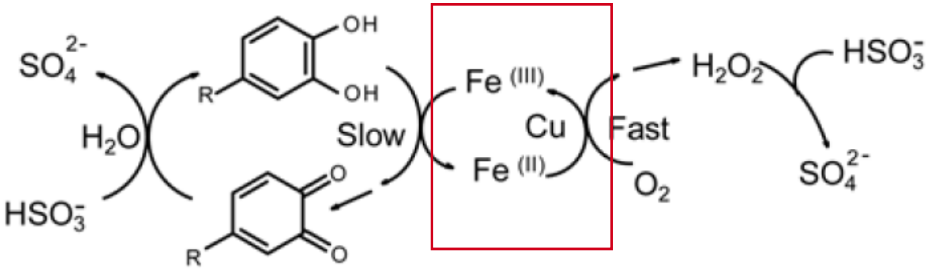
CHEMICAL OXIDATION



Scheme 1 Proposed mechanism of catechol oxidation in wine. Fe(III)/Fe(II) redox cycling and involvement of SO_2.

Danilewicz J. Interaction of sulfur dioxide, polyphenols, and Oxygen in a Wine – Model System: Centrol Role of Iron and Copper. Am. J. Enol. Vitic. 58:1 (2007)

METALS EFFECT ON SO_2 LOSSES



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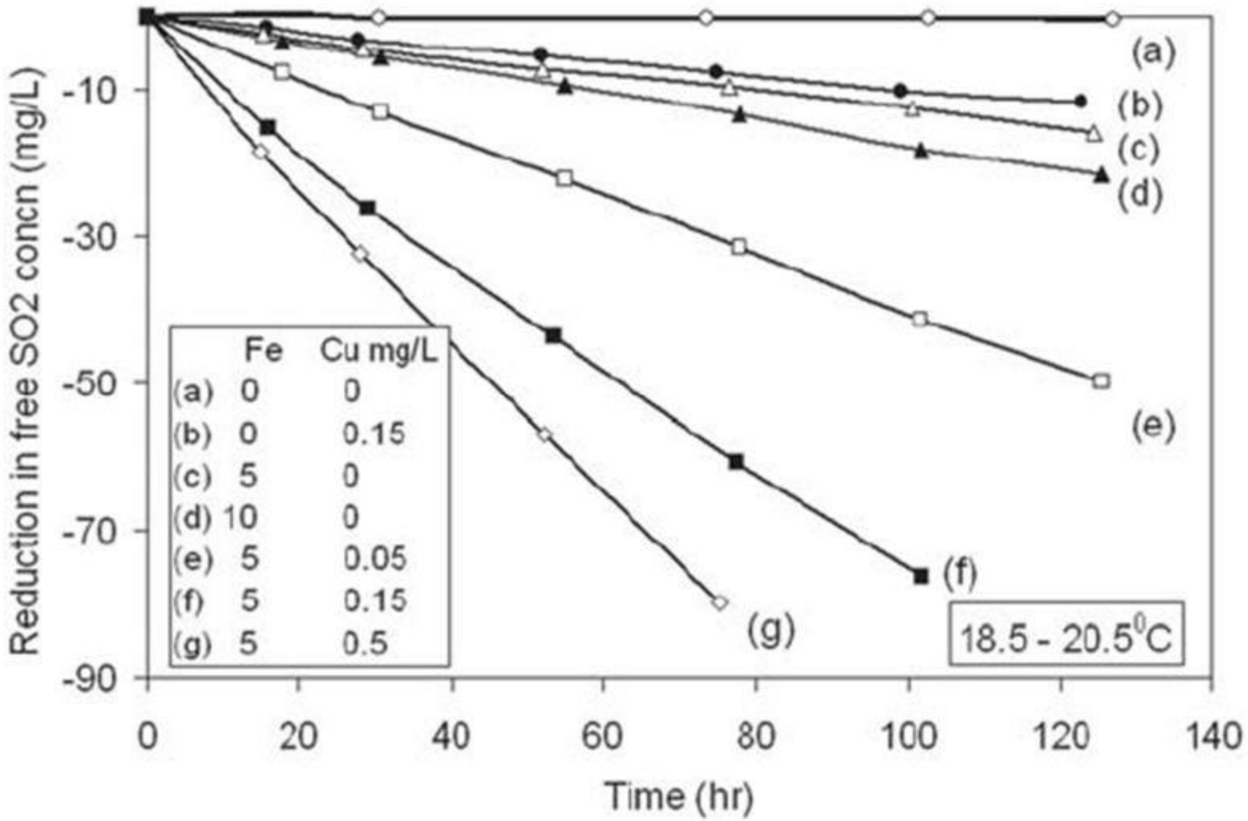
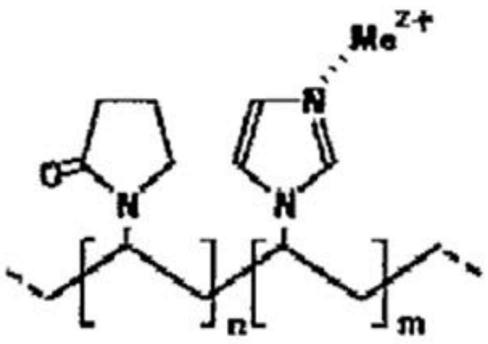
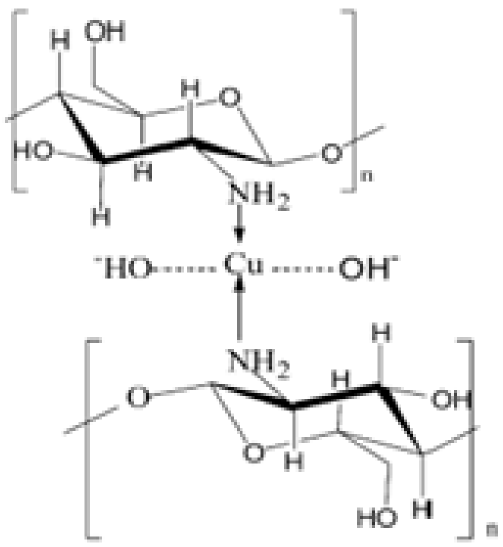


METAL REMOVERS PVI/PVP & CHITOSAN

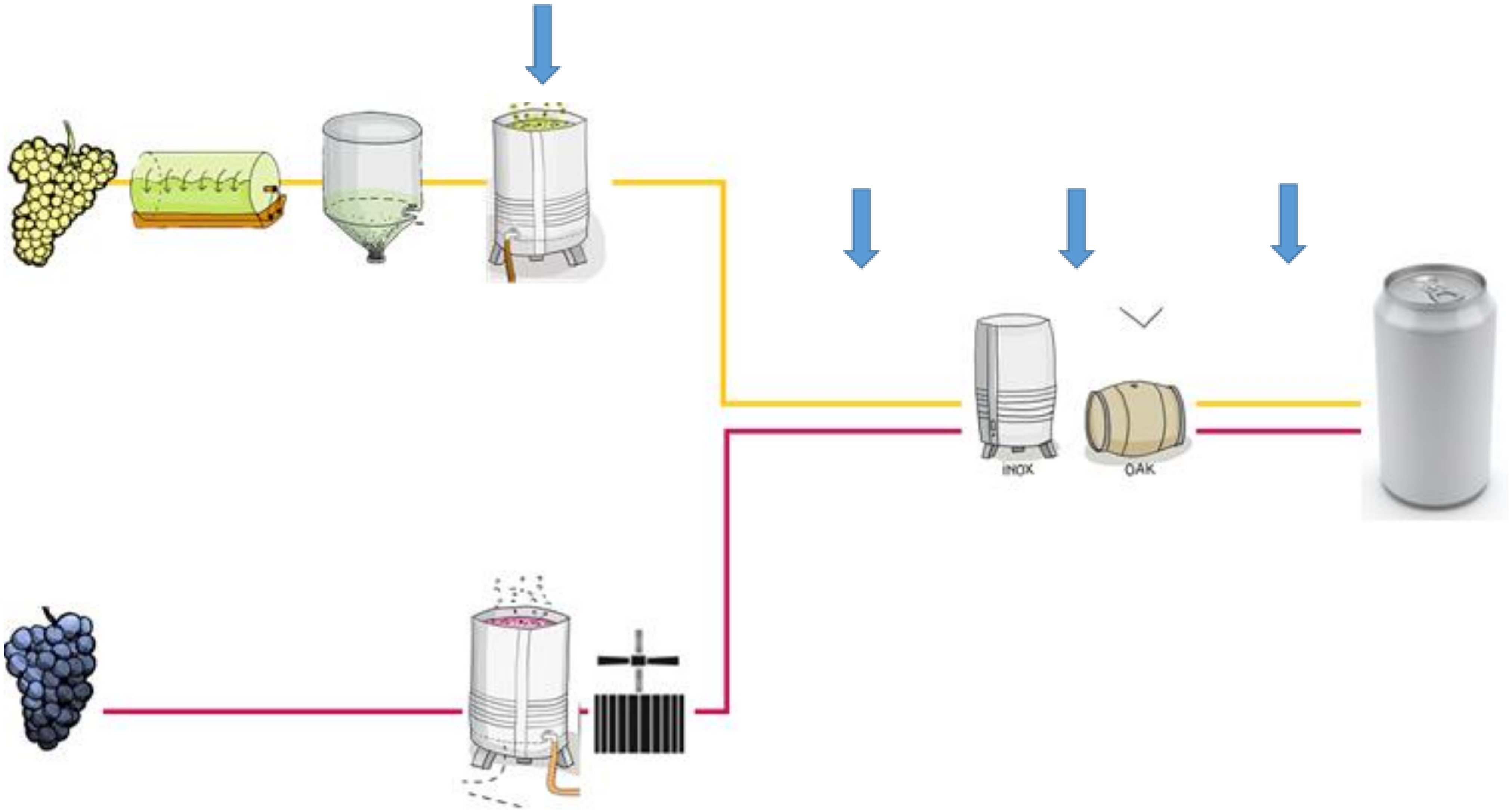




PVI/PVP
Vinylimidizole vinylpyrollidone
- Polymer which binds several different metal types.
- Also removes smaller phenolics like hydroxycinnamates

CHITOSAN
- Different forms available and vary in activities
- Processing can improve metal removal capacity
- Also removes smaller phenolics like catechins

POINTS WHERE METAL REMOVAL CAN OCCUR



METAL REMOVING OPTIONS

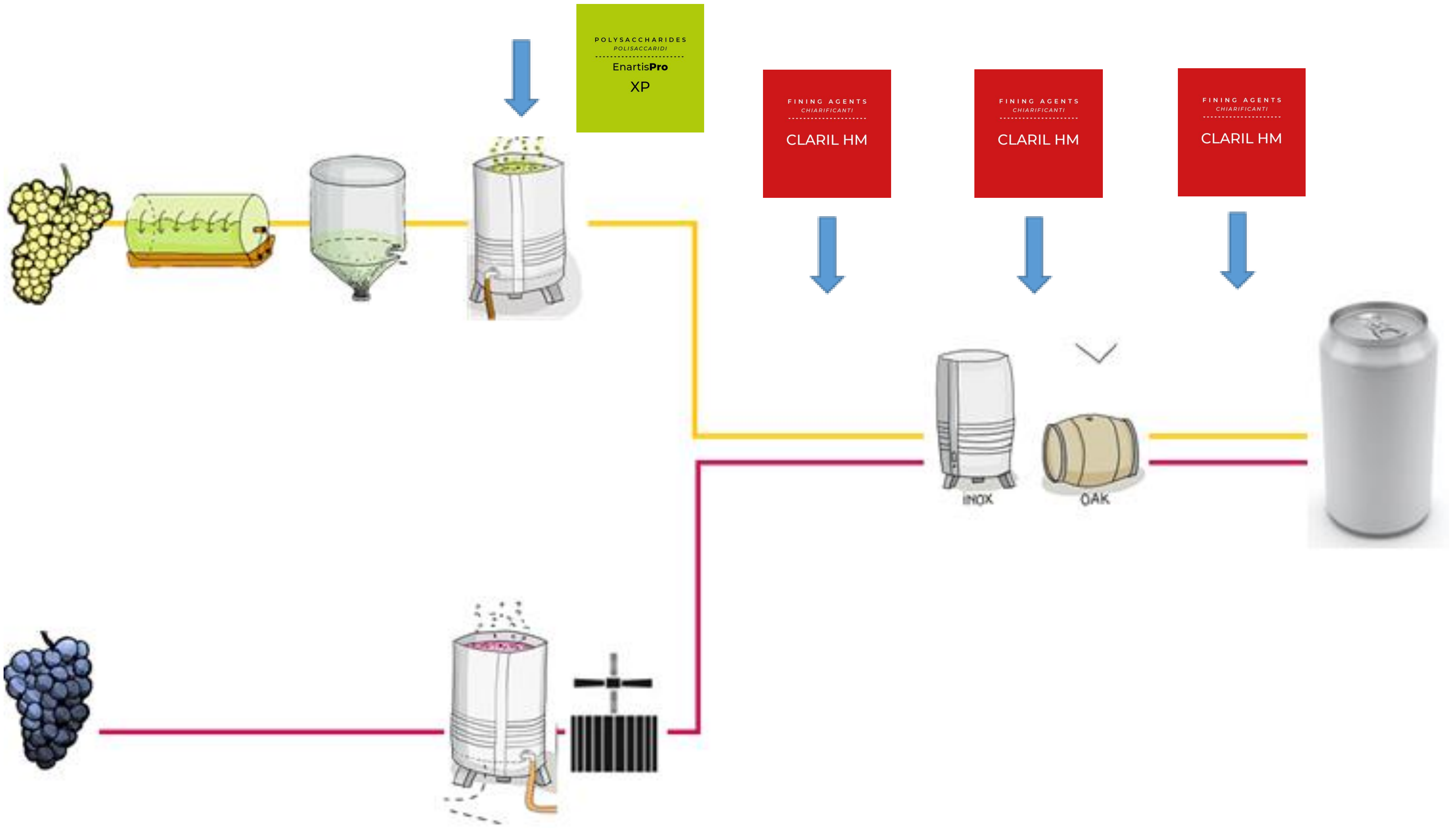
POLYSACCHARIDES
POLISACCARIDI
EnartisPro
XP

POLYSACCHARIDES
POLISACCARIDI
EnartisPro
FT

FINING AGENTS
CHIARIFICANTI
CLARIL HM

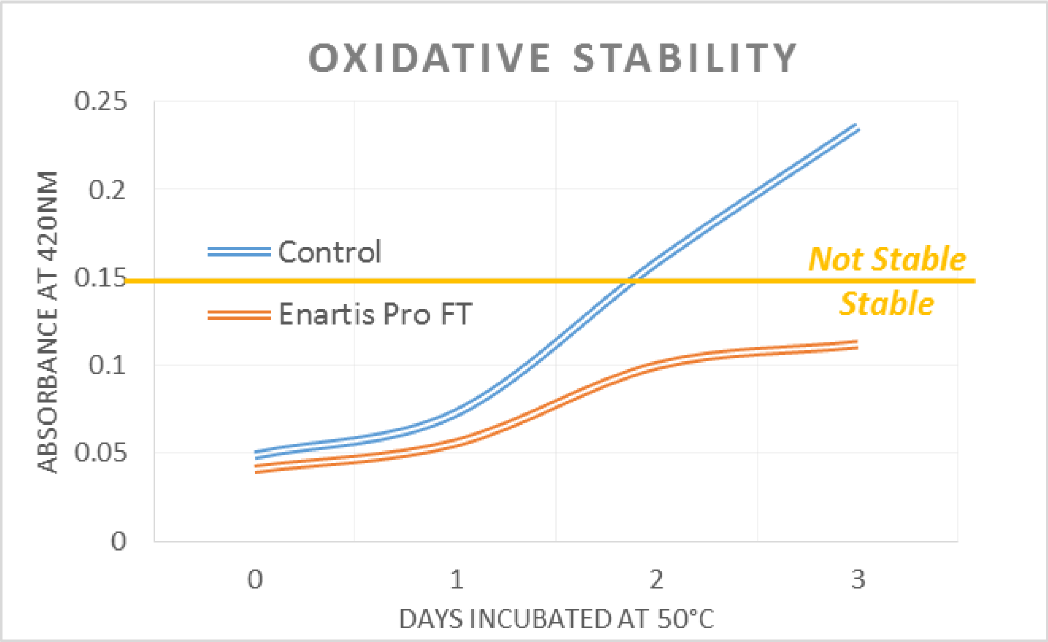
FINING AGENTS
CHIARIFICANTI
STABYL MET

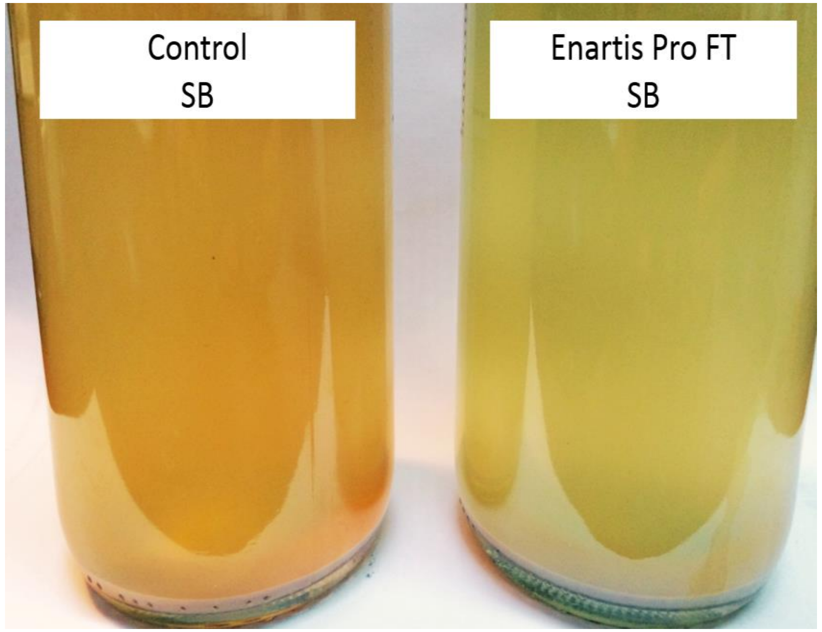
POINTS WHERE METAL REMOVAL CAN OCCUR



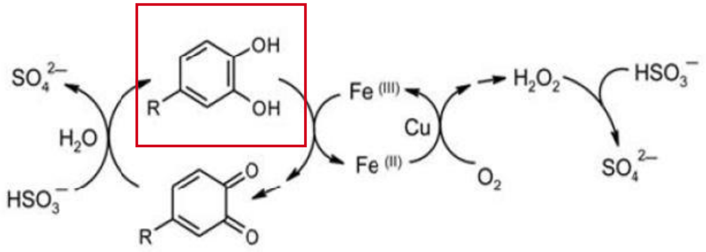
Stabyl Met Containing Polysaccharide Blends

Pro FT/XP – Yeast hulls rich in polysaccharides blended with PVI/PVP





ROLE OF PHENOLICS SO_2 LOSSES



Scheme 1 Proposed interaction of a catechol and O_2 in the presence of sulfite.

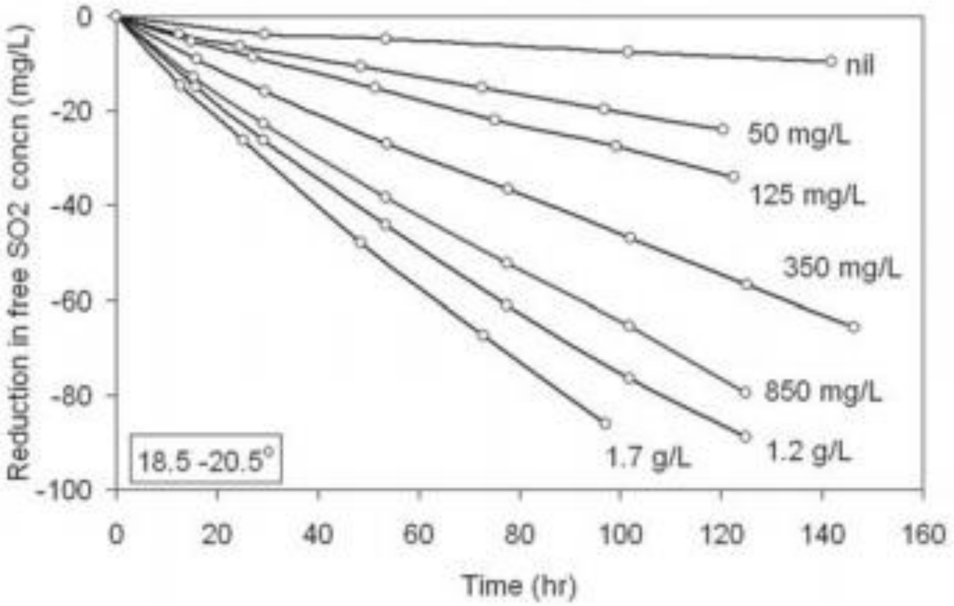


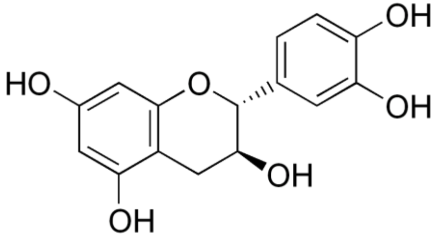
Figure 2 The effect of 4-MeC concentration on the reaction rate of SO_2 in the presence of Fe (5 mg/L) and Cu (0.15 mg/L) in the wine-model system.

Danilewicz J. Interaction of sulfur dioxide, polyphenols, and Oxygen in a Wine – Model System: Centrol Role of Iron and Copper. Am. J. Enol. Vitic. 58:1 (2007)

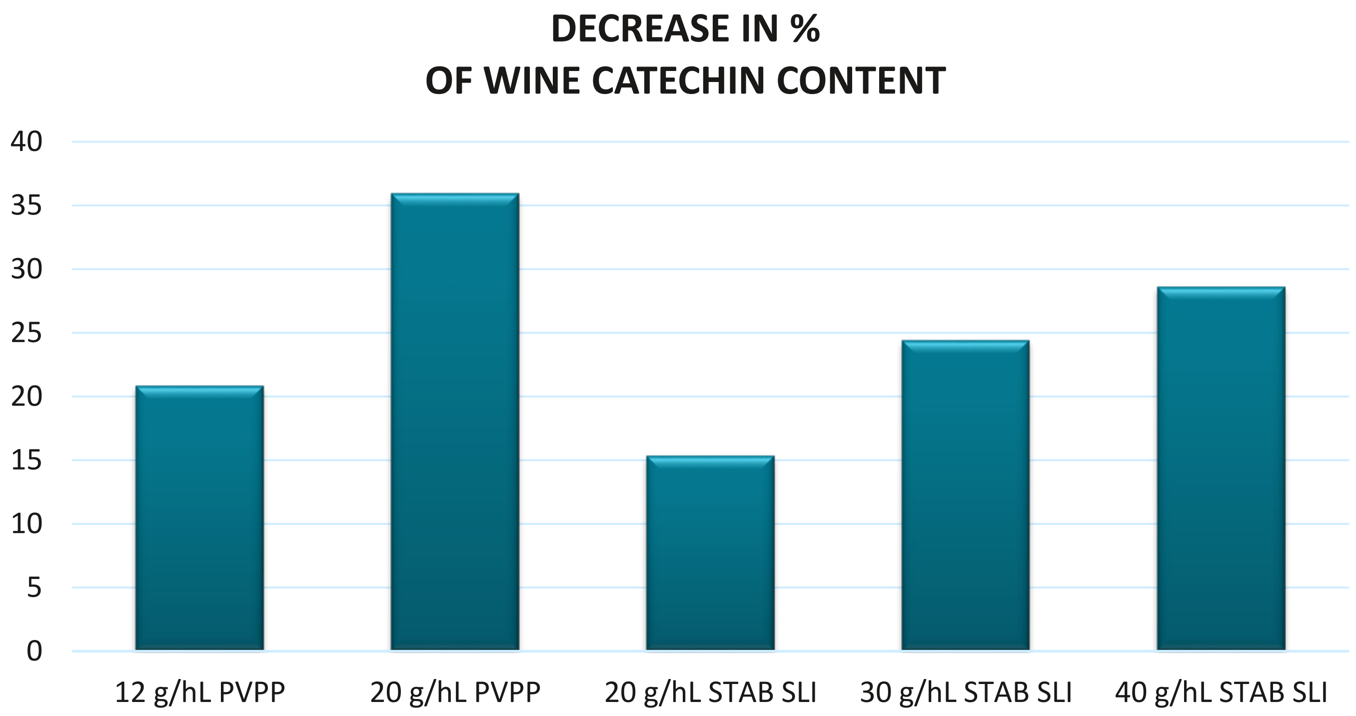
WAYS TO DECREASE OXIDATIVE PRECURSORS

Tools for decreasing oxidative precursors

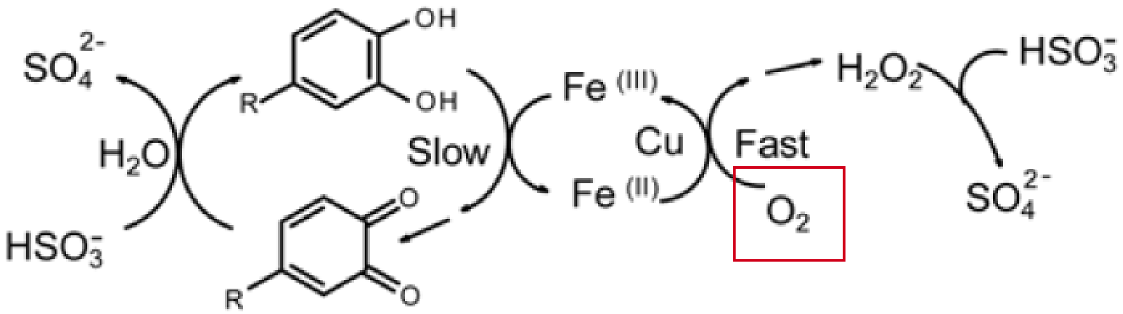
- PVPP – Stabyl PVPP
- PVI/PVP - Stabyl Met
- Polymer Blends – Claril HM
- Chitosan – Stab Micro
- Casein
- Hyperoxidation (not aromatic varieties)
- Separate hard press fractions



Catechin



CHEMICAL OXIDATION



Scheme 1 Proposed mechanism of catechol oxidation in wine. Fe(III)/Fe(II) redox cycling and involvement of SO_2.

Danilewicz J. Interaction of sulfur dioxide, polyphenols, and Oxygen in a Wine – Model System: Centrol Role of Iron and Copper. Am. J. Enol. Vitic. 58:1 (2007)

PREVENTING SO_2 LOSSES – AVOIDING OXYGEN PICKUP

These are processes where oxygen pickup is highest

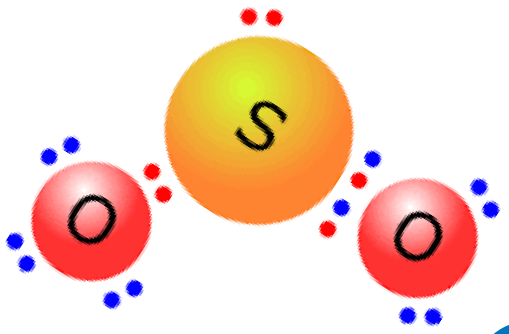
Operation	Range O_2 pickup (mg/L)
Racking	0.20 - 1.50
Pumping	0.10 - 0.20
Plate filtration	0.04 - 2.20
DE filtration	0.24 - 1.10
Cross Flow filtration	0.20 - 4.30
Membrane filtration	0.20 – 2.10
Cold stabilization	1.20 - 7.80
Electrodialysis	0.20 - 2.70
Bottling	0.38 - 9.10

Adapted from : Morozova, K., Schmidt, O. (2011) Oxygen uptake during winemaking. FDW conference, Freiburg, April 6, 2011.

SO_2 PROTECTION

ANTIMICROBIAL

(microbial control)

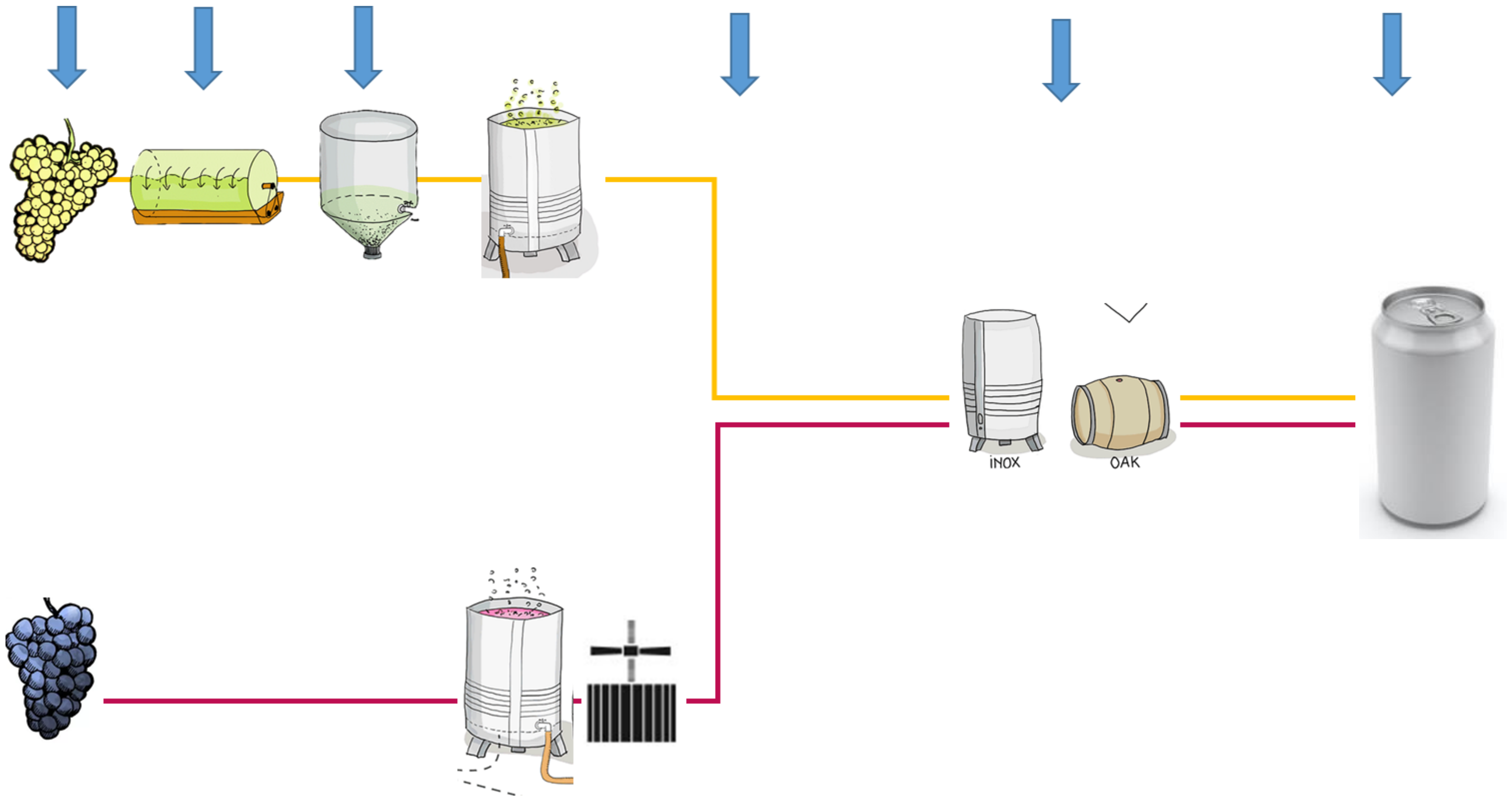


ANTIOXIDANT
(chemical oxidation)

ANTIOXIDASIC

(enzymatic oxidation)

APPLICATION OF SO_2 FOR MICROBIAL PROTECTION

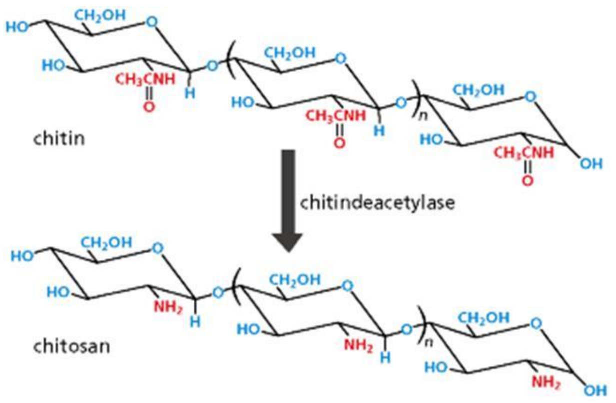


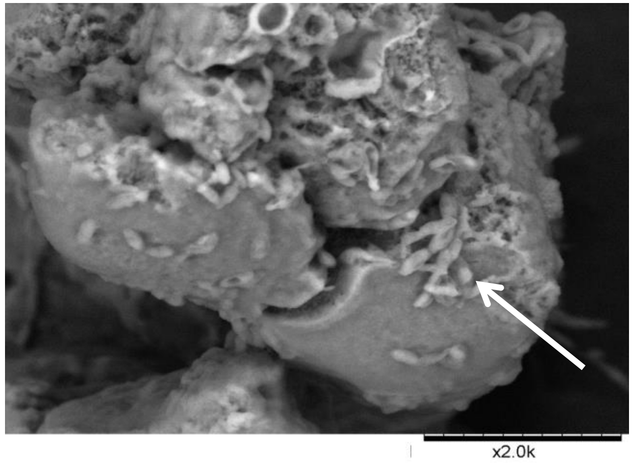
MICROBIAL CONTROL WITH STAB MICRO + STAB MICRO M

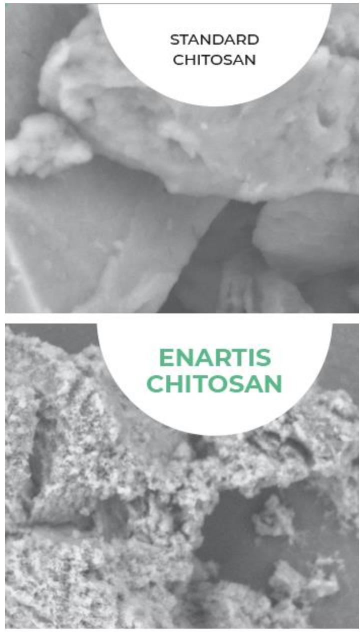
Chitosan: de-acetylation of chitin, polysaccharide derived from *Aspergillus niger*

Attraction chitosan (+) and microbe cell walls (-) => Death of cells

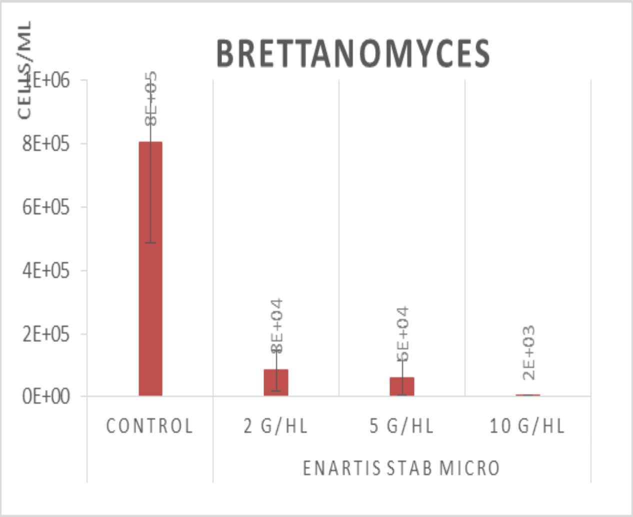
Enartis Stab Micro and Enartis Stab Micro M: Pre-activated chitosan, higher charge, higher contact surface, better efficiency

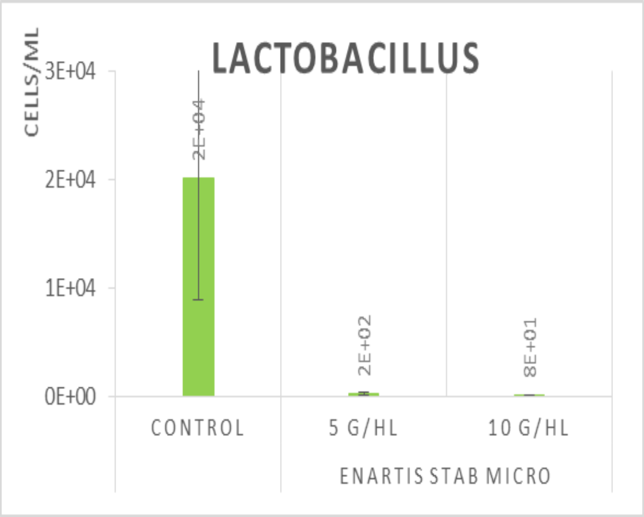


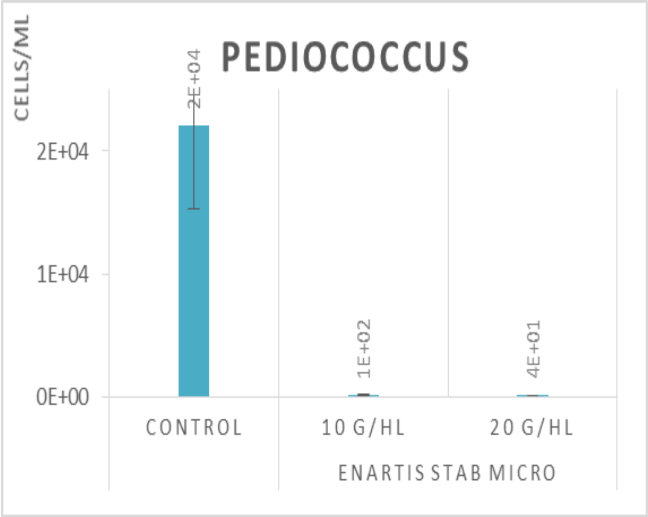


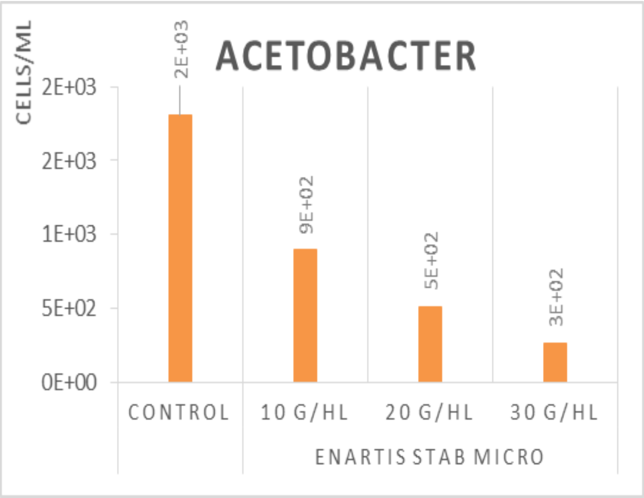


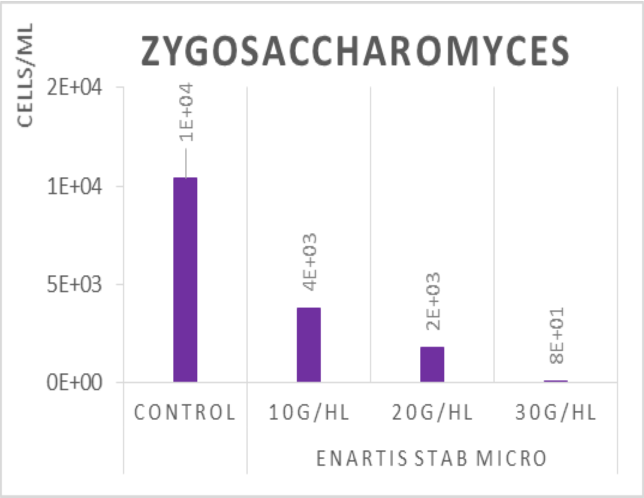
STAB MICRO EFFECT ON SPOILAGE MICROORGANISMS

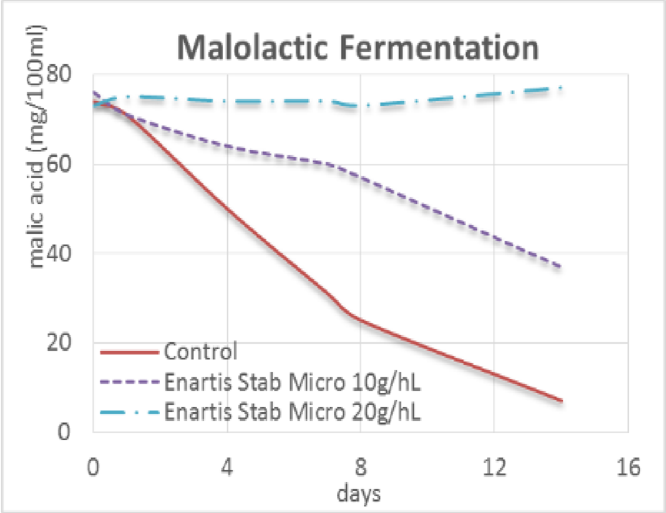




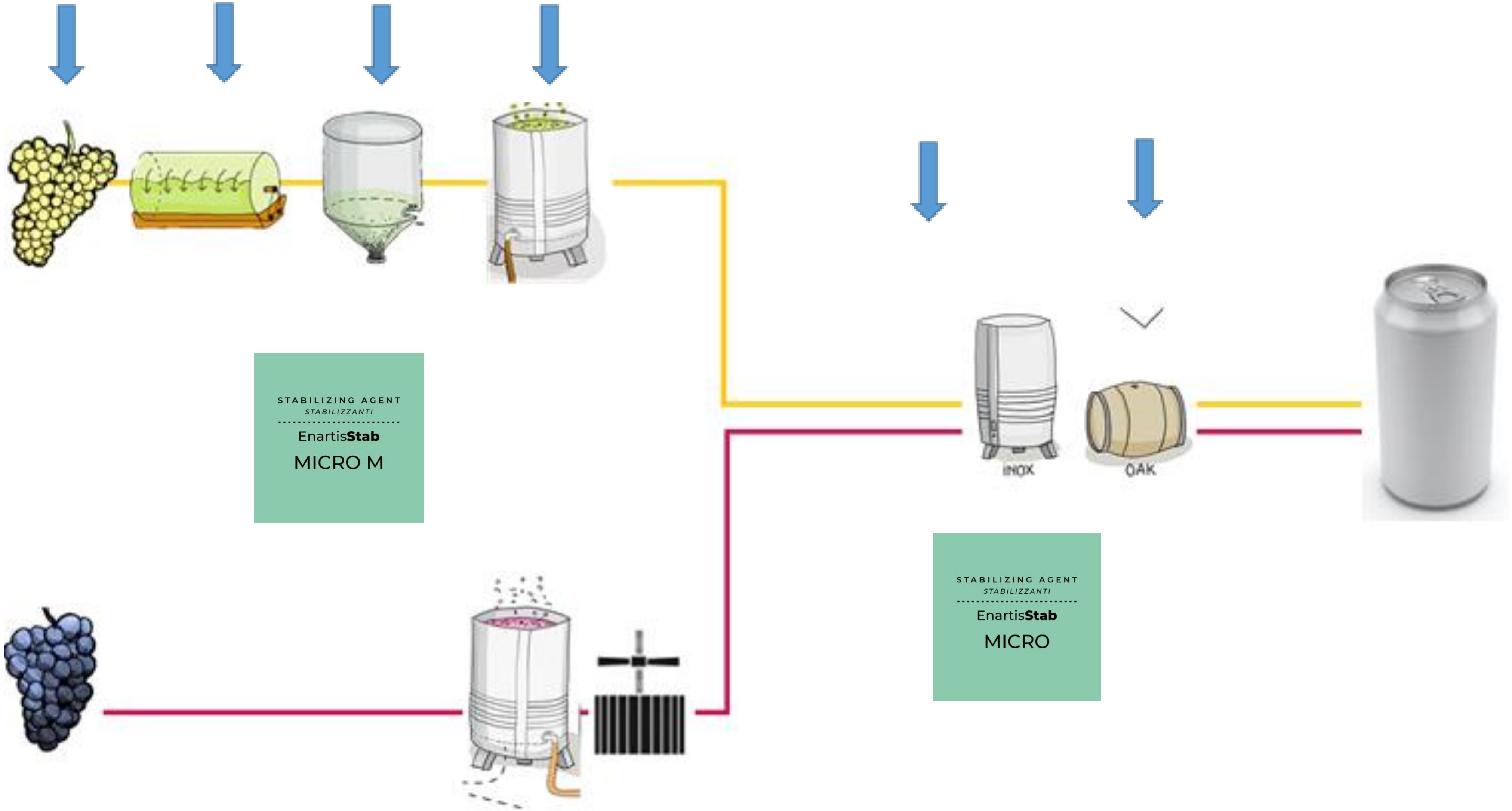








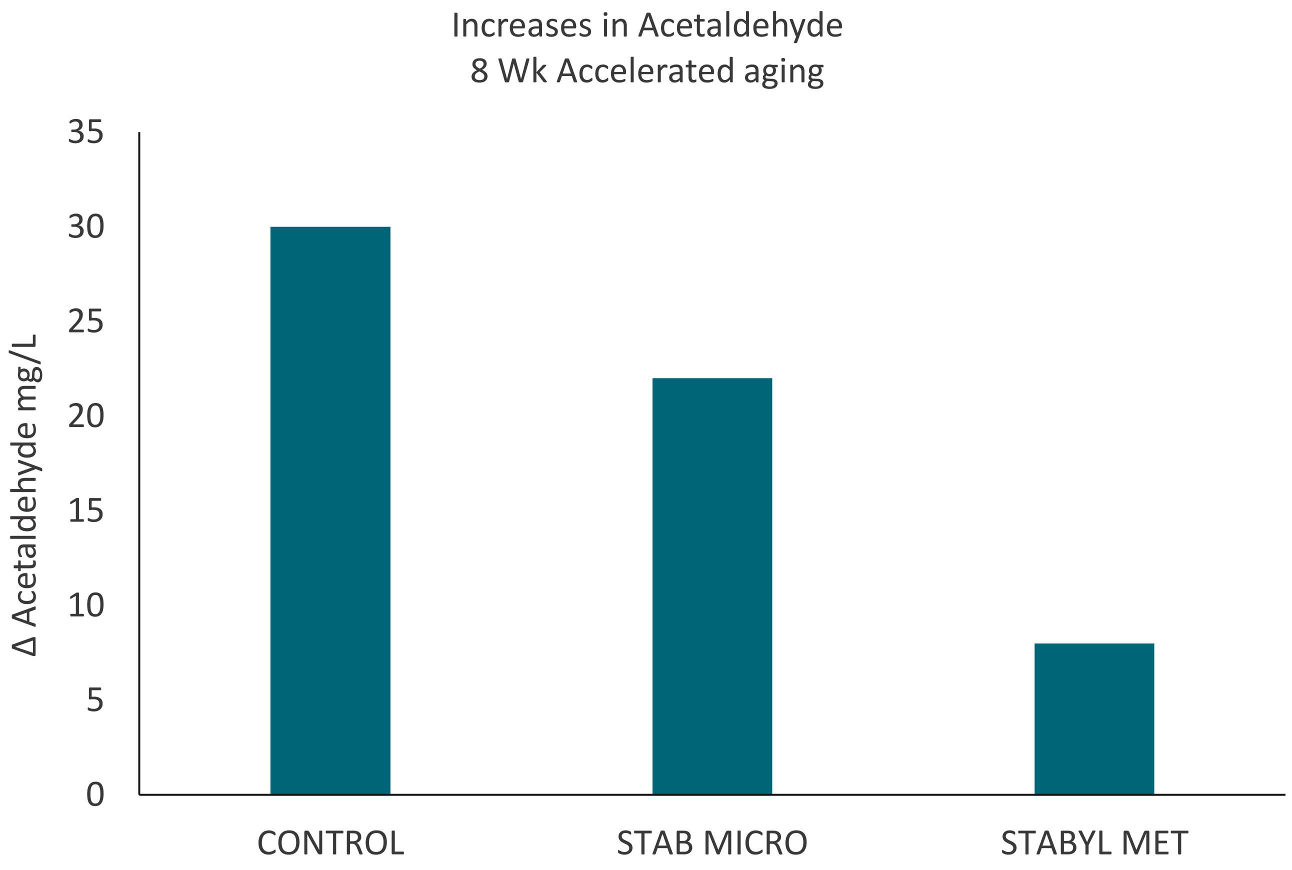
POINTS WHERE STAB MICRO CAN BE APPLIED



FULL ENARTIS LOW SO_2 PROTOCOL COMPARISON

PARAMETER	+ SO_2	LOW SO_2
pH	3.56	3.54
Free SO_2 (mg/L)	29	0
Total SO_2 (mg/L)	61	1
VA (g/100 mL)	0.061	0.054
PCR Pedio (cell/mL)	ND	ND
PCR Lacto (cell/mL)	1.06 x 10^4	ND
PCR Zygo (cell/mL)	ND	ND
PCR Brett (cell/mL)	ND	ND

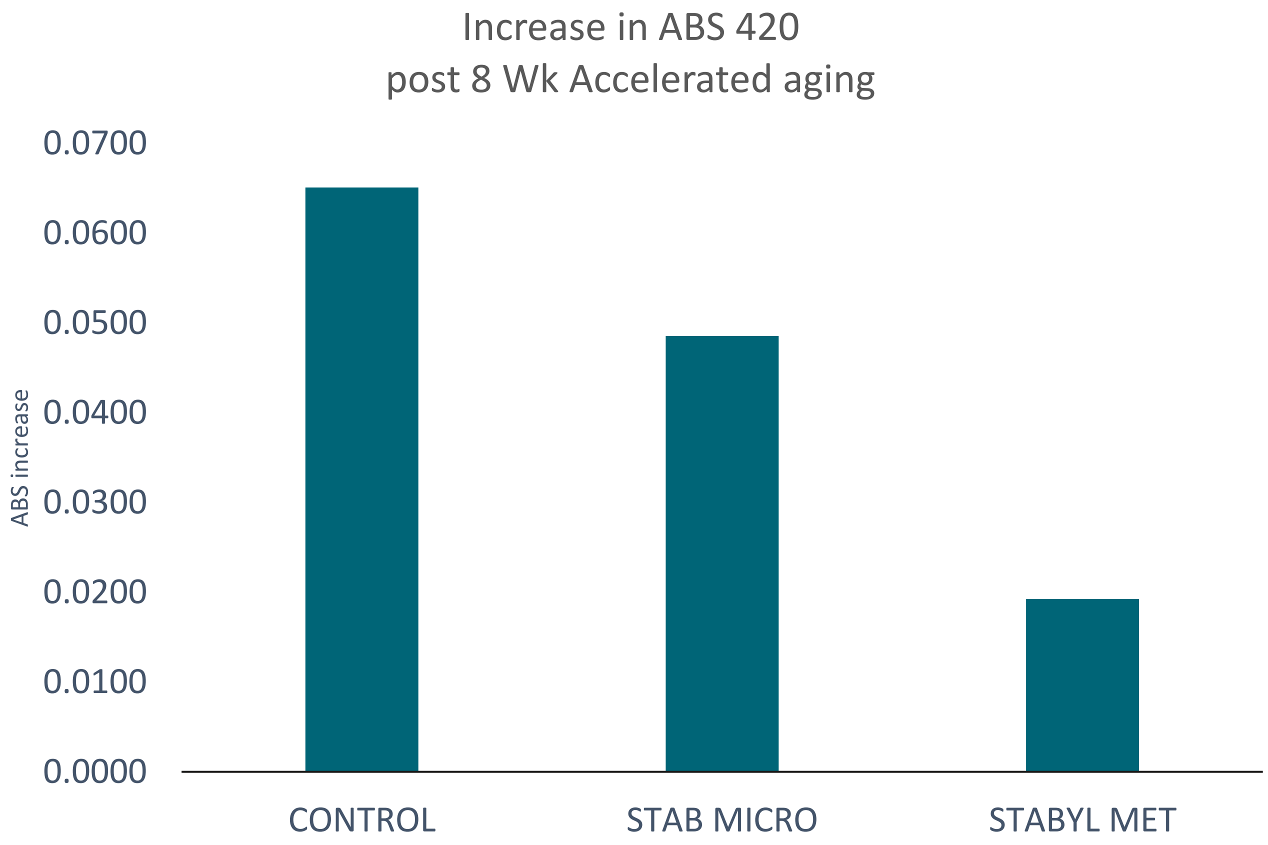
ACCELERATED AGING TRIALS - ACETALDEHYDE



FINING AGENTS
CHIARIFICANTI
STABYL MET

STABILIZING AGENT
STABILIZZANTI
Enartis**Stab**
MICRO

ACCELERATED AGING TRIALS – CHANGE IN ABS 420

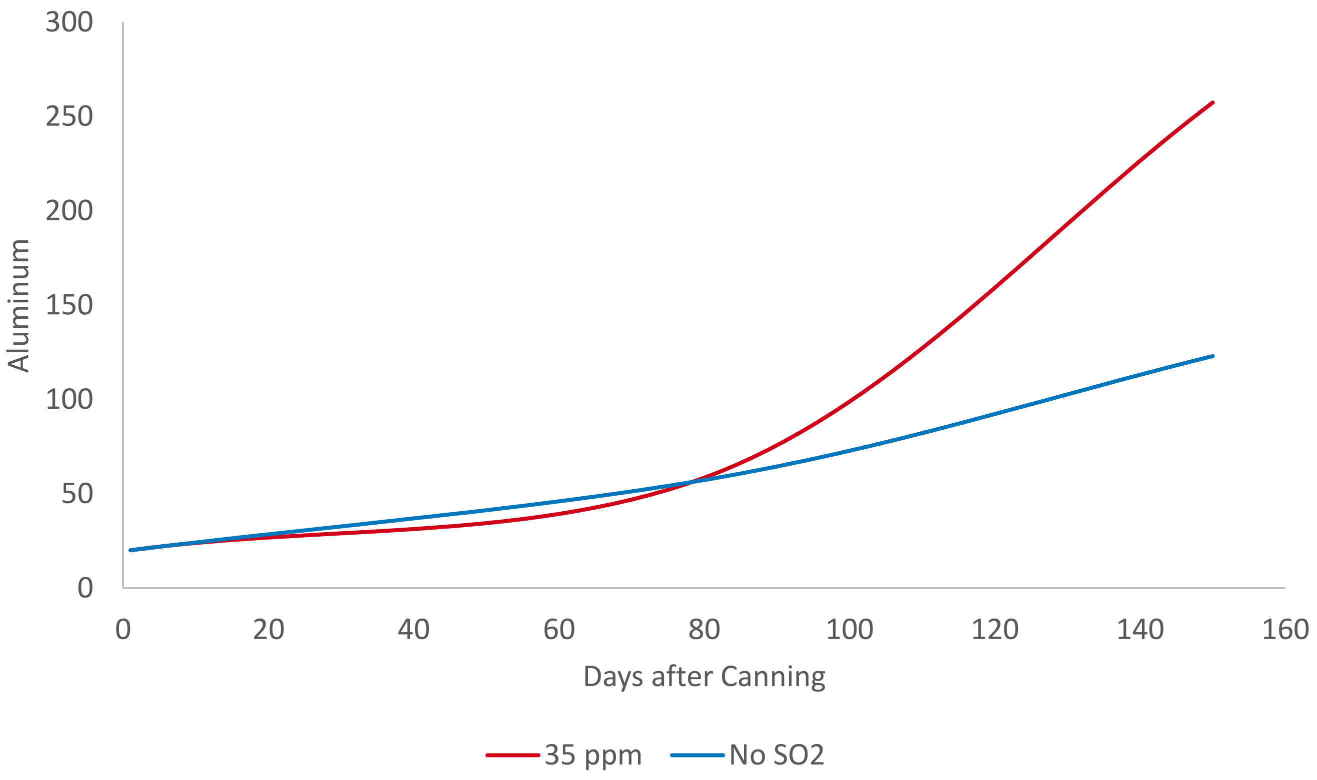


Trial Setup -

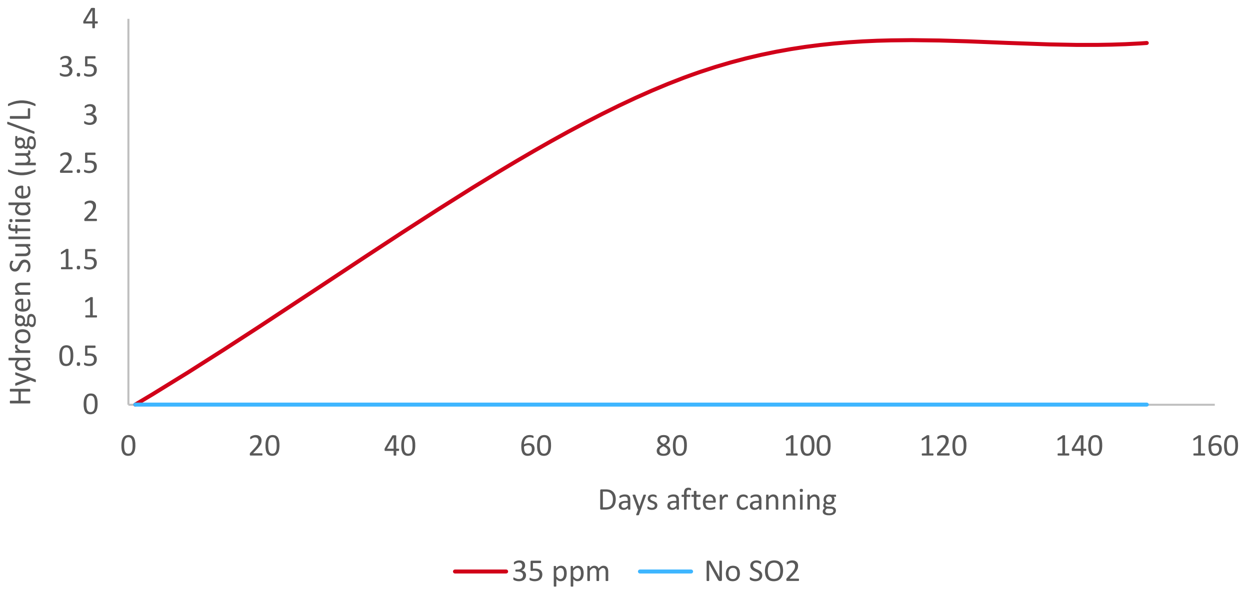
- Cider fermented with 10 g/hL Stab Micro M
- Treated with .1 ppm of Cu, then removed Cu with 10 g/hL Claril HM
- Canned with 0 ppm SO_2

- Same batch fermented without Stab Micro M
- Treated with .1 ppm of Cu, no addition of Claril HM
- Canned with 35 ppm Free SO_2, 70 ppm total

COMPLETE PROTOCOL CIDER EXAMPLE – NO SO_2, Cu REMOVED



Comparing Low SO_2 and Copper removal impact



TAKE AWAYS

- Limiting SO_2 can help with reduction appearing in canned products
- Understanding the activities of SO_2 can help us to find ways to lower levels in canned wine production
- There is good evidence that low SO_2 and removing Copper may help with reduction.

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