

Transport of lipid oxidation intermediates

and its impact on the lipid oxidation rate in a model food emulsion

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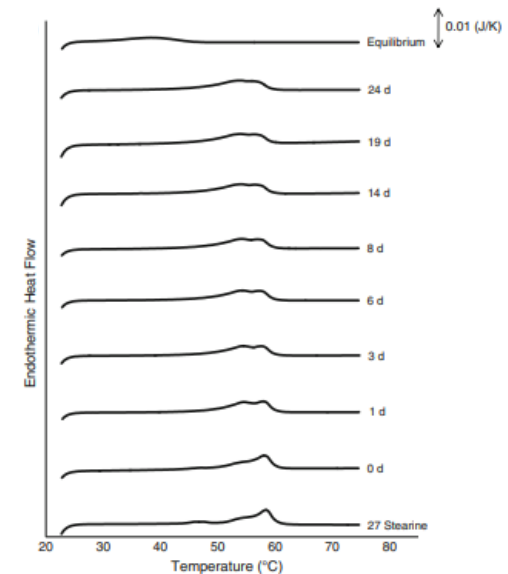
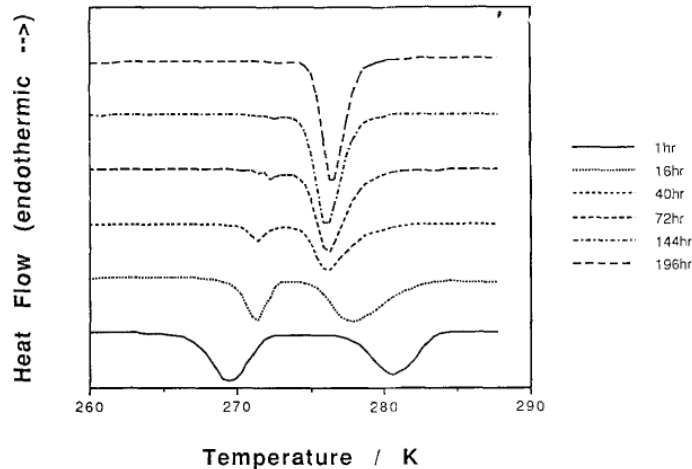
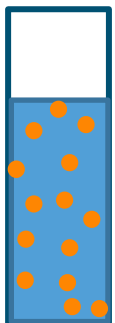
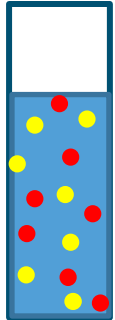


Transport of lipids in emulsions

■ Compositional ripening:

- Mixing of n-hexane and n-octadecane droplets (1)
- Mixing of palm stearin and MCT oil droplets (2)

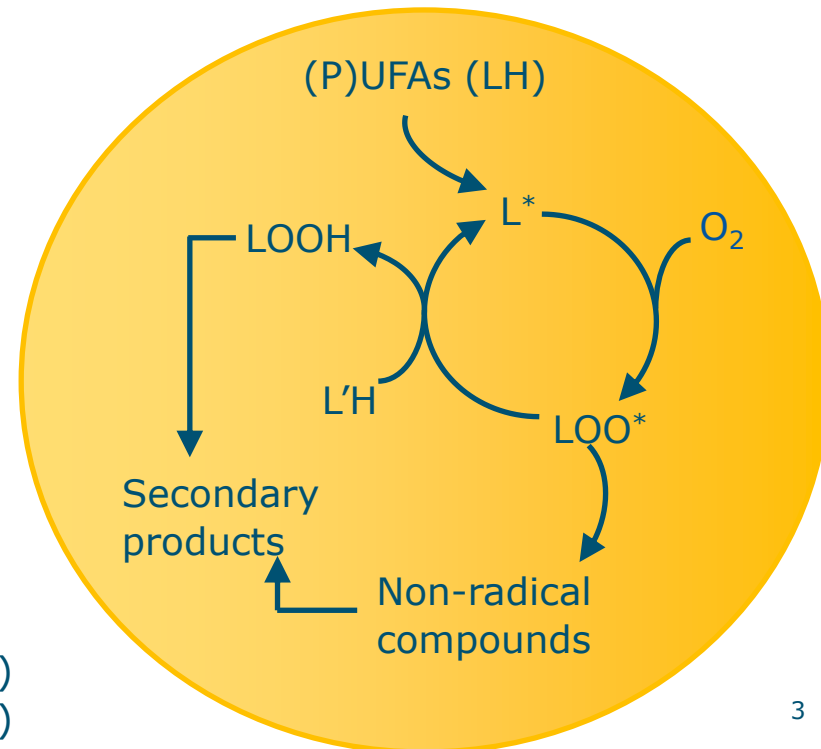
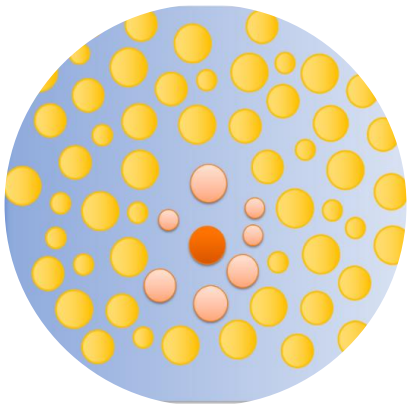
■ Droplets can exchange lipids



One droplet contaminating another?

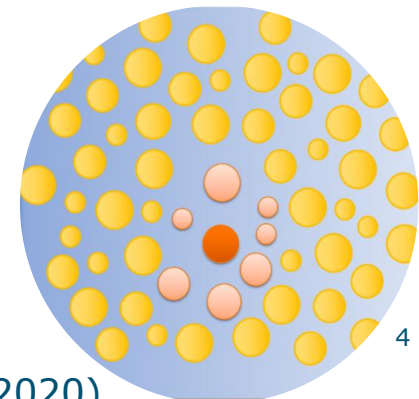
- Transport phenomena in lipid oxidation (3,4)
- Reaction scheme of lipid oxidation
- Hydroperoxides (5)

- $LOOH + Fe^{3+} \rightarrow LOO^* + Fe^{2+}$
 - $LOO^* + L'H \rightarrow +LOOH + L^*$
- $LOOH + Fe^{2+} \rightarrow LO^* + Fe^{3+}$
 - $LO^* + L'H \rightarrow +LOH + L^*$
- Secondary initiation: faster



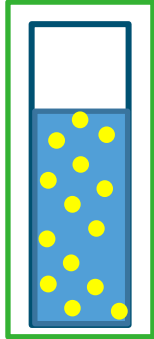
One droplet contaminating another?

- Flow cytometry and mass transport phenomena (6)
 - Bodipy in MCT droplets oxidizes faster when oxidizing oil droplets present
- Two remaining questions:
 1. How can one droplet contaminate another?
 - a. Which molecules play a role?
 2. What is the influence of spreading of oxidation?



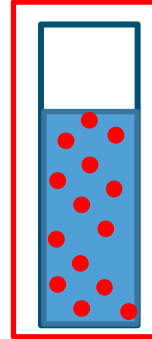
Methodology

Emulsion A – clean droplets



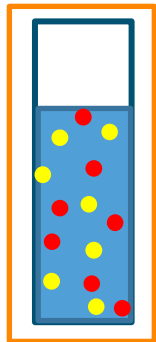
- 10 wt.% stripped rapeseed oil
density: 0.92 g/mL
- 0.5 / 2 wt.% Tween 20
- 75 mg/kg EDTA

Emulsion B – oxidized heavy droplets



- 10 wt.% oil
65 wt.% stripped, oxidized rapeseed oil
35 wt.% brominated oil
Density: 1.08 g/mL
- 75 mg/kg EDTA
- 0.5 / 2 wt.% Tween 20

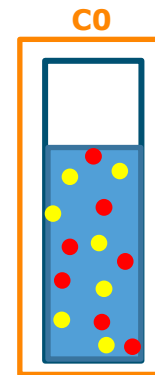
Emulsion C



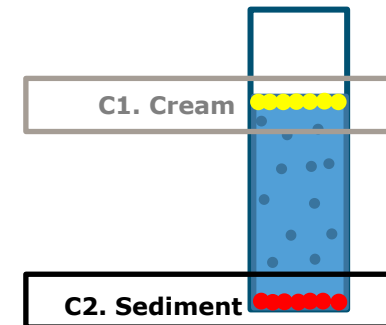
- 50:50 v/v mix of A and B

**Incubation: nitrogen blanket,
(slowly) rotating horizontally,
25 °C in the dark**

Over time, samples are taken from:



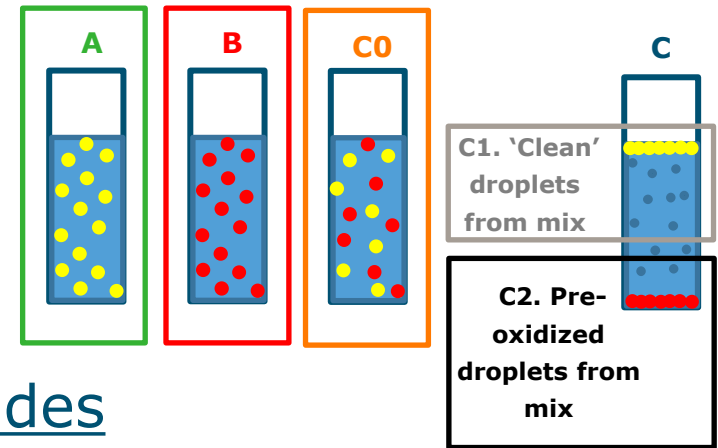
**Centrifuge C
(28,000xg, 30 min at 4 °C)**



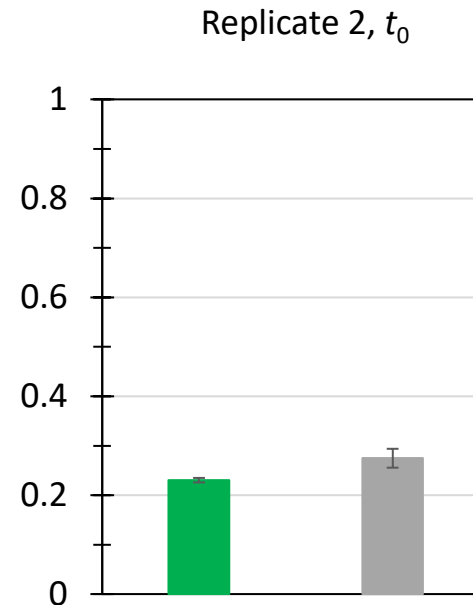
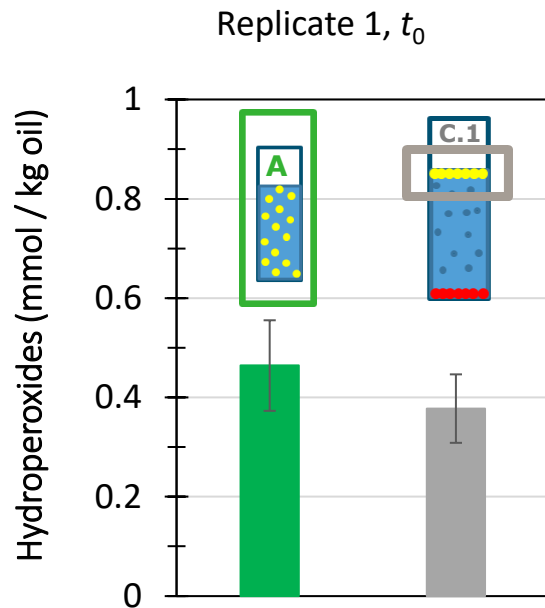
**Droplet size measurements
Primary/secondary oxidation**

**- Static light scattering
- ¹H NMR (7)**

Results – 0.5 wt.% Tween 20

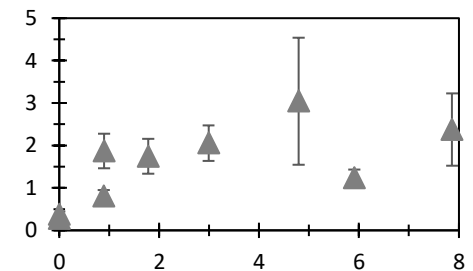
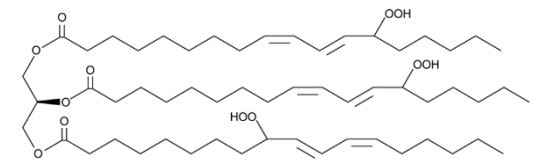
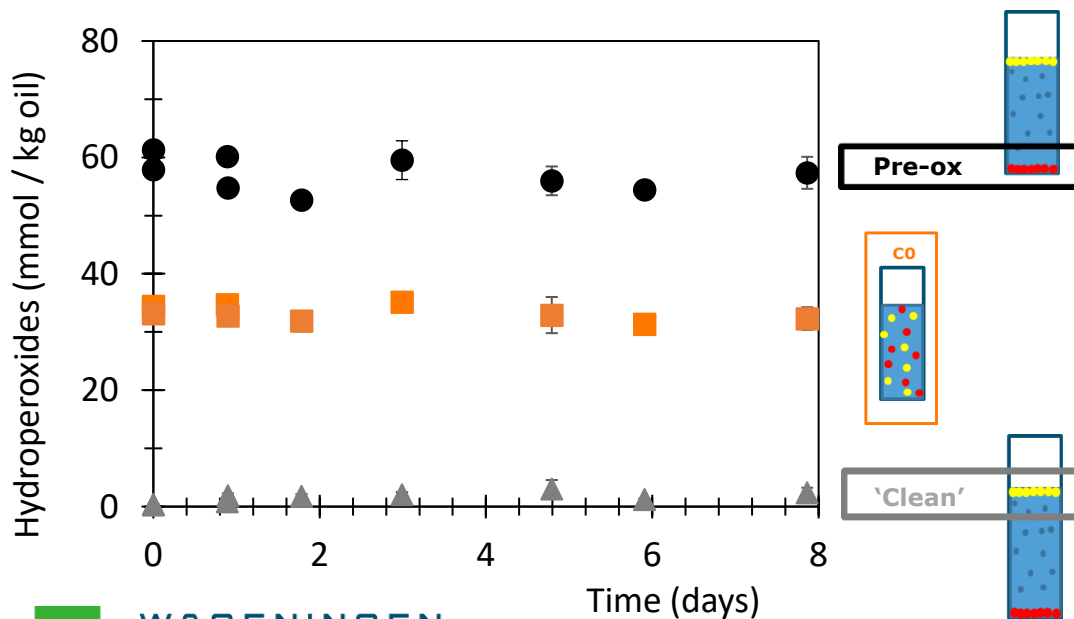


- No instant transfer of hydroperoxides
- Able to separate the droplets properly



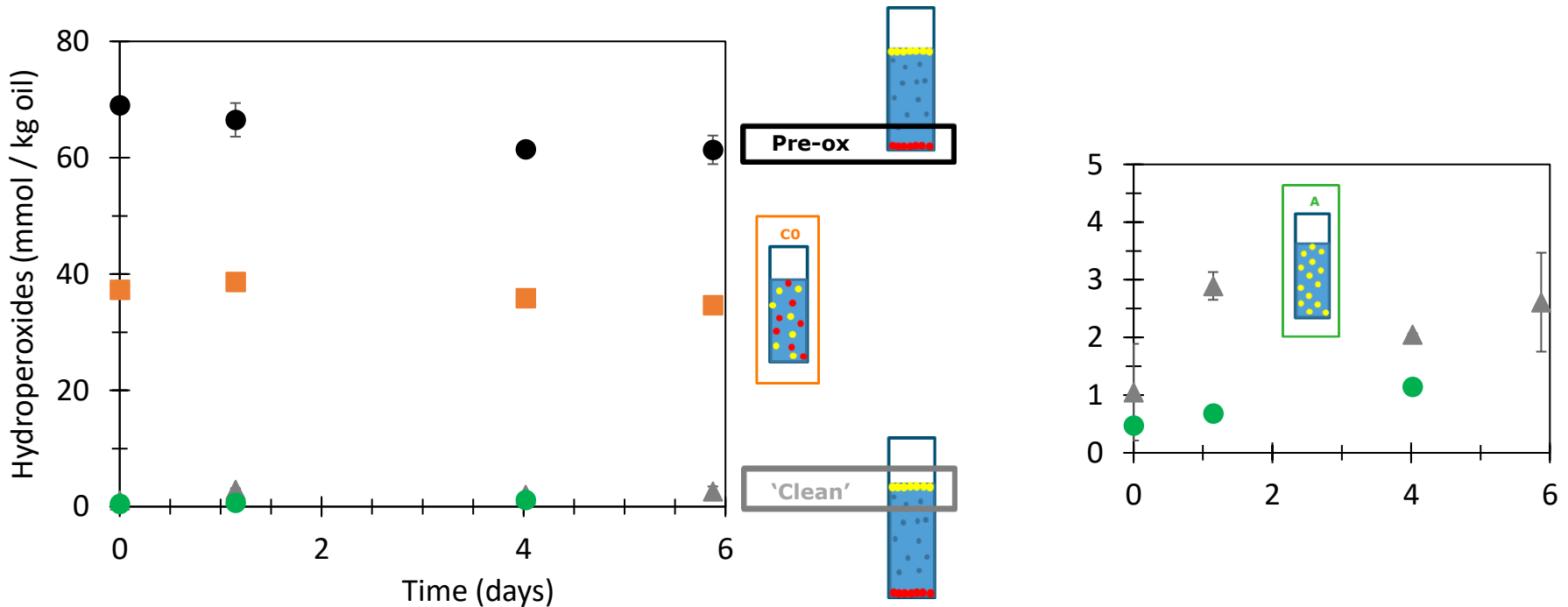
Results – 0.5 wt.% Tween 20

- Hydroperoxide transport over time
 - No massive transport of hydroperoxides
 - Slight increase after ~ 1 day
 - Due to transport or *in situ* oxidation?



Results – 2 wt.% Tween 20

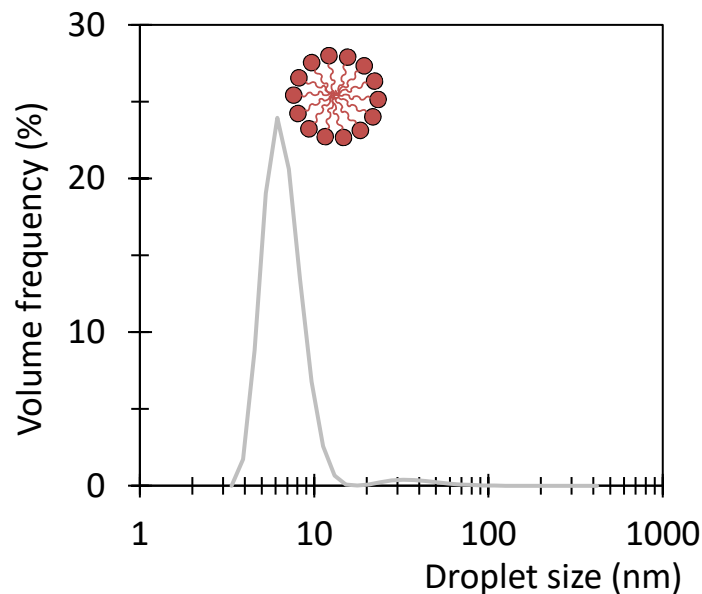
- 2% Tween 20 emulsions
- Still no massive transport of hydroperoxides



Results

■ Micelles

- Centrifuge (1 h, 20,000xg)
- Centrifuge 100 kDa spin filters (10 min, 1,000xg)



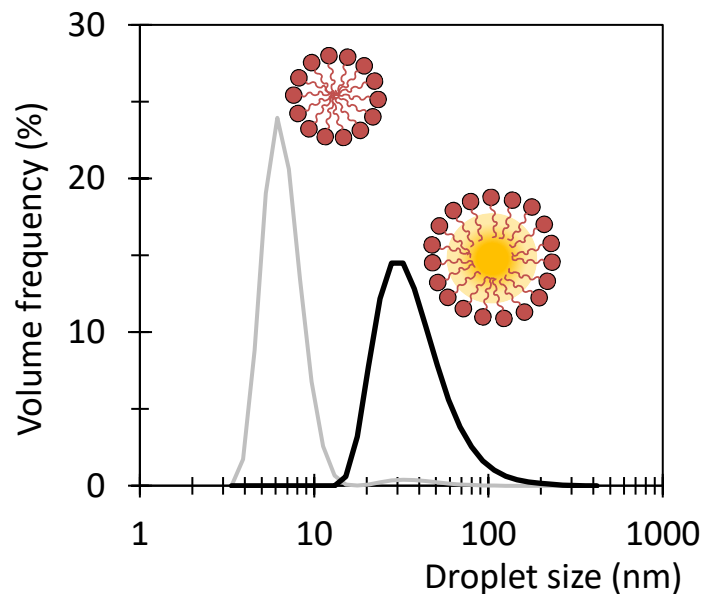
- 1:1 mix of 2% Tween 20-stabilised emulsion and 2% Tween 20 solution

Results

■ Micelles

- Centrifuge (1 h, 20,000xg)
- Centrifuge 100 kDa spin filters (10 min, 1,000xg)

■ No micelles present in homogenized emulsion?

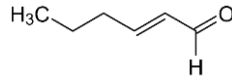
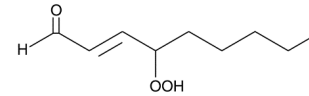


- **2% Tween 20-stabilised emulsion**
- **1:1 mix of 2% Tween 20-stabilised emulsion and 2% Tween 20 solution**

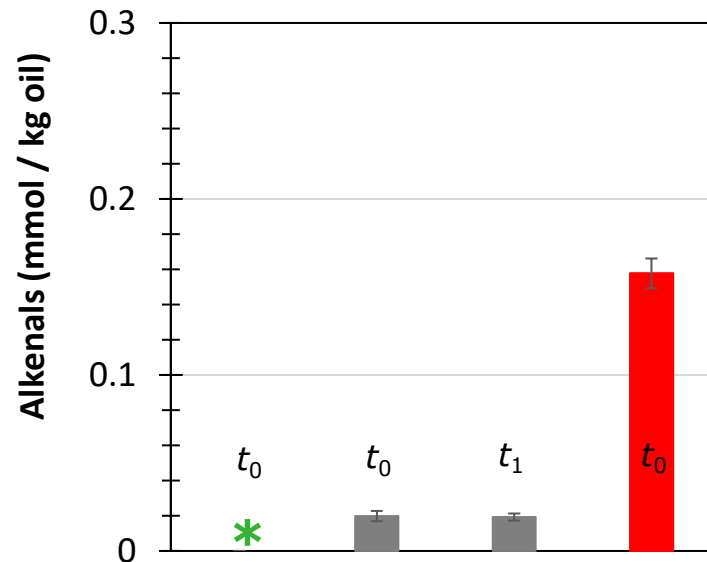
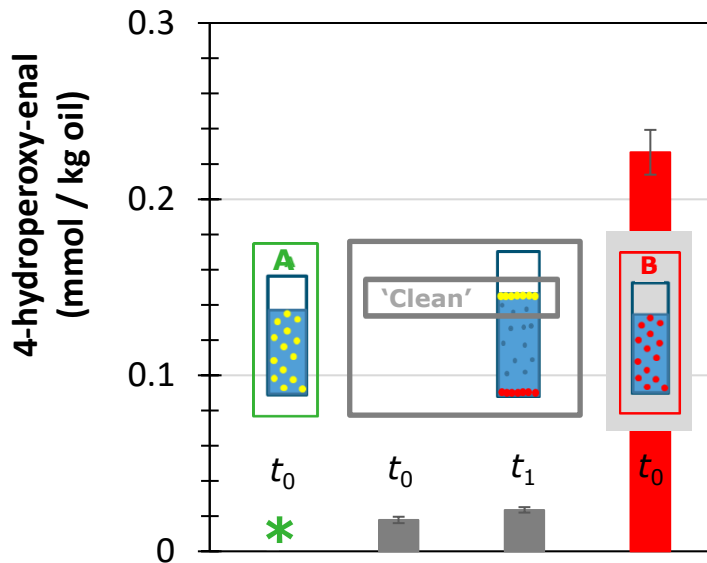
Results

■ Specific aldehyde transport

- 4-hydroperoxy-enals
- Alkenals



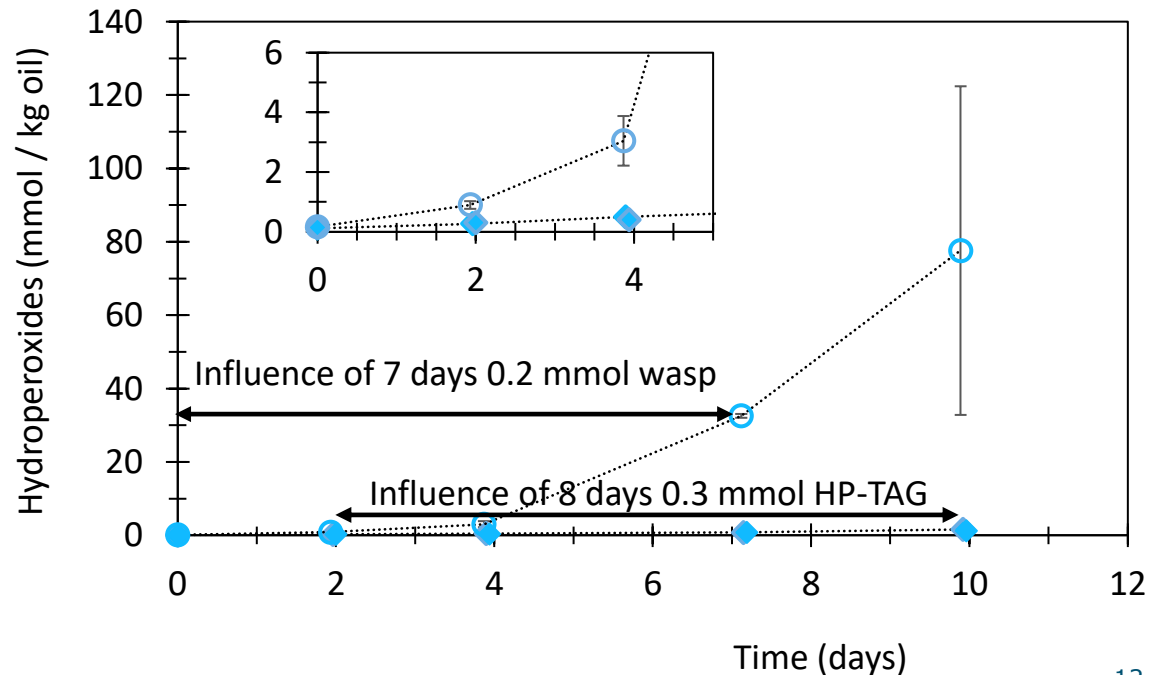
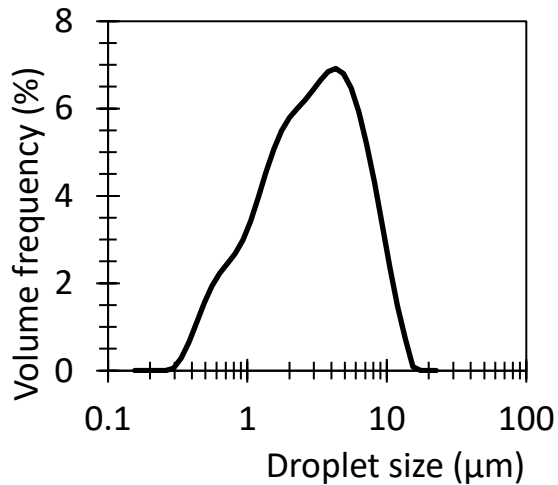
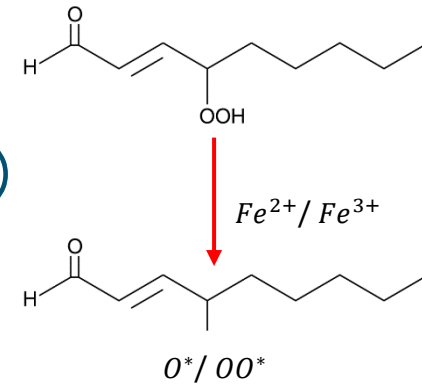
■ Smaller (more hydrophilic) aldehydes can transport



Results

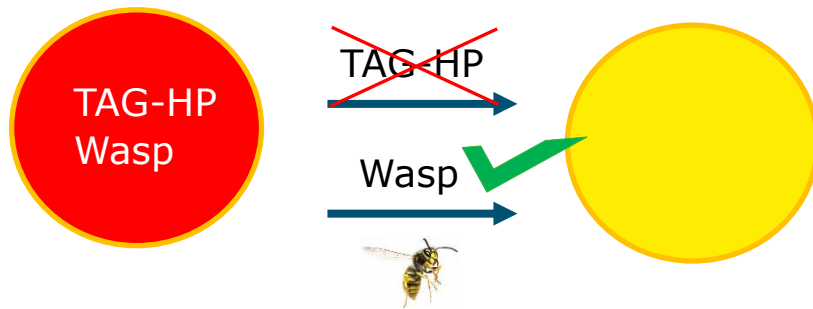


- 4-hydroperoxy 2-nonenal (wasp)
 - Added: 0.2 mmol / kg oil (○), control (●)
- Easily transported (more than HP-TAGs)
- Pro-oxidant effect



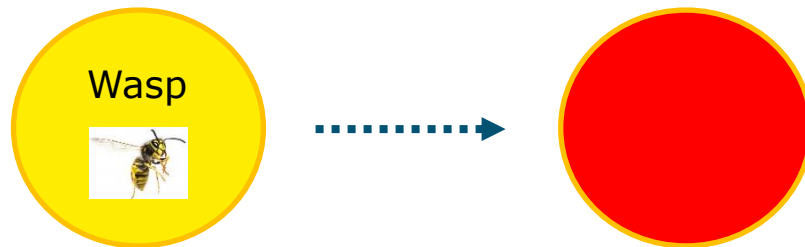
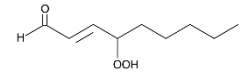
Conclusions

Under these conditions

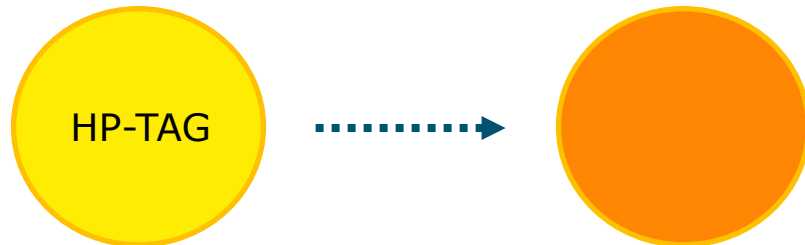


Barely any TAG-HP transport (if any)

Small amounts of wasp



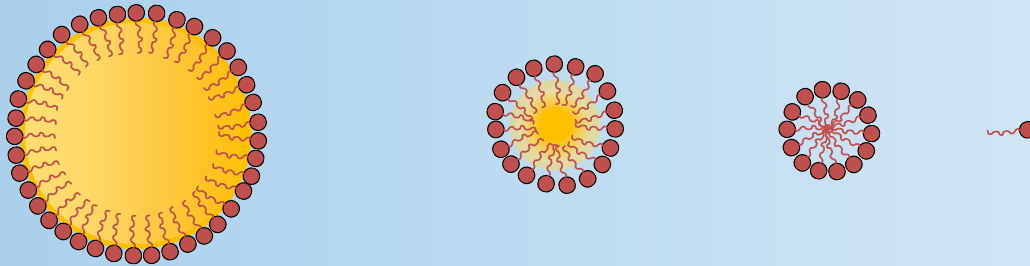
Wasp pro-oxidant



HP-TAG less pro-oxidant

Outlook

- What if micelles are present?
- When do we have micelles in continuous phase?
- What if only small amounts of (HP-)alkenals are added?
- Contribution of transport to total oxidation?



Thank you!



Acknowledgements

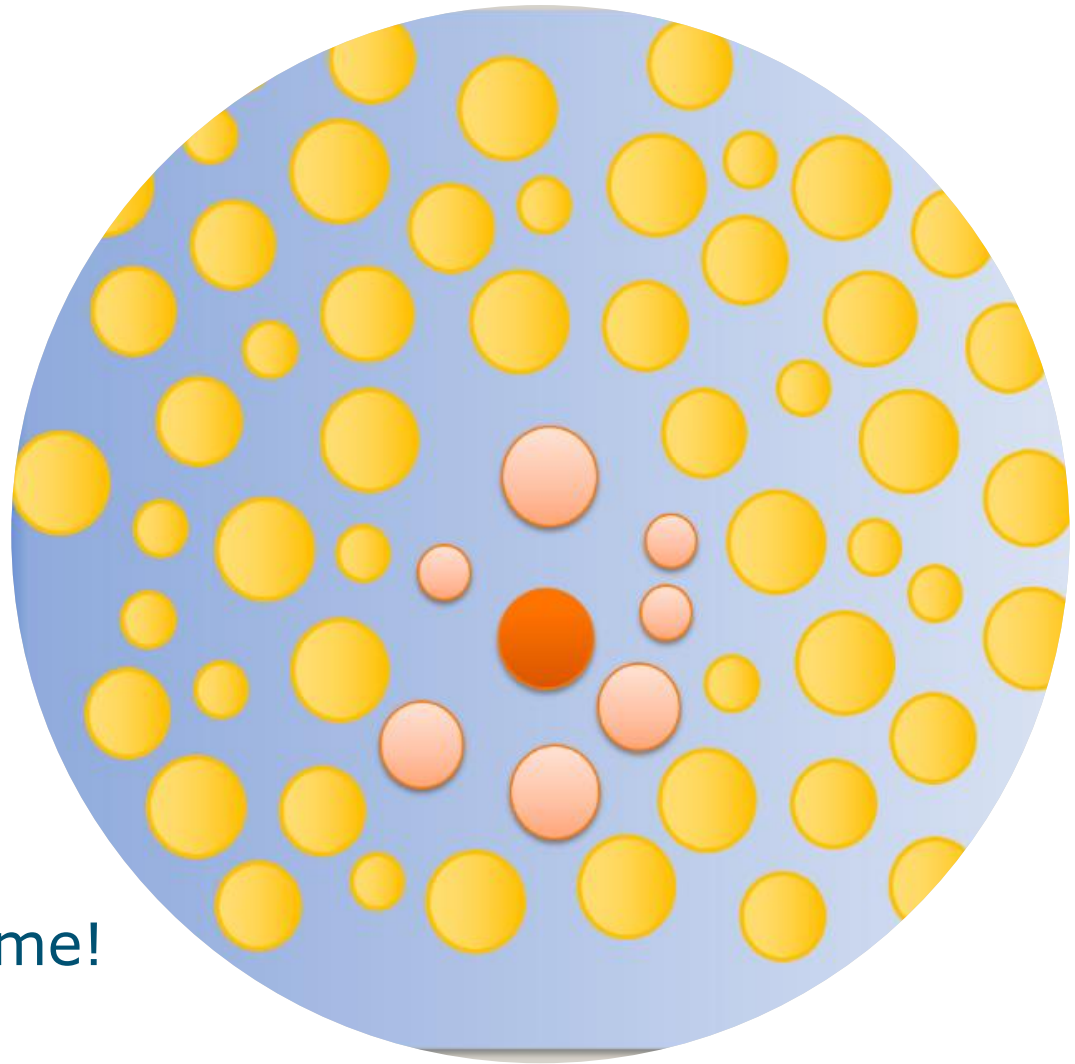
Donny Merkx

Unilever

Danone

NWO

Questions are very welcome!



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