

# Dynamic aroma release from complex food emulsions

Pu, Xiaolu; Linforth, Robert; Dragosavac, Marijana; Wolf, Bettina

DOI:

[10.1021/acs.jafc.9b02304](https://doi.org/10.1021/acs.jafc.9b02304)

License:

None: All rights reserved

*Document Version*

Peer reviewed version

*Citation for published version (Harvard):*

Pu, X, Linforth, R, Dragosavac, M & Wolf, B 2019, 'Dynamic aroma release from complex food emulsions', *Journal of Agricultural and Food Chemistry*, vol. 67, no. 33, pp. 9325-9334.  
<https://doi.org/10.1021/acs.jafc.9b02304>

[Link to publication on Research at Birmingham portal](#)

**Publisher Rights Statement:**

Checked for eligibility: 23/07/2019

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Journal of Agricultural and Food Chemistry*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see: <https://doi.org/10.1021/acs.jafc.9b02304>.

**General rights**

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

**Take down policy**

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

### Dynamic Aroma Release from Complex Food Emulsions

Journal:	<i>Journal of Agricultural and Food Chemistry</i>
Manuscript ID	jf-2019-02304t.R4
Manuscript Type:	Article
Date Submitted by the Author:	16-Jul-2019
Complete List of Authors:	Pu, Xiaolu; University of Nottingham Faculty of Sciences, Food Science; Hebei University of Science and Technology, College of Bioscience and Bioengineering Linthorpe, Robert; University of Nottingham Faculty of Sciences, food science Dragosavac, Marijana; Loughborough University, Chemical Engineering Department Wolf, Betina; University of Birmingham, School of Chemical Engineering; University of Nottingham Faculty of Sciences, food science

SCHOLARONE™  
Manuscripts

## Dynamic Aroma Release from Complex Food Emulsions

Xiaolu Pu<sup>a1\*</sup>, Robert Linforth<sup>a</sup>, Marijana M. Dragosavac<sup>b</sup>, Bettina Wolf<sup>a2</sup>

<sup>a</sup>School of Biosciences, University of Nottingham, Sutton Bonington Campus, Loughborough  
LE12 5RD, UK

<sup>b</sup>Chemical Engineering Department, Loughborough University, Loughborough LE11 3TU, UK

\*correspondence: xiaolu.pu@outlook.com

---

<sup>1</sup> Present address: College of Bioscience and Bioengineering, Hebei University of Science and Technology 050000, China

<sup>2</sup> Present address: School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

## 1 **Abstract**

2 *In-vitro* dynamic aroma release over oil-in-water (o/w) and water-in-oil-in-water (w/o/w)  
3 emulsions stabilised with Tween 20 or octenyl succinic anhydride (OSA) starch as a hydrophilic  
4 emulsifier and polyglycerol polyricinoleate (PGPR) as a hydrophobic emulsifier was  
5 investigated. The equal-molecular-weight hydrophilic aroma diacetyl (2,3-butanedione) or  
6 relatively-more-hydrophobic 3-pentanone was added to the emulsions prepared by high  
7 speed mixing, or membrane emulsification followed by thickened with xanthan gum  
8 removing droplet size distribution and creaming as variables affecting dynamic release.  
9 Results showed the differences of w/o/w emulsions in the dynamic release compared to o/w  
10 emulsions mainly depended on aroma hydrophobicity, emulsion type, emulsifier-aroma  
11 interactions and creaming. Xanthan led to a reduced headspace replenishment. Interfacially  
12 adsorbed OSA starch and xanthan-OSA starch interaction influenced diacetyl release over  
13 emulsions. OSA starch alone interacted with 3-pentanone. This study demonstrates the  
14 potential impact of emulsifying and thickening systems on aroma release systems and  
15 highlights that specific interactions may compromise product quality.

16

17 **Keywords:** dynamic aroma release; OSA starch; xanthan gum; w/o/w emulsions

18

## 19 Introduction

20 The aroma of a processed food is one of the key quality parameters for its success in the  
21 market place, and aroma release over simple oil-in-water (o/w) emulsions (for example, milk,  
22 cream, mayonnaise, salad dressing)<sup>1</sup> has been studied widely.<sup>2-9</sup> Complex water-in-oil-in-  
23 water (w/o/w) emulsions are emulsions where the oil phase of o/w emulsions is partly  
24 replaced by an inner aqueous phase. Due to the complex structure, w/o/w systems can be  
25 used for bioactive encapsulation.<sup>10, 11</sup> w/o/w emulsions have been shown to have advantages  
26 over o/w emulsions for fat reduction<sup>12, 13</sup> and salt reduction.<sup>14, 15</sup> Although food applications  
27 in low calorie cream or fat-reduced mayonnaise,<sup>16</sup> fat substitutes in meat emulsions,<sup>17</sup>  
28 substitutes for dairy fat in cheese<sup>12</sup> and so on have been reported, compared to o/w  
29 emulsions aroma release over w/o/w emulsions has obtained far less attention in the  
30 published literature.<sup>18, 19</sup> This might be at least in part due to the fact that w/o/w emulsions  
31 are more difficult to stabilise than o/w emulsions. For the successful application in low-fat  
32 and salt-reduced foods, an understanding of their aroma release properties is desirable.

33 The consumption of a food is a dynamic process as air is continuously exhaled and inhaled,  
34 rendering the acquisition of dynamic aroma release profiles more relevant to real foods,  
35 compared to static methods. If the dynamic aroma release is only affected by oil, the ability  
36 of an aroma compound to replenish a diluting headspace can be predicted by the equilibrium  
37 headspace partition coefficient (water: air-water partition coefficient  $K_{aw}$ ; emulsions: air-  
38 emulsion partition coefficient  $K_{ae}$ ).<sup>20, 21</sup> A low  $K_{aw}$  or  $K_{ae}$  value will lead to a more stable  
39 headspace concentration against headspace dilution.<sup>20, 21</sup> In that case,  $K_{ae}$  is calculated by  
40 Eq.1:<sup>22</sup>

41 
$$K_{ae} = \frac{1}{\left(\frac{\Phi_o}{K_{ao}} + \frac{\Phi_w}{K_{aw}}\right)}$$
 Eq.1

42 where  $\Phi_o$  and  $\Phi_w$  are the oil and water volume fraction respectively,  $K_{ao}$  is the air-oil  
43 partition coefficient.

44 If there are other non-volatile solute-aroma interactions that limit aroma release to the  
45 headspace, the hypothesis is that there would be differences in the headspace replenishment  
46 compared to the prediction by  $K_{ae}$  above. Factors such as emulsion composition and aroma  
47 hydrophobicity (the octanol-water partition coefficient,  $\log P$  or  $\log K_{ow}$ ) influence dynamic  
48 aroma release over o/w emulsions.<sup>3, 4, 6-9</sup> With regard to the impact of emulsion droplet size,  
49 dispersed volume fraction and emulsifier concentration on dynamic aroma release, published  
50 literature paints a controversial picture. On one hand side these factors are reported to have  
51 no impact,<sup>4, 6</sup> on the other hand side impact of droplet size, affecting emulsion viscosity, on  
52 dynamic aroma release has been reported.<sup>3</sup> Further, decreasing release rates with increasing  
53 fat level,<sup>9</sup> decreasing lipophilicity<sup>9</sup> and increasing gel strength<sup>8</sup> for lipophilic compounds have  
54 been reported. Undoubtedly, emulsifiers may interact with aroma compounds. For example,  
55 micelles of low molecular weight (LMW) surfactants forming above their critical micelle  
56 concentration in solution can solubilise hydrophobic<sup>23, 24</sup> or hydrophilic<sup>25</sup> molecules, or aroma  
57 compounds as of interest in this study, in their core. Polymeric emulsifiers such as starches  
58 are known to interact with aroma compounds<sup>26, 27</sup>. The suggested mechanisms is via hydrogen  
59 bonding between the hydrophilic aroma compounds and the hydroxyl groups of starch,<sup>28</sup> or  
60 inclusion complexes between the hydrophobic aroma compounds and amylose.<sup>29</sup> A  
61 consequence of these interactions is that, when used as emulsifier, the relative distribution  
62 of interfacially adsorbed to non-adsorbed starch can affect aroma distribution in emulsions  
63 and the headspace.<sup>24, 30-32</sup> This ratio is affected by the total surface area of the dispersed

64 emulsion phase, thus the droplet size characteristics for emulsions formulated at the same  
65 dispersed phase volume. Nonetheless, there is a lack of understanding of how those factors  
66 impact on dynamic release over w/o/w emulsions and their release behaviour compared to  
67 o/w emulsions.

68 In this study, *in-vitro* dynamic headspace analysis was carried out to evaluate the  
69 replenishment of two selected aroma compounds into the gas phase over w/o/w emulsions  
70 compared to o/w emulsions during headspace dilution. Water controls were also analysed to  
71 identify whether the emulsifier impacted dynamic aroma release. The overall aim of this study  
72 was to investigate the dynamic aroma release behaviour in fat-reduced complex food  
73 emulsions, w/o/w emulsions compared to o/w emulsions, and explore the emulsifier-aroma  
74 interaction as well as emulsion microstructure (size distribution, droplet size, specific surface  
75 area, Span and creaming) influence on dynamic release.

76

77 Materials and methods

78 Materials and sample composition

79 The oil phase in the emulsions comprised sunflower oil (density:  $0.916 \pm 0.003$  g/cm<sup>3</sup>; viscosity  
80 presented in supporting information Table S1) purchased from a local supermarket. All  
81 aqueous phases were prepared with deionised water unless otherwise stated.  
82 Polyoxyethylene 20 sorbitan monolaurate (Tween 20) (HLB = 16.7), diacetyl, 3-pentanone and  
83 sodium azide, added to prevent microbial spoilage, were obtained from Sigma Aldrich  
84 (Gillingham, UK), polyglycerol polyricinoleate PGPR (PGPR 90) from Danisco (Kettering, UK),  
85 octenyl succinic anhydride (OSA) starch (N-creamer 46) from Univar (Widnes, UK) and

86 xanthan gum (Keltrol RD) from CP Kelco (San Diego, USA). Sodium chloride to aid  
87 microstructure stabilisation<sup>33</sup> was purchased from Fisher Scientific (Loughborough, UK). All  
88 concentrations are provided on a weight by weight basis, unless stated otherwise.

89 The composition of all liquid samples is listed in Table 1. Two hydrophilic emulsifiers including  
90 the LMW surfactant Tween 20<sup>33, 34</sup> and the polymeric emulsifier OSA starch<sup>14, 15</sup> to stabilise  
91 the external w/o/w emulsion interface were selected in this study to assess the interaction of  
92 hydrophilic emulsifier type with aroma compounds and its impact on dynamic aroma release.  
93 PGPR was chosen as the hydrophobic emulsifier due to most successfully stabilising w/o/w  
94 emulsions.<sup>35</sup> Simple o/w emulsions were included in the experimental design to compare with  
95 w/o/w emulsions, formulated at the same dispersed phase volume of o and w/o respectively  
96 in the emulsion system. Emulsions were initially processed with a high speed mixer. Then,  
97 emulsions were also processed via a previously reported stirred cell membrane  
98 emulsification,<sup>34</sup> thereby removing droplet size variation as a factor impacting aroma release.  
99 Since our initial analysis of the high speed processed emulsions suggested that droplet  
100 creaming, which was observed for all emulsions produced, might have affected aroma release,  
101 creaming was suppressed in the membrane processed emulsions by adding the viscosifying  
102 agent xanthan gum. At the same time, PGPR was added also to the oil phase of the o/w  
103 emulsions, although not required to stabilise an internalised aqueous phase, in order to retain  
104 similarity in formulation for better comparison of the aroma release results. The thickened  
105 emulsions had a comparatively lower dispersed phase volume due to the method of  
106 preparation, outlined in the following.

107

108 Preparation of emulsions by high shear mixing



109 w/o/w emulsions

110 A two-step emulsification method with a batch high speed overhead mixer (L5M fitted with  
111 emulsor screen, Silverson, Chesham, UK) was used to produce the w/o/w emulsions. Initially,  
112 the internal  $w_1/o$  emulsion was prepared by slowly adding  $w_1$  into oil while mixing at 7000  
113 rpm for 4 min and cooling the process beaker (4-6 °C). Batch size was kept constant at 100 g  
114 with a ratio of  $w_1:o$  of 2:3. This primary w/o emulsion was then added to  $w_2$  during mixing at  
115 6700 rpm for 4 min while cooling (4-6 °C). Batch size was also 100 g with a ratio of  $w_1/o:w_2$  of  
116 3:7. Finally, 1 mL of aqueous sodium azide solution was added to the w/o/w emulsions to  
117 obtain a final sodium azide concentration of 0.02% and the emulsion was stored at room  
118 temperature ( $21 \pm 5$  °C) until further use.

119

120 o/w emulsions and water controls

121 o/w emulsions manufactured by high speed mixing were prepared by adding the oil to the  
122 water. The same high speed overhead mixer as for preparation of the w/o/w emulsions was  
123 used, operated at 6700 rpm for 4 min while cooling (4-6 °C). The mixing ratio of oil to water  
124 was 3:7 and batches of 100 g were processed. The water controls contained Tween 20 or OSA  
125 starch as the hydrophilic emulsifier at the same concentration as the external water phase of  
126 w/o/w emulsions.

127

128 Preparation of xanthan gum thickened emulsions with stirred cell membrane emulsification

129 w/o/w emulsions

130 w/o/w emulsions were manufactured in two steps followed by the addition of xanthan gum.

131 First, w/o emulsions were produced by slowly adding  $w_1$  into o under high shear mixing (Ultra

132 Turrax, model T25, IKA Works, Staufen, Germany) at 24000 rpm for 5 min while cooling the

133 process beaker (4-6°C). Batch size was kept constant at 100 g with a ratio of  $w_1$ :o of 2:3. The

134 w/o/w emulsions were then manufactured using stirred cell membrane emulsification. w/o

135 emulsions were injected through a microporous membrane surface into the external aqueous

136 phase stirred by a paddle stirrer. Maximum shear stress at the membrane surface was

137 controlled by the rotational speed. The experimental conditions were a maximum shear stress

138 of 14 and 36 Pa for the continuous aqueous phase containing Tween 20 and OSA starch

139 respectively, and a constant w/o emulsion injection speed of 1 mL min<sup>-1</sup> corresponding to a

140 transmembrane flux of 70 L h<sup>-1</sup> m<sup>-2</sup>. The experiments were run until the dispersed phase

141 volume fraction reached 30 vol.% as determined by reading from the syringe scale. Batches

142 of 100 g were prepared, transferred into a glass beaker followed by the addition of 1 mL of

143 aqueous sodium azide solution to obtain a final sodium azide concentration of 0.02% and

144 stored at room temperature (21 ± 5 °C) until further use.

145

146 o/w emulsions

147 o/w emulsions manufactured by stirred cell membrane emulsification were prepared

148 following the actual membrane emulsification step of preparing the w/o/w emulsions, with

149 the difference that the dispersed phase corresponded to a single oil phase. In order to obtain

150 a droplet size similar to that of the w/o/w emulsions, the process parameters were tested in

151 preliminary experiments. These were a maximum shear stress at the membrane surface of 10

152 Pa and 36 Pa respectively for Tween 20 and OSA starch as emulsifier, and an oil phase injection  
153 speed of 1 mL min<sup>-1</sup>.

154

155 Xanthan gum solution preparation and addition

156 A 1% xanthan gum solution was prepared and added to the membrane processed w/o/w and  
157 o/w emulsions as follows. Initially, the appropriate amount of xanthan gum was dispersed  
158 into 0.1 M NaCl and 0.02% sodium azide solution pre-heated to 80 °C while stirring at 1500  
159 rpm with an overhead mixer (RW20 fitted with a Propeller 4-bladed stirrer, IKA, Staufen,  
160 Germany). Temperature was maintained at 80°C during 1 h of mixing after which the solution  
161 was allowed to cool down at room temperature and left overnight for complete hydration  
162 before use. 70 g of xanthan gum solution was then added to 100 g of membrane processed  
163 emulsion sample contained in a 600 mL glass beaker followed by mixing at 600 rpm on a  
164 magnetic stirrer for 30 min. The resulting xanthan gum concentration in the external aqueous  
165 phase of the w/o/w and o/w emulsions was 0.5%.

166 To prepare the xanthan gum thickened water controls, 100 g of the xanthan gum solution was  
167 mixed with 100 g of w<sub>2</sub> at 600 rpm to also obtain a final xanthan gum concentration of 0.5%.

168

169 Emulsion characterisation

170 Emulsions were analysed immediately after manufacturing and then regularly during 6-day  
171 storage at room temperature (21 ± 5 °C).

172

173 Microscopy

174 The microstructure of the w/o/w and o/w emulsions was visualised using bright field  
175 microscopy (EVOS FL, Life Technologies, USA). Slides were prepared by placing a small drop  
176 of emulsion diluted with water onto a glass slide and placed onto the optical stage without  
177 adding cover slips. Objective lenses x4, x10 and x20 were fitted and at least three randomly  
178 selected areas of each slide were imaged with each objective. Three slides were prepared for  
179 each emulsion.

180

181 Droplet size measurement

182 Droplet size distributions were acquired with a laser diffraction particle size analyser  
183 (Beckman-Coulter LS 13 320, Meritics Ltd, Dunstable, UK) fitted with a dispersion cell  
184 containing deionized water. Measurement set up and analysis was controlled by the  
185 instrument's software package. Once the emulsion was dispersed in the water, three  
186 measurements were taken and the raw data was averaged before analysis based on the input  
187 of the refractive indices of the dispersion medium (water; 1.33) and the dispersed phase (oil;  
188 1.47). The absorption value of the dispersed phase was set to 0. Samples were prepared in  
189 triplicates. The results are reported as the averaged droplet size distributions on a volume  
190 basis, the mean droplet size on a volume basis ( $d_{4,3}$ ), the specific surface area (SSA) and the  
191 span of the monomodal size distributions.

192

193 *In-vitro* dynamic headspace analysis

194 A volume (95 mL) of w/o/w emulsion or o/w emulsion or water control were placed into a  
195 134 mL total volume glass bottle with a 25 x 6 mm magnetic stirrer bar at the bottom and  
196 stored at room temperature. Diacetyl or 3-pentanone was added to the liquid samples after,  
197 rather than prior to, emulsion preparation, including addition of xanthan gum to the  
198 membrane processed emulsions, in order to reduce aroma loss during processing due to  
199 exposure to open air. These two aroma compounds were selected as they vary in log P (the  
200 hydrophilic aroma, diacetyl: -1.34; the relatively more hydrophobic aroma, 3-pentanone: 0.75  
201 estimated from EPI SUITE (EPA's and Syracuse Research Corp., USA) at 20 °C) whilst being  
202 equal in molecular weight (diacetyl: 86.09 g/mol; 3-pentanone: 86.13 g/mol) to eliminate the  
203 effect of molecular mass on aroma release. 400  $\mu\text{L L}^{-1}$  of aroma standard solution containing  
204 0.1 M NaCl was prepared in a 100 mL volumetric flask. 5 mL of the aroma standard solution  
205 was added into each bottle to obtain a final aroma concentration of 20  $\mu\text{L L}^{-1}$  in the liquid  
206 sample and a headspace volume of 34 mL. The bottles were immediately sealed and stirred  
207 at 200 rpm for 1 min to ensure rapid distribution of the aroma compounds before the dynamic  
208 headspace analysis. Samples were then allowed to equilibrate for at least 4 h at room  
209 temperature ( $21 \pm 5$  °C) to equilibrate aroma distribution between liquid and headspace. 4 h  
210 was chosen because it was the minimum time required for the aromas to reach equilibrium,  
211 as determined in preliminary tests. Samples were prepared in triplicate.

212 To dilute the headspace, nitrogen gas ( $\text{N}_2$ ) was introduced into the bottle at a flow rate of 70  
213  $\text{mL min}^{-1}$  measured using an electronic flow meter (vary-flow 500, Agilent Technologies,  
214 Berkshire, UK). 5  $\text{mL min}^{-1}$  of the gas phase was sampled into the APCI-MS (Ultima Micromass,  
215 Manchester, UK) over 10 min. The transfer line to the mass spectrometer was heated (140 °C)  
216 and the source was operated in positive ionisation mode (4kV corona discharge). The  
217 compounds were measured in selected ion mode at 87  $\text{mz}^{-1}$  (molecular weight +1) with a

218 dwell time of 0.1 s. Raw data was exported to Excel (Microsoft Corporation) and graphs were  
219 plotted as the average headspace intensity (%). The first peak of average headspace intensity  
220 was set to 100%. The points measured after the first peak were divided by the first peak of  
221 average headspace intensity.

222

## 223 Statistics

224 The mean values and their standard deviations were calculated using the spreadsheet  
225 software Microsoft Excel. Statistical analysis of the dynamic headspace intensity by MANOVA  
226 statistical analysis with least significant difference (LSD) post hoc test ( $p < 0.05$ ) using the SPSS  
227 software (IBM Statistics 21, USA) at 2, 5 and 9 min, as early, mid and late stage of dynamic  
228 headspace analysis was carried out to explore significant differences in data sets.

229

## 230 Results and discussion

### 231 Emulsion characteristics

232 The o/w and w/o/w emulsions, stabilised with Tween 20 or OSA starch and processed by high  
233 speed or membrane emulsification, were viewed under a bright field microscope and it was  
234 confirmed that the expected emulsion structure had formed. The oil continuous droplet  
235 phase of the w/o/w emulsions showed their previously noted characteristic dark appearance  
236 (micrographs shown in supporting information Figure S1).<sup>36</sup> The volume based droplet size  
237 distributions of all of the prepared o/w and w/o/w emulsions are presented in Figure 1.

238 The droplet size distribution of each type of the high speed mixed emulsions (Figure 1A) was  
239 not affected by the choice of emulsifier. This indicates that the outcome of the high speed

240 process was controlled by the processing parameters rather than the emulsifier type and its  
241 concentration. The droplet size distributions were broad showing a shoulder at smaller  
242 droplet diameters, which was more pronounced for the o/w emulsions and shifted slightly to  
243 larger droplet diameters for the w/o/w emulsions. With around 20  $\mu\text{m}$ , the main distribution  
244 peak of the w/o/w emulsions was also slightly larger compared to 10  $\mu\text{m}$  for the o/w  
245 emulsions. Since the same processing conditions were used for emulsifying the oil and the  
246 w/o into their respective external emulsion phase, it can only be concluded that the increased  
247 viscosity of the o/w emulsion compared to the oil (see supporting information Table 1), and  
248 the additional presence of PGPR in the oil phase of the w/o/w emulsion led to this result. As  
249 a consequence of these differences in droplet size distribution between the o/w and w/o/w  
250 emulsions, the specific surface area of the oil droplets was larger in the case of the o/w  
251 emulsions and thus the proportion of adsorbed emulsifier rendering the interpretation of  
252 aroma release data in terms of aroma-emulsifier interactions challenging.

253 The droplet size distributions of the xanthan gum thickened membrane processed emulsions  
254 (Figure 1B) were monomodal and the volume based mean diameter,  $d_{4,3}$ , of all of these  
255 emulsions was approximately 60-70  $\mu\text{m}$  resulting in the specific surface area of around 0.1  $\text{m}^2$   
256  $\text{mL}^{-1}$ , independent of the type of emulsion. Both types of Tween 20 stabilised emulsions had  
257 a span of around 0.6, whereas both types of OSA starch stabilised emulsions had slightly larger  
258 span of approximately 0.7.

259 All emulsions were tested in terms of microstructure stability by checking droplet size  
260 distribution over a storage period of 6 days, during which the aroma release experiments  
261 were conducted. There were no changes for any of the emulsions (data not shown for the  
262 sake of brevity).

263

264 Dynamic headspace analysis

265 The theoretical equilibrium headspace partition coefficients ( $K_{ae}$ ) calculated by Eq.1 are  
266 reported in Table 2. According to Table 2, it is expected that if there were only oil-aroma  
267 interactions, diacetyl would most easily replenish the diluting headspace over water controls,  
268 then w/o/w and finally o/w emulsions. This would be the opposite for 3-pentanone. If the  
269 headspace replenishment did not meet that predicted by  $K_{ae}$ , this would suggest emulsifier-  
270 aroma interactions and an impact of emulsion microstructure on dynamic release.

271 The first peak in the dynamic headspace analysis was effectively representative of the  
272 undiluted headspace and therefore regarded as the equilibrium headspace intensity, which  
273 was set to 100%. Afterwards the equilibrium was disturbed during headspace dilution, so the  
274 headspace intensity decreased over the course of the measurement. The values shown in the  
275 following were normalised by the first peak headspace intensity (signal = 100%).

276

277 High speed mixed emulsions

278 *Diacetyl*

279 Figures 2A and B show the changes of dynamic headspace intensity of diacetyl over water,  
280 the water controls and the emulsions for Tween 20 and OSA starch as emulsifier respectively.  
281 Across all samples, the diacetyl headspace intensity decreased by 20 to 40% during headspace  
282 dilution. Over water and water containing emulsifier (water controls), the diacetyl headspace  
283 intensity decreased initially but then stabilised at approximately 80%. According to the  
284 statistics reported in Table 3, the headspace concentration of all emulsions was significantly



285 lower than that over water at 9 min ( $p < 0.05$ ). This behaviour was expected because  
286 emulsions had higher air-emulsion partition coefficients than water as reported in Table 2.

287 Diacetyl initially showed less replenishment into the headspace over the o/w and w/o/w  
288 emulsions than water controls. Then the intensity of diacetyl progressively decreased more  
289 than over the water controls, without asymptotically reaching an equilibrium value. In Table  
290 3, at 2 min and for Tween 20 as surfactant, the diacetyl concentration over the o/w emulsion  
291 was higher than that over the w/o/w emulsion ( $p < 0.05$ ). Thus, the fat-reduced w/o/w  
292 emulsion system showed an inhibition of the dynamic diacetyl release compared to the o/w  
293 emulsion.

294 Aroma release under dynamic condition is mainly affected by the air-liquid interface, as this  
295 interface replenishes the headspace with volatile compounds as the headspace is diluted. All  
296 of the high speed mixed emulsions creamed; a cream phase on top and a serum phase at  
297 bottom was observed visually. Hence, underneath the layer of emulsifier molecules at the air-  
298 emulsion interface there was a layer of creamed oil droplets representing an additional  
299 barrier affecting aroma release. Due to the broad droplet size distribution (Figure 1), the  
300 creamed layer of oil droplets would have contained larger droplets towards its top and  
301 smaller droplet towards its bottom. So the higher diacetyl release over the o/w emulsion  
302 contrary to expectation was probably due to the cream layer acting as a barrier for diacetyl  
303 movement from the continuous water phase underneath the creamed oil droplets. The  
304 thickness of the cream layer was different between the emulsions due to the difference in  
305 the droplet size, size distribution and density in addition to the viscosity of the continuous  
306 phase. The w/o/w emulsions had a thicker cream layer due to their larger main distribution  
307 peak compared to the o/w emulsions (Figure 1), leading to the poorer headspace

308 replenishment of diacetyl over the w/o/w emulsions. Another reason could be the presence  
309 of PGPR in the oil phase of the w/o/w emulsions, which was absent in the o/w emulsions.  
310 PGPR could have trapped diacetyl molecules, partitioned into the oil phase, in the hydrophilic  
311 core of their micelles thereby slowing transfer into the aqueous phase as a result of  
312 equilibrium disturbance and ultimately aroma release.

313 However, the release of diacetyl over the o/w emulsion and the w/o/w emulsion was not  
314 different for the OSA starch as emulsifier (Table 3). Hence, the w/o/w emulsion had a similar  
315 ability to maintain the headspace concentration of diacetyl as the o/w emulsion. This could  
316 be because diacetyl interacted with the interfacially adsorbed starch at the oil-water  
317 interface. There was a higher amount of the starch adsorbed at the creamed oil droplet  
318 interface of o/w emulsions than that of the w/o/w emulsions due to its smaller main  
319 distribution peak (Figure 1) resulting in a larger SSA of o/w emulsions, which led to no  
320 significant difference in the diacetyl release over OSA starch stabilised o/w and w/o/w  
321 emulsions.

322 In summary, the dynamic release behaviour of diacetyl over high speed mixed emulsions was  
323 mainly driven by emulsion type, creaming resulting from the broad droplet size distribution  
324 and SSA of the emulsion characteristics and diacetyl-OSA starch interactions.

325

### 326 *3-pentanone*

327 Figures 2C and D show the changes of dynamic headspace intensity of 3-pentanone over  
328 emulsions and water controls. The headspace intensity decreased by 20% to 60 % for 3-  
329 pentanone during headspace dilution for all samples. This was more than for diacetyl (Figures  
330 2A and B), the lower headspace replenishment would be caused by 3-pentanone's higher  $K_{aw}$

331 compared to diacetyl (Table 2). The water control and the emulsifier alone showed an initial  
332 major decrease in headspace intensity, which stabilised at about 40%. As expected in Table  
333 2, they had the lowest headspace 3-pentanone intensity over time, which suggests the  
334 weakest headspace replenishment among all samples. As reported in Table 4, OSA starch  
335 alone led to a significant decrease in the dynamic headspace intensity compared to the water  
336 control at 2, 5 and 9 min ( $p < 0.05$ ), which suggests an interaction of starch with 3-pentanone  
337 possibly through hydrophobic interaction or a starch barrier effect at the air-water interface  
338 reducing volatile movement.

339 According to Figures 2C and D and Table 4, 3-pentanone had the strongest headspace  
340 replenishment ( $p < 0.05$ ) over the o/w emulsions over 10 min without asymptotically reaching  
341 an equilibrium value, then w/o/w emulsions and last water. It met the expectation as  $K_{ae}$   
342 predicts in Table 2. It has been reported previously that an o/w emulsion system stabilised  
343 the hydrophobic aroma headspace concentration during headspace dilution relative to the  
344 water system<sup>37, 38</sup> as a direct result of the emulsion decreasing the air-liquid partition  
345 coefficient. There was no significant difference among o/w or w/o/w emulsions (Table 4). This  
346 is probably due to 3-pentanone favouring oil so the oil phase played a major role in 3-  
347 pentanone release and the hydrophilic emulsifier type could not limit the headspace intensity.  
348 The cream layer of the emulsions could facilitate the replenishment of 3-pentanone into the  
349 gas phase during headspace dilution.

350 Thus, the dynamic release behaviour of 3-pentanone over high speed mixed emulsions was  
351 mainly driven by emulsion type and creaming.

352

353 Membrane processed and xanthan gum thickened emulsions

354 *Diacetyl*

355 Figures 3A and B reveal the dynamic headspace release of diacetyl over xanthan gum-  
356 thickened samples. The headspace intensity decreased by approximately 40% for diacetyl  
357 during dilution for all samples. All samples showed a progressive decrease in the headspace  
358 intensity without asymptotically reaching an equilibrium value. The xanthan gum thickened  
359 water had a lower headspace intensity at mid and late stage compared to water in the  
360 absence of xanthan gum (Figures 2A and B). This was probably caused by the xanthan gum  
361 increasing the viscosity of the water (supporting information Table S1) such that the xanthan  
362 gum network at the air-water interface delayed the release of diacetyl. It has been reported  
363 that significant binding of all tested compounds (diacetyl, 1-octen-3-ol, diallyl sulfide, diallyl  
364 disulfide) occurred at 0.1% xanthan under equilibrium headspace analysis and hydrogen  
365 bonding was found in 1-octen-3-ol-xanthan interactions by exclusion chromatography.<sup>39</sup> It  
366 can be speculated that hydrogen bonding between diacetyl and xanthan gum may also have  
367 occurred.

368 For Tween 20 (Table 5), diacetyl showed the most stable headspace intensity over water and  
369 Tween 20 alone, then w/o/w and last o/w emulsions. This is as expected on the basis of the  
370  $K_{ae}$  values. For the membrane emulsification processed and xanthan gum thickened  
371 emulsions, creaming was reduced due to the increased viscosity of the continuous aqueous  
372 phase (supporting information Table S1). The impact of emulsion microstructure on dynamic  
373 release was also minimised because all the emulsions had a similar size distribution (Figure  
374 1), droplet size, SSA and a low Span. The emulsion droplets were homogeneously dispersed in

375 the continuous water phase. Hence, oil was the only factor influencing on the diacetyl release  
376 over water and emulsions in the presence of Tween 20.

377 For OSA starch (Table 5), the OSA starch and xanthan gum water control showed a  
378 significantly lower headspace concentration than the xanthan gum alone only at 2 min ( $p <$   
379 0.05), which indicates an interaction of diacetyl with OSA starch or with OSA starch and  
380 xanthan gum. It was reported above that there was no interaction of diacetyl with OSA starch  
381 under dynamic headspace conditions in the absence of xanthan gum. Therefore, this  
382 interaction of diacetyl was associated with xanthan gum and OSA starch. Furthermore, the  
383 viscosity of these water controls and emulsions was measured revealing an interaction of  
384 xanthan gum with OSA starch as its addition lowered the viscosity of the xanthan gum  
385 (supporting information Table S1). Thus, a xanthan gum-OSA starch interaction influenced the  
386 dynamic release of diacetyl. However, there was no significant difference among o/w or  
387 w/o/w emulsions. Hence, interaction of diacetyl with xanthan gum and OSA starch appeared  
388 to be absent in o/w and w/o/w emulsions (Table 5). It is worth noting thought that in the  
389 presence of xanthan gum the viscosity of the OSA starch stabilised emulsions was lower  
390 compared to those stabilised with Tween 20 (supporting information Table S1). Consequently,  
391 while xanthan gum-OSA starch interactions are evident, these did not impact on the dynamic  
392 release of diacetyl in the emulsion systems whereas they did in the control system. Further  
393 detailed analysis of this system is required to understand why the fact that a proportion of  
394 the OSA starch molecules adsorbed at the oil droplet interface, therefore not available to  
395 interact with xanthan gum, might be the reason for the dynamic release of diacetyl  
396 observation.

397 Hence, the dynamic release behaviour of diacetyl over membrane processed and xanthan  
398 gum thickened emulsions was mainly driven by emulsion type and interactions between  
399 diacetyl and xanthan-OSA starch association.

400

401 *3-pentanone*

402 Figures 3C and D show the changes of dynamic headspace of 3-pentanone over xanthan gum  
403 thickened samples. The headspace intensity decreased by approximately 60% for 3-  
404 pentanone during dilution for all samples. All samples also showed a progressive decrease in  
405 the headspace intensity without asymptotically reaching an equilibrium value. The xanthan  
406 gum thickened emulsions had no difference in dynamic headspace intensity with the xanthan  
407 gum solution (Table 6). They also showed a much weaker resistance to dilution compared  
408 with the high speed mixed emulsions (Figure 2C and D). This may have been due to diffusion  
409 barriers that limited headspace replenishment,<sup>8</sup> or increased viscosity<sup>40</sup> that decreased  
410 droplet mobility, or, abundance of droplets at the air-emulsion interface. The droplets in high  
411 speed mixed emulsions on the other hand were more mobile as these emulsions were not  
412 thickened and 3-pentanone continually released into the headspace. There was no significant  
413 factor influencing the dynamic release behaviour of 3-pentanone over membrane processed  
414 and xanthan gum thickened emulsions.

415

416 Conclusions

417 The conclusions that could be drawn based on the experimental data acquired in this study  
418 are summarised in Table 7. Xanthan gum led to a reduced aroma headspace replenishment

419 mainly due to the effect of increased viscosity. OSA starch alone interacted with 3-pentanone  
420 possibly through hydrophobic interaction or a starch barrier effect. Dynamic diacetyl release  
421 was affected by the OSA starch adsorbed at the oil-water interface and xanthan gum-OSA  
422 starch interaction. This study demonstrates the potential impact of emulsifying and  
423 thickening systems on aroma release systems and highlights that specific interactions may  
424 compromise product quality.

425

#### 426 **Acknowledgement and Declaration**

427 Pu acknowledges a scholarship from China Scholarship Council (CSC).

428

#### 429 **Supporting Information**

430 Micrographs of high speed mixed or membrane processed and xanthan thickened w/o/w and  
431 o/w emulsions, see Figure S1.

432 Viscosity results of oil and external water phase of w/o/w emulsions and xanthan gum  
433 thickened w/o/w emulsions, see Table S1.

434 This material is available free of charge via the Internet at  
435 <https://nam02.safelinks.protection.outlook.com/?url=http%3A%2F%2Fpubs.acs.org&data=02%7C01%7C%7C2dd9e187411645add5c408d709dcf7b2%7C84df9e7fe9f640afb435aaaaaaa%7C1%7C0%7C636988716956319662&sdata=1%2FDMBBa7pYiIF4b0Y6QT06tgIN7F256Vi0FTulnuAI%3D&reserved=0>.  
438

439

## 440 References

- 441 1. McClements, D.J., *Food emulsions: principles, practice and techniques*. **2005**, Bora Raton: CRC  
442 press. 422-428.
- 443 2. Tamaru, S., Igura, N., and Shimoda, M., *Effectiveness of water-air and octanol-air partition*  
444 *coefficients to predict lipophilic flavor release behavior from O/W emulsions*. *Food Chem.*,  
445 **2018**. 239: p. 712-717.
- 446 3. van Ruth, S.M., King, C., and Giannouli, P., *Influence of lipid fraction, emulsifier fraction, and*  
447 *mean particle diameter of oil-in-water emulsions on the release of 20 aroma compounds*. *J.*  
448 *Agric. Food Chem.*, **2002a**. 50(8): p. 2365-2371.
- 449 4. Rabe, S., Krings, U., and Berger, R.G., *Influence of oil-in-water emulsion characteristics on*  
450 *initial dynamic flavour release*. *J. Sci. Food Agric.*, **2003**. 83: p. 1124-1133.
- 451 5. Mao, L., Roos, Y.H., and Miao, S., *Flavour Release from Monoglyceride Structured Oil-in-Water*  
452 *Emulsions through Static Headspace Analysis*. *Food Biophysics*, **2014**. 9(4): p. 359-367.
- 453 6. Bortnowska, G., *Effect of composition, stability and microstructure of o/w emulsions on the*  
454 *retention and release characteristics of diacetyl and (-)-alpha-pinene*. *J. Food Nutr. Sci.*, **2011**.  
455 61(2): p. 125-135.
- 456 7. Frank, D., Appelqvist, I., Piyasiri, U., Wooster, T.J., and Delahunty, C., *Proton Transfer Reaction*  
457 *Mass Spectrometry and Time Intensity Perceptual Measurement of Flavor Release from Lipid*  
458 *Emulsions Using Trained Human Subjects*. *J. Agric. Food Chem.*, **2011**. 59(9): p. 4891-4903.
- 459 8. Frank, D., Eyres, G.T., Piyasiri, U., Cochet-Broch, M., Delahunty, C.M., Lundin, L., and  
460 Appelqvist, I.M., *Effects of Agar Gel Strength and Fat on Oral Breakdown, Volatile Release, and*  
461 *Sensory Perception Using in Vivo and in Vitro Systems*. *J. Agric. Food Chem.*, **2015**. 63(41): p.  
462 9093-9102.
- 463 9. Frank, D., Appelqvist, I., Piyasiri, U., and Delahunty, C., *In vitro measurement of volatile release*  
464 *in model lipid emulsions using proton transfer reaction mass spectrometry*. *J. Agric. Food*  
465 *Chem.*, **2012**. 60(9): p. 2264-73.
- 466 10. Chen, X., McClements, D.J., Wang, J., Zou, L., Deng, S., Liu, W., Yan, C., Zhu, Y., Cheng, C., and  
467 Liu, C., *Coencapsulation of (-)-Epigallocatechin-3-gallate and Quercetin in Particle-Stabilized*  
468 *W/O/W Emulsion Gels: Controlled Release and Bioaccessibility*. *J. Agric. Food Chem.*, **2018**.  
469 66(14): p. 3691-3699.
- 470 11. Malone, M.E., Appelqvist, I.A.M., and Norton, I.T., *Oral behaviour of food hydrocolloids and*  
471 *emulsions. Part 2. Taste and aroma release*. *Food Hydrocolloids*, **2003**. 17(6): p. 775-784.
- 472 12. Lobato-Calleros, C., Rodriguez, E., Sandoval-Castilla, O., Vernon-Carter, E.J., and Alvarez-  
473 Ramirez, J., *Reduced-fat white fresh cheese-like products obtained from W1/O/W2 multiple*  
474 *emulsions: Viscoelastic and high-resolution image analyses*. *Food Res. Int.*, **2006**. 39(6): p. 678-  
475 685.
- 476 13. Lobato-Calleros, C., Recillas-Mota, M.T., Espinosa-Solares, T., Alvarez-Ramirez, J., and Vernon-  
477 Carter, E.J., *Microstructural and rheological properties of low-fat stirred yoghurts made with*  
478 *skim milk and multiple emulsions*. *Journal of Texture Studies*, **2009**. 40(6): p. 657-675.
- 479 14. Chiu, N., Tarrega, A., Parmenter, C., Hewson, L., Wolf, B., and Fisk, I.D., *Optimisation of octinyl*  
480 *succinic anhydride starch stabilised w1/o/w2 emulsions for oral destablisation of encapsulated*  
481 *salt and enhanced saltiness*. *Food Hydrocolloids*, **2017**. 69: p. 450-458.
- 482 15. Chiu, N., Hewson, L., Fisk, I., and Wolf, B., *Programmed emulsions for sodium reduction in*  
483 *emulsion based foods*. *Food & Function*, **2015**. 6(5): p. 1428-1434.
- 484 16. S., M. and M., K., *Rheological properties of W/O/W - type multiple phase systems.*, in *Food*  
485 *texture and rheology*, P., S., Editor. **1979**, Academic Press: London. p. 437-452.
- 486 17. Serdaroglu, M., Öztürk, B., and Urgan, M., *Emulsion characteristics, chemical and textural*  
487 *properties of meat systems produced with double emulsions as beef fat replacers*. *Meat*  
488 *Science*, **2016**. 117: p. 187-195.



- 489 18. Gerald, M. and Eric, D., *Double Emulsions Relevant to Food Systems: Preparation, Stability,*  
490 *and Applications*. Comprehensive Reviews in Food Science and Food Safety, **2017**. 16(3): p.  
491 532-555.
- 492 19. Garti, N., *Progress in stabilization and transport phenomena of double emulsions in food*  
493 *applications*. Lebensm.-Wiss.u.-Technol, **1997**. 30: p. 222-235.
- 494 20. Fernández-Vázquez, R., Linforth, R., Hort, J., Hewson, L., Vila, D.H., Heredia Mira, F.J., Vicario,  
495 I.M., and Fisk, I., *Headspace delivery of limonene from the serum and non-serum fractions*  
496 *of orange juice in-vitro and in-vivo*. LMT - Food Sci. Technol., **2013**. 51(1): p. 65-72.
- 497 21. Linforth, R. and Taylor, A., *Expression of multidisciplinary flavour science. Flavour delivery from*  
498 *the oral cavity to the nose*. Expression of multidisciplinary flavour science, **2010**: p. 101e104.
- 499 22. Buttery, R.G., Guadagni, D.G., and Ling, L.C., *Flavour compounds: volatiles in vegetable oil and*  
500 *oil-water mixtures*. J. Agric. Food Chem., **1973**. 21: p. 198.
- 501 23. Benjamin, O., Silcock, P., Beauchamp, J., Buettner, A., and Everett, D.W., *Emulsifying*  
502 *properties of legume proteins compared to  $\beta$ -lactoglobulin and tween 20 and the volatile*  
503 *release from oil-in-water emulsions*. J. Food Sci., **2014**. 79(10): p. E2014-E2022.
- 504 24. van Ruth, S.M., de Vries, G., Geary, M., and Giannouli, P., *Influence of composition and*  
505 *structure of oil-in-water emulsions on retention of aroma compounds*. J. Sci. Food Agric., **2002b**.  
506 82(9): p. 1028-1035.
- 507 25. Eisinaite, V., Duque Estrada, P., Schroën, K., Berton-Carabin, C., and Leskauskaite, D., *Tailoring*  
508 *W/O/W emulsion composition for effective encapsulation: The role of PGPR in water transfer-*  
509 *induced swelling*. Food Res. Int., **2018**. 106: p. 722-728.
- 510 26. Madene, A., Jacquot, M., Scher, J., and Desobry, S., *Flavour encapsulation and controlled*  
511 *release - a review*. Int. J. Food Sci. Technol., **2006**. 41(1): p. 1-21.
- 512 27. Boutboul, A., Giampaoli, P., Feigenbaum, A., and Ducruet, V., *Influence of the nature and*  
513 *treatment of starch on aroma retention*. Carbohydrate Polymers, **2002a**. 47(1): p. 73-82.
- 514 28. Boutboul, A., Giampaoli, G., Feigenbaum, A., and Duvruet, V., *Use of inverse gas*  
515 *chromatography with humidity control of the carrier gas to characterize aroma-starch*  
516 *interactions*. Food Chem., **2002b**. 71: p. 387-392.
- 517 29. Naknean, P. and Meenune, M., *Factors affecting retention and release of flavour compounds*  
518 *in food carbohydrates*. International Food Research Journal, **2010**. 17: p. 23-34.
- 519 30. van Ruth, S.M., King, C., Delarue, M., and Giannouli, P., *Release of volatile compounds from*  
520 *emulsions: Influence of  $\beta$ -lactoglobulin and pH*. Italian journal of food science, **2002c**. 14(2).
- 521 31. Miettinen, S.-M., Tuorila, H., Piironen, V., Vehkalahti, K., and Hyvönen, L., *Effect of Emulsion*  
522 *Characteristics on the Release of Aroma As Detected by Sensory Evaluation, Static Headspace*  
523 *Gas Chromatography, and Electronic Nose*. J. Agric. Food Chem., **2002**. 50(15): p. 4232-4239.
- 524 32. Paraskevopoulou, A., Tsoukala, A., and Kiosseoglou, V., *Monitoring air/liquid partition of*  
525 *mastic gum oil volatiles in model alcoholic beverage emulsions: effect of emulsion composition*  
526 *and oil droplet size*. Food Hydrocolloids, **2009**. 23(4): p. 1139-1148.
- 527 33. Pawlik, A., Cox, P.W., and Norton, I.T., *Food grade duplex emulsions designed and stabilised*  
528 *with different osmotic pressures*. J. Colloid Interface Sci., **2010**. 352(1): p. 59-67.
- 529 34. Pu, X., Wolf, B., and Dragosavac, M., *Generation of magnesium enriched water-in-oil-in-water*  
530 *food emulsions by stirred cell membrane emulsification*. J. Food Eng., **2018**.
- 531 35. Muschiolik, G. and Dickinson, E., *Double Emulsions Relevant to Food Systems: Preparation,*  
532 *Stability, and Applications*. **2017**. 16(3): p. 532-555.
- 533 36. Lad, M., Hewson, L., and Wolf, B., *Enhancing saltiness in emulsion based foods*. Flavour, **2012**.  
534 1(1): p. 13.
- 535 37. Doyen, K., Carey, M., Linforth, R.S.T., Marin, M., and Taylor, A.J., *Volatile release from an*  
536 *emulsion: Headspace and in-mouth studies*. J. Agric. Food Chem., **2001**. 49(2): p. 804-810.
- 537 38. Bahtz, J., Gunes, D.Z., Syrbe, A., Mosca, N., Fischer, P., and Windhab, E.J., *Quantification of*  
538 *spontaneous w/o emulsification and its impact on the swelling kinetics of multiple w/o/w*  
539 *emulsions*. Langmuir, **2016**. 32(23): p. 5787-5795.

- 540 39. Yven, C., Guichard, E., Giboreau, A., and Roberts, D.D., *Assessment of Interactions between*  
541 *Hydrocolloids and Flavor Compounds by Sensory, Headspace, and Binding Methodologies*. J.  
542 Agric. Food Chem., **1998**. 46(4): p. 1510-1514.
- 543 40. Bylaite, E., Jens Adlernissen, A., and Meyer, A.S., *Effect of Xanthan on Flavor Release from*  
544 *Thickened Viscous Food Model Systems*. J. Agric. Food Chem., **2005**. 53(9): p. 3577-83.

545

546

547 List of figure captions

548 Figure 1 Averaged droplet size distributions on a volume basis of A) high speed mixed or B)  
549 membrane processed and xanthan thickened o/w (ow) and w/o/w (wow) emulsions stabilised  
550 with Tween 20 (T) or OSA starch (S): □ Day of making; ■ Day 6.

551

552 Figure 2 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan  
553 gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,  
554 C) Tween 20 (T) or B, D) OSA starch (S). Values are based on 3 replicates.

555

556 Figure 3 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan  
557 gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,  
558 C) Tween 20 (T) or B, D) OSA starch (S) in the absence or presence of xanthan gum (XG). Values  
559 are based on 3 replicates.

560

Table 1 Composition of w/o/w and o/w emulsions and water control.  $w_1$ : the internal water phase.  $w_2$ : the external water phase. T20: Tween 20. S: OSA starch. XG: xanthan gum. For each emulsion, the dispersed phase mass fraction of the xanthan gum thickened membrane processed emulsions lowered compared to that of high shear mixed emulsions due to the experiment design.

sample ID	$w_1$ (wt.%)	composition of $w_1$	oil (wt.%)	composition of oil	$w_2$ (wt.%)	composition of $w_2$
wT	-	-	-	-	100	2% T20, 0.1 M NaCl
wS	-	-	-	-	100	4% S, 0.1 M NaCl
owT	-	-	30	-	70	2% T20
owS	-	-	30	-	70	4% S
wowT	12	0.1 M NaCl	18	4% PGPR	70	2% T20, 0.1 M NaCl
wowS	12	0.1 M NaCl	18	4% PGPR	70	4% S, 0.1 M NaCl
XG	-	-	-	-	100	0.5 % XG
wT+XG	-	-	-	-	100	2% T20, 0.1 M NaCl, 0.5 % XG
wS+XG	-	-	-	-	100	4% S, 0.1 M NaCl, 0.5 % XG
owT+XG	-	-	18	4% PGPR	82	1% T20, 0.1 M NaCl, 0.5 % XG
owS+XG	-	-	18	4% PGPR	82	2% S, 0.1 M NaCl, 0.5 % XG
wowT+XG	7	0.1 M NaCl	11	4% PGPR	82	1% T20, 0.1 M NaCl, 0.5 % XG
wowS+XG	7	0.1 M NaCl	11	4% PGPR	82	2% S, 0.1 M NaCl, 0.5 % XG

Table 2 Theoretical equilibrium headspace partition coefficients ( $K_{ae}$ ) of two aroma compounds, diacetyl and 3-pentanone, calculated by Eq.1 at 20 °C under dynamic headspace analysis conditions: water: air-water partition coefficient ( $K_{aw}$ ) estimated from EPI SUITE (EPA's and Syracuse Research Corp., USA) at 20 °C.; emulsions: air-emulsion partition coefficient. XG: xanthan gum.

XG addition	aroma type	water	o/w emulsion	w/o/w emulsion
No XG	diacetyl	$5.4 \times 10^{-4}$	$7.6 \times 10^{-4}$	$6.6 \times 10^{-4}$
	3-pentanone	$3.6 \times 10^{-3}$	$1.5 \times 10^{-3}$	$2 \times 10^{-3}$
+XG	diacetyl	$5.4 \times 10^{-4}$	$6.5 \times 10^{-4}$	$6.1 \times 10^{-4}$
	3-pentanone	$3.6 \times 10^{-3}$	$2 \times 10^{-3}$	$2.4 \times 10^{-3}$

561

562

Table 3 Dynamic headspace intensity (%) of diacetyl above water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
water	83.9±1.0 <sup>a*</sup>	80.4±1.9 <sup>a</sup>	80.4±1.9 <sup>a</sup>
wT	82.8±1.4 <sup>ab</sup>	80.6±3.1 <sup>a</sup>	81.0±3.9 <sup>a</sup>
wS	81.1±2.5 <sup>ab</sup>	76.8±1.2 <sup>ab</sup>	79.9±7.8 <sup>a</sup>
owT	85.0±3.4 <sup>a</sup>	77.9±3.5 <sup>ab</sup>	70.3±3.9 <sup>b</sup>
owS	84.7±1.9 <sup>a</sup>	75.0±3.7 <sup>ab</sup>	67.8±4.1 <sup>b</sup>
wowT	78.9±3.1 <sup>b</sup>	73.0±6.2 <sup>b</sup>	66.0±5.9 <sup>b</sup>
wowS	83.0±0.7 <sup>a</sup>	75.9±2.4 <sup>ab</sup>	68.5±1.7 <sup>b</sup>

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

\* Within a column, different letters indicate statistically significant values ( $p < 0.05$ ).

Table 4 Dynamic headspace intensity (%) of 3-pentanone above water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
water	58.0±1.7 <sup>a*</sup>	48.6±1.7 <sup>a</sup>	45.0±1.7 <sup>b</sup>
wT	52.6±2.5 <sup>ab</sup>	44.7±3.5 <sup>ab</sup>	42.0±4.7 <sup>b</sup>
wS	50.9±1.4 <sup>b</sup>	40.2±0.2 <sup>b</sup>	35.3±0.4 <sup>a</sup>
owT	87.4±0.8 <sup>d</sup>	78.6±1.5 <sup>d</sup>	70.6±1.3 <sup>d</sup>
owS	89.4±7.9 <sup>d</sup>	77.1±7.4 <sup>d</sup>	67.3±6.5 <sup>d</sup>
wowT	73.1±0.2 <sup>c</sup>	62.1±2.7 <sup>c</sup>	53.0±3.7 <sup>c</sup>
wowS	72.1±2.2 <sup>c</sup>	59.7±2.6 <sup>c</sup>	51.1±2.4 <sup>bc</sup>

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

\* Within a column, different letters indicate statistically significant values ( $p < 0.05$ ).

Table 5 Dynamic headspace intensity (%) of diacetyl above xanthan thickened (+XG) water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
w+XG	89.0±1.0 <sup>ab*</sup>	79.5±1.2 <sup>a</sup>	70.2±2.5 <sup>ab</sup>
wT+XG	90.0±1.4 <sup>a</sup>	79.8±3.4 <sup>a</sup>	72.4±4.1 <sup>a</sup>
wS+XG	79.5±1.9 <sup>cd</sup>	73.8±3.8 <sup>ab</sup>	68.2±6.5 <sup>ab</sup>
owT+XG	80.1±4.2 <sup>cd</sup>	69.4±5.2 <sup>b</sup>	63.6±4.0 <sup>ab</sup>
owS+XG	75.7±2.2 <sup>d</sup>	68.4±3.3 <sup>b</sup>	63.2±4.3 <sup>b</sup>
wowT+XG	83.7±4.0 <sup>bc</sup>	74.4±4.7 <sup>ab</sup>	67.7±6.6 <sup>ab</sup>
wowS+XG	79.4±5.7 <sup>cd</sup>	73.5±4.0 <sup>ab</sup>	68.5±6.0 <sup>ab</sup>

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

\* Within a column, different letters indicate statistically significant values ( $p < 0.05$ ).



Table 6 Dynamic headspace intensity (%) of 3-pentanone above xanthan thickened (+XG) water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
w+XG	64.1±2.0 <sup>ab*</sup>	49.7±2.0 <sup>ab</sup>	39.1±1.0 <sup>ab</sup>
wT+XG	60.6±4.9 <sup>ab</sup>	49.9±2.6 <sup>ab</sup>	38.8±1.3 <sup>ab</sup>
wS+XG	61.4±6.0 <sup>ab</sup>	47.7±2.9 <sup>a</sup>	34.9±2.1 <sup>a</sup>
owT+XG	67.1±4.1 <sup>a</sup>	51.6±4.8 <sup>ab</sup>	39.8±4.0 <sup>ab</sup>
owS+XG	56.6±6.0 <sup>b</sup>	44.8±6.3 <sup>a</sup>	35.8±4.7 <sup>a</sup>
wowT+XG	69.0±6.3 <sup>a</sup>	56.4±5.2 <sup>b</sup>	44.5±2.8 <sup>b</sup>
wowS+XG	60.0±6.9 <sup>ab</sup>	44.9±3.3 <sup>a</sup>	38.7±5.0 <sup>ab</sup>

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

\* Within a column, different letters indicate statistically significant values ( $p < 0.05$ ).

Table 7 Results summary of the inhibition, enhancement or similar ability of w/o/w emulsions in the dynamic headspace release of diacetyl or 3-pentanone compared to o/w emulsions and the main factors driving the phenomenon. A) High speed mixed or B) membrane processed and xanthan gum thickened emulsions stabilised with Tween 20 or OSA starch as the hydrophilic emulsifier.

Preparation method	Aroma compounds	Tween 20	OSA starch	Main factors
A)	Diacetyl	Inhibition	Similar	Emulsion type, creaming and diacetyl-OSA starch interactions
	3-pentanone	Inhibition	Inhibition	Emulsion type and creaming
B)	Diacetyl	Enhancement	Similar	Emulsion type and diacetyl-xanthan gum-OSA starch interactions
	3-pentanone	Similar	Similar	None

Figure 1 Page 1

A)

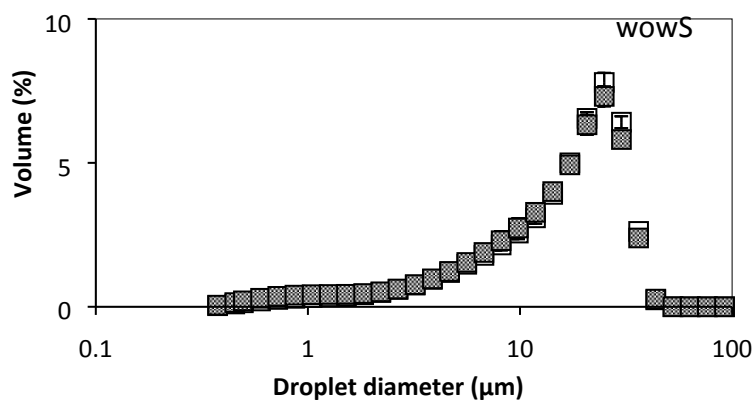
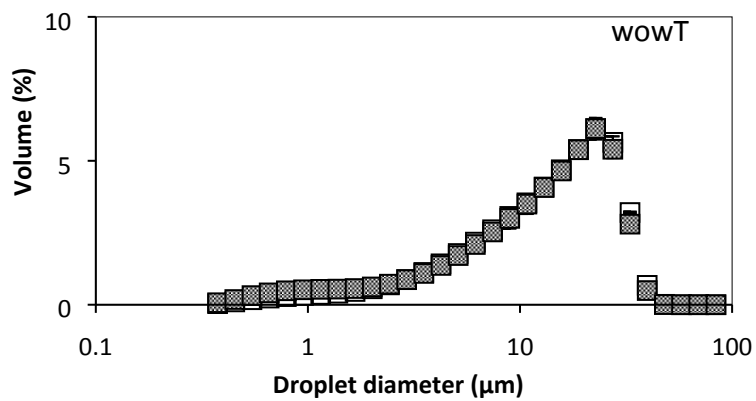
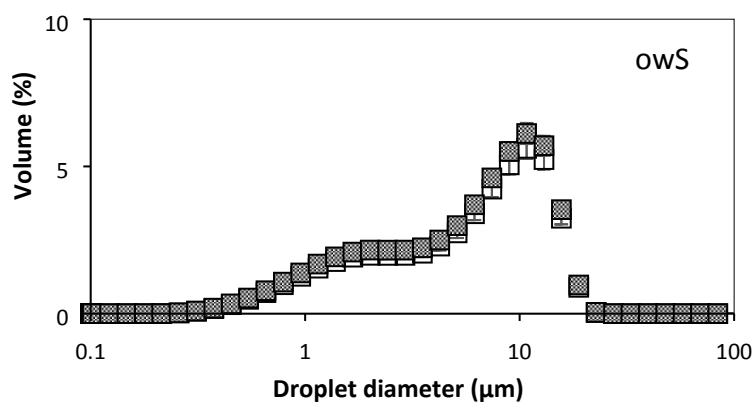
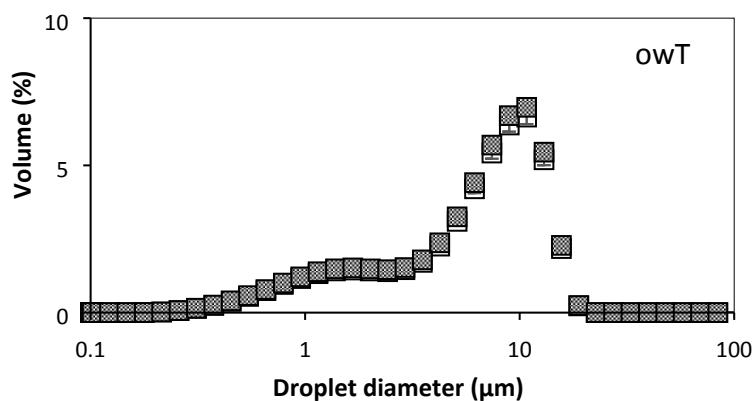
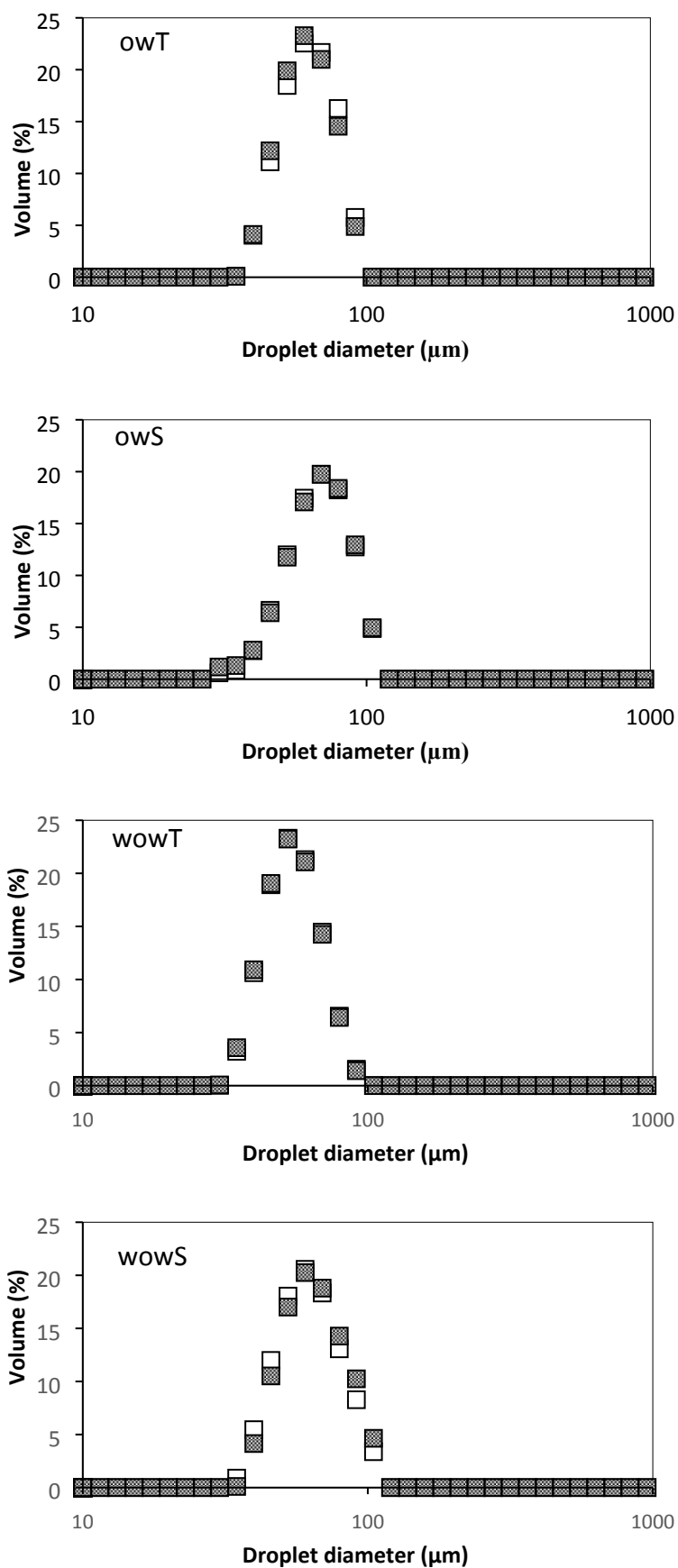


Figure 1 Page 2

B)

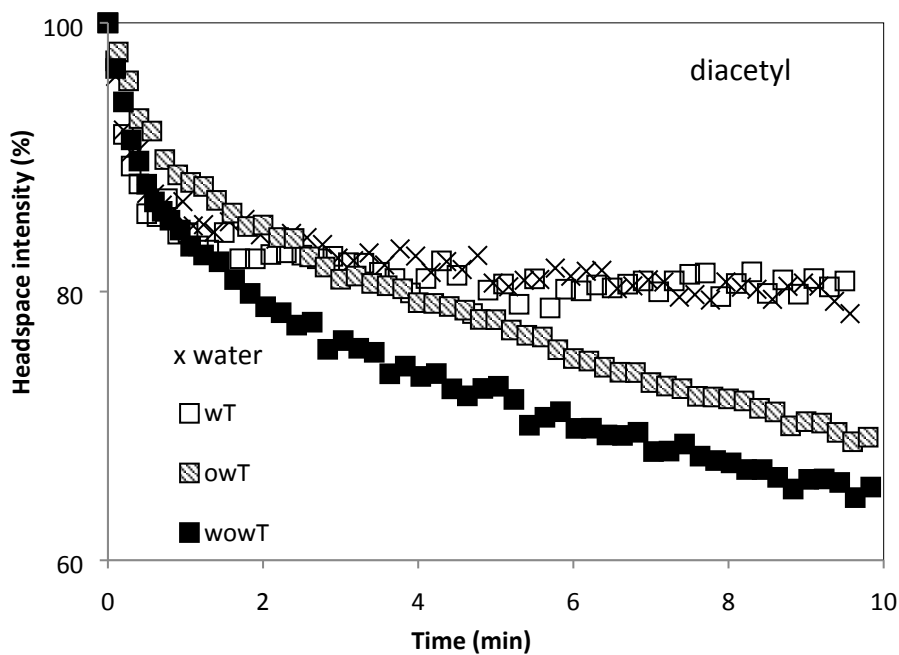


## Figure 1 Page 3

Figure 1 Averaged droplet size distributions on a volume basis of A) high speed mixed or B) membrane processed and xanthan thickened o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S): □ Day of making; ▣ Day 6.

Figure 2 Page 1

A)



B)

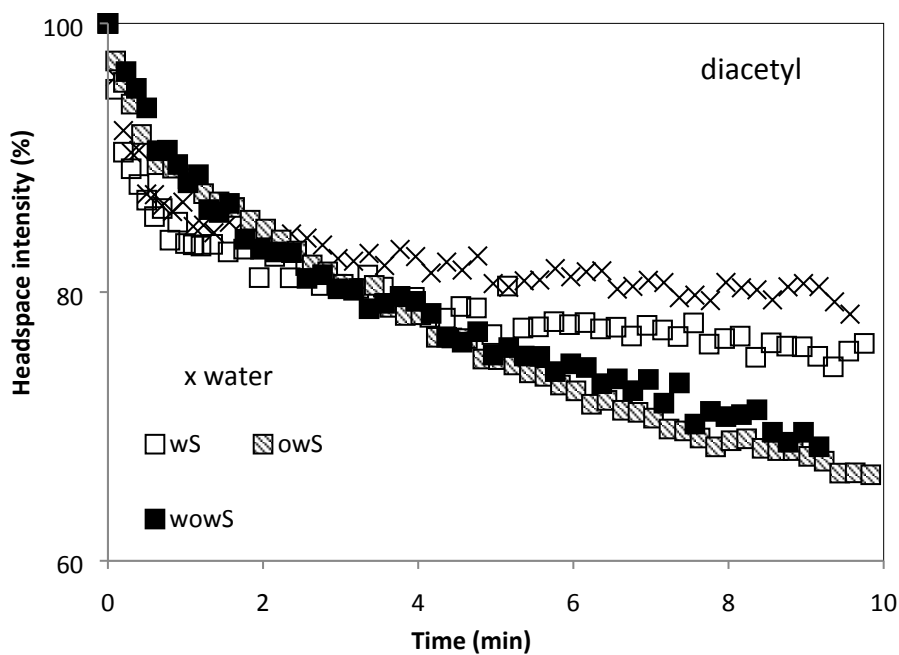
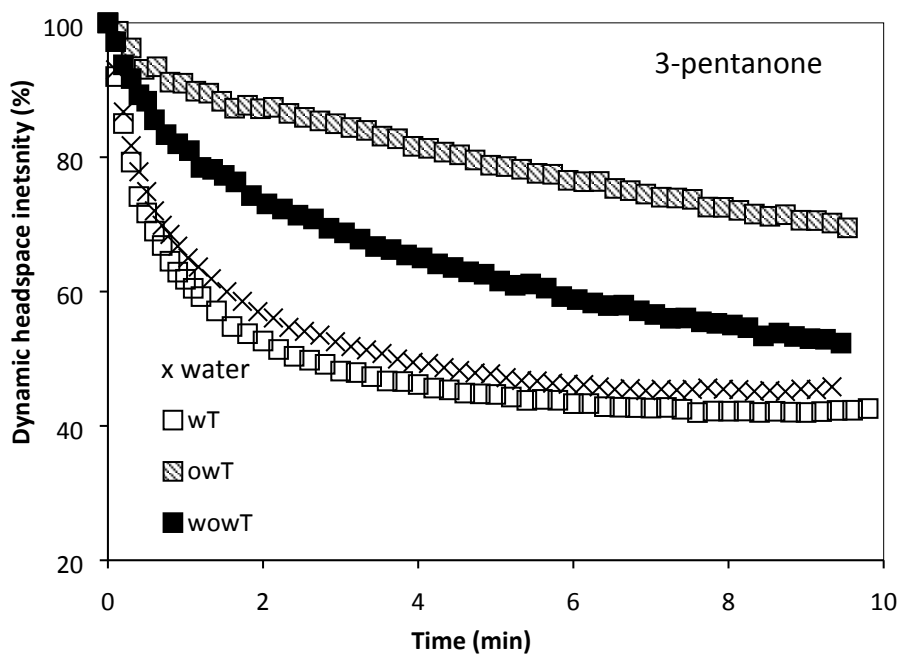


Figure 2 Page 2

C)



D)

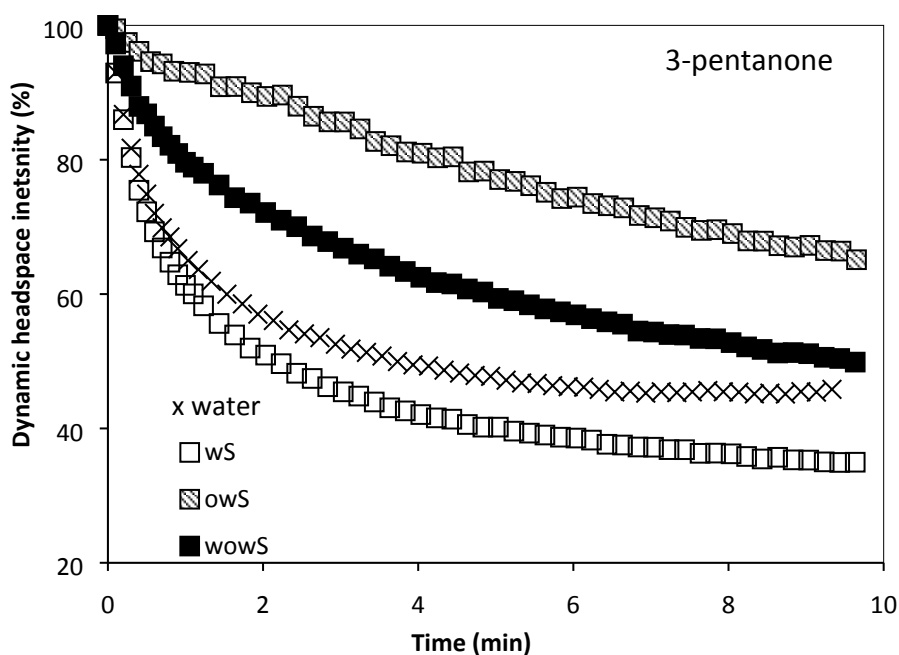
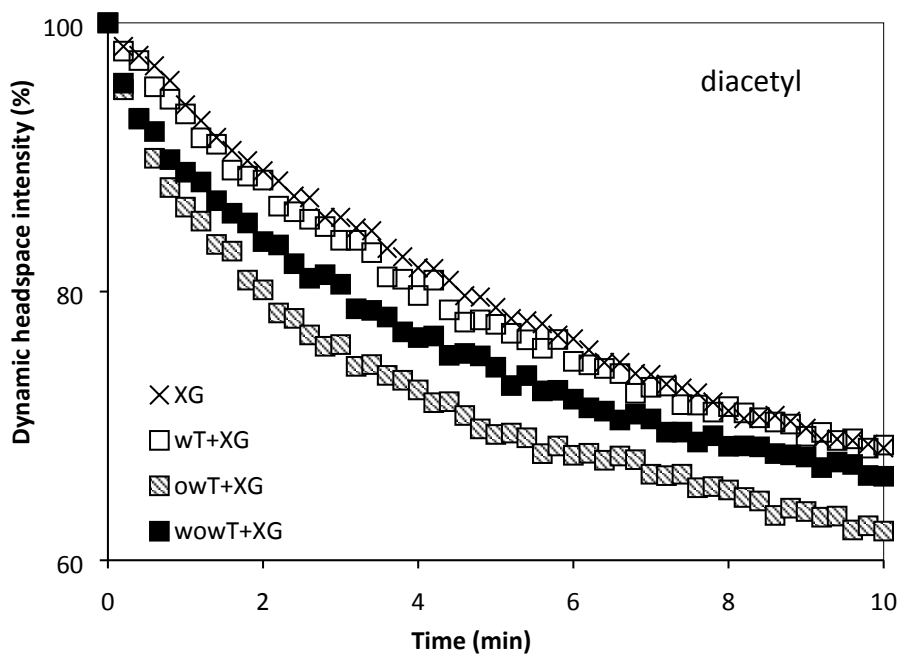


Figure 2 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A, C) Tween 20 (T) or B, D) OSA starch (S). Values are based on 3 replicates.

Figure 3 Page 1

A)



B)

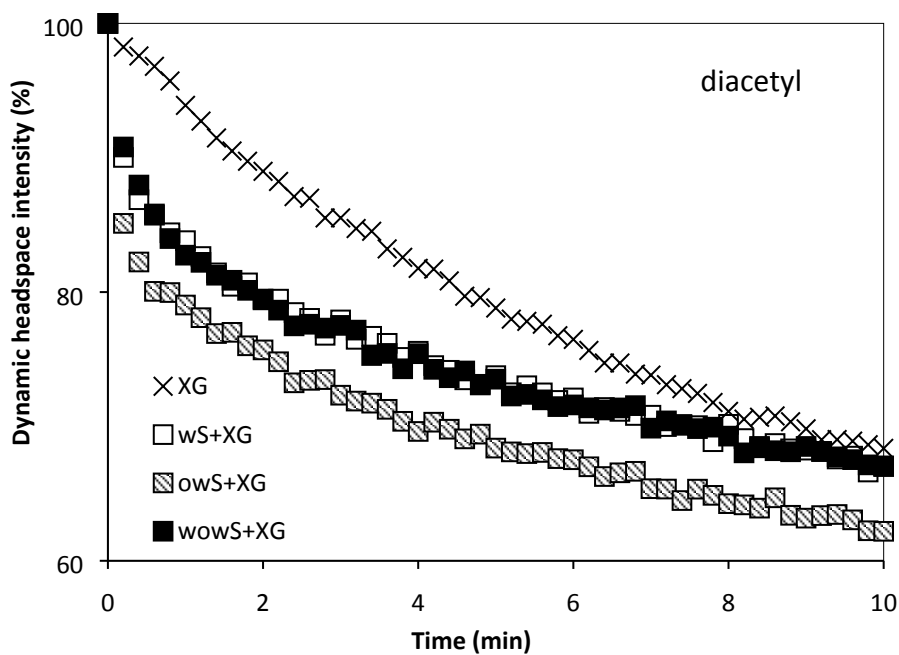
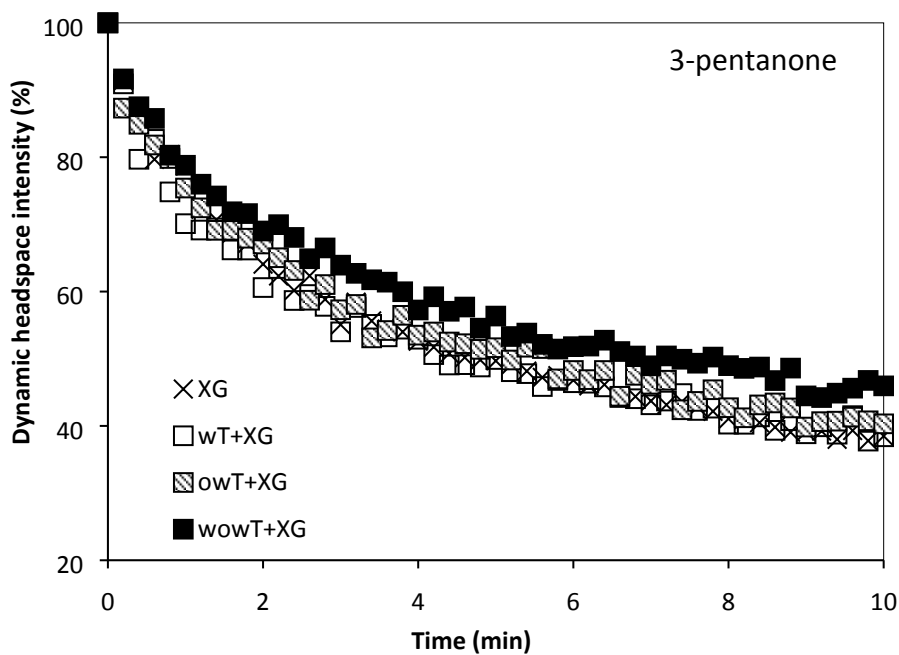




Figure 3 Page 3

C)



D)

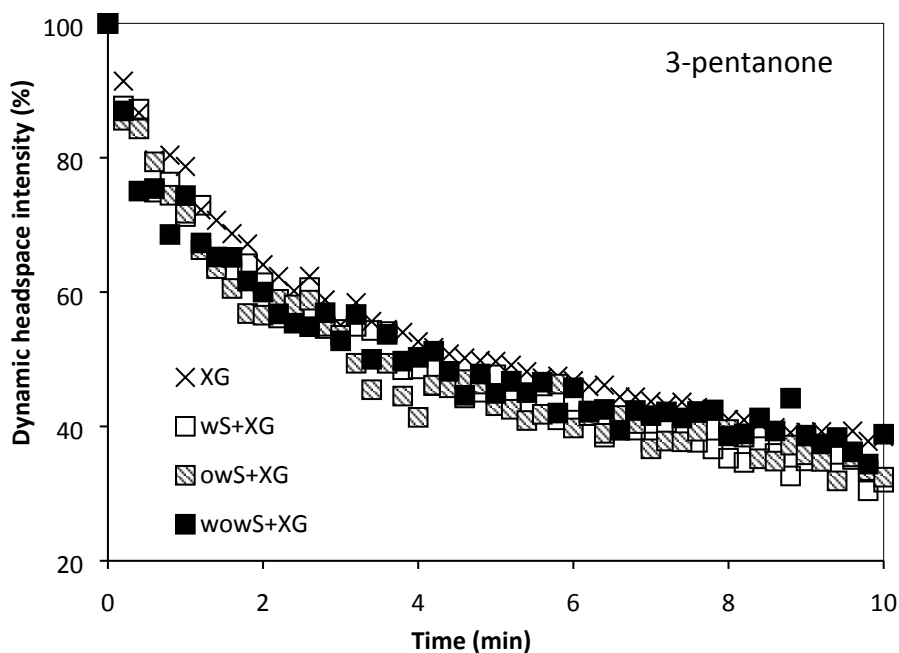


Figure 3 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,

Figure 3 Page 3

C) Tween 20 (T) or B, D) OSA starch (S) in the absence or presence of xanthan gum (XG). Values are based on 3 replicates.

## TOC graphic

