UNIVERSITY OF BIRMINGHAM

Dynamic aroma release from complex food emulsions

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

Document Version
Peer reviewed version

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

Dynamic Aroma Release from Complex Food Emulsions

Journal:	*Journal of Agricultural and Food Chemistry*
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 Linforth, 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[a][1][*], Robert Linforth[a], Marijana M. Dragosavac[b], Bettina Wolf[a][2]

[a]School of Biosciences, University of Nottingham, Sutton Bonington Campus, Loughborough

LE12 5RD, UK

[b]Chemical Engineering Department, Loughborough University, Loughborough LE11 3TU, UK

[*]correspondence: xiaolu.pu@outlook.com

[1] Present address: College of Bioscience and Bioengineering, Hebei University of Science and Technology 050000, China
[2] Present address: School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

1

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

2

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)[1] has been studied widely.[2-9] 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.[10, 11] w/o/w emulsions have been shown to have advantages

26   over o/w emulsions for fat reduction[12, 13] and salt reduction.[14, 15] Although food applications

27   in low calorie cream or fat-reduced mayonnaise,[16] fat substitutes in meat emulsions,[17]

28   substitutes for dairy fat in cheese[12] 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.[18, 19] 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}).[20, 21] A low K_{aw} or K_{ae} value will lead to a more stable

39   headspace concentration against headspace dilution.[20, 21] In that case, K_{ae} is calculated by

40   Eq.1:[22]

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

42 where Φ_o and Φ_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.[3, 4, 6-9] 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,[4, 6] on the other hand side impact of droplet size, affecting emulsion viscosity, on

52 dynamic aroma release has been reported.[3] Further, decreasing release rates with increasing

53 fat level,[9] decreasing lipophilicity[9] and increasing gel strength[8] 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[23, 24] or hydrophilic[25] 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[26, 27]. The suggested mechanisms is via hydrogen

59 bonding between the hydrophilic aroma compounds and the hydroxyl groups of starch,[28] or

60 inclusion complexes between the hydrophobic aroma compounds and amylose.[29] 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.[24, 30-32] This ratio is affected by the total surface area of the dispersed

4

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±0.003 g/cm^3; 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

5

86 xanthan gum (Keltrol RD) from CP Kelco (San Diego, USA). Sodium chloride to aid

87 microstructure stabilisation[33] 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[33, 34] and the polymeric emulsifier OSA starch[14, 15] 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.[35] 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,[34] 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

6

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 ± 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

7

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^{-1} corresponding to a

140   transmembrane flux of 70 L h^{-1} m^{-2}. 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^{-1}.

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_2 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

9

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 μL 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 μL 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 ± 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 (N$_2$) was introduced into the bottle at a flow rate of 70

213   mL min^{-1} measured using an electronic flow meter (vary-flow 500, Agilent Technologies,

214   Berkshire, UK). 5 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 mz^{-1} (molecular weight +1) with a

11

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).[36] 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 μm, the main distribution

244   peak of the w/o/w emulsions was also slightly larger compared to 10 μm 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 μm resulting in the specific surface area of around 0.1 m^2

256   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

14

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}

16

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[37, 38] 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.[39] 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 homogenously 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,[8] or increased viscosity[40] 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**

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&d

436   ata=02%7C01%7C%7C2dd9e187411645add5c408d709dcf7b2%7C84df9e7fe9f640afb435aaa

437   aaaaaaaaaa%7C1%7C0%7C636988716956319662&sdata=1%2FDMBBa7pYiIlF4b0Y6QT0

438   6tglN7F256Vi0FTulnuAI%3D&reserved=0.

439

References

1. McClements, D.J., *Food emulsions: principles, practice and techniques.* **2005**, Bora Raton: CRC press. 422-428.

2. Tamaru, S., Igura, N., and Shimoda, M., *Effectiveness of water-air and octanol-air partition coefficients to predict lipophilic flavor release behavior from O/W emulsions.* Food Chem., **2018**. 239: p. 712-717.

3. van Ruth, S.M., King, C., and Giannouli, P., *Influence of lipid fraction, emulsifier fraction, and mean particle diameter of oil-in-water emulsions on the release of 20 aroma compounds.* J. Agric. Food Chem., **2002a**. 50(*8*): p. 2365-2371.

4. Rabe, S., Krings, U., and Berger, R.G., *Inlfuence of oil-in-water emulsion characteristics on initial dynamic flavour release.* J. Sci. Food Agric., **2003**. 83: p. 1124-1133.

5. Mao, L., Roos, Y.H., and Miao, S., *Flavour Release from Monoglyceride Structured Oil-in-Water Emulsions through Static Headspace Analysis.* Food Biophysics, **2014**. 9(*4*): p. 359-367.

6. Bortnowska, G., *Effect of composition, stability and microstructure of o/w emulsions on the retention and release characteristics of diacetyl and (-)-alpha-pinene.* J. Food Nutr. Sci., **2011**. 61(*2*): p. 125-135.

7. Frank, D., Appelqvist, I., Piyasiri, U., Wooster, T.J., and Delahunty, C., *Proton Transfer Reaction Mass Spectrometry and Time Intensity Perceptual Measurement of Flavor Release from Lipid Emulsions Using Trained Human Subjects.* J. Agric. Food Chem., **2011**. 59(*9*): p. 4891-4903.

8. Frank, D., Eyres, G.T., Piyasiri, U., Cochet-Broch, M., Delahunty, C.M., Lundin, L., and Appelqvist, I.M., *Effects of Agar Gel Strength and Fat on Oral Breakdown, Volatile Release, and Sensory Perception Using in Vivo and in Vitro Systems.* J. Agric. Food Chem., **2015**. 63(*41*): p. 9093-9102.

9. Frank, D., Appelqvist, I., Piyasiri, U., and Delahunty, C., *In vitro measurement of volatile release in model lipid emulsions using proton transfer reaction mass spectrometry.* J. Agric. Food Chem., **2012**. 60(*9*): p. 2264-73.

10. Chen, X., McClements, D.J., Wang, J., Zou, L., Deng, S., Liu, W., Yan, C., Zhu, Y., Cheng, C., and Liu, C., *Coencapsulation of (−)-Epigallocatechin-3-gallate and Quercetin in Particle-Stabilized W/O/W Emulsion Gels: Controlled Release and Bioaccessibility.* J. Agric. Food Chem., **2018**. 66(*14*): p. 3691-3699.

11. Malone, M.E., Appelqvist, I.A.M., and Norton, I.T., *Oral behaviour of food hydrocolloids and emulsions. Part 2. Taste and aroma release.* Food Hydrocolloids, **2003**. 17(*6*): p. 775-784.

12. Lobato-Calleros, C., Rodriguez, E., Sandoval-Castilla, O., Vernon-Carter, E.J., and Alvarez-Ramirez, J., *Reduced-fat white fresh cheese-like products obtained from W1/O/W2 multiple emulsions: Viscoelastic and high-resolution image analyses.* Food Res. Int., **2006**. 39(*6*): p. 678-685.

13. Lobato-Calleros, C., Recillas-Mota, M.T., Espinosa-Solares, T., Alvarez-Ramirez, J., and Vernon-Carter, E.J., *Microstructural and rheological properties of low-fat stirred yoghurts made with skim milk and multiple emulsions.* Journal of Texture Studies, **2009**. 40(*6*): p. 657-675.

14. Chiu, N., Tarrega, A., Parmenter, C., Hewson, L., Wolf, B., and Fisk, I.D., *Optimisation of octinyl succinic anhydride starch stablised w1/o/w2 emulsions for oral destabilisation of encapsulated salt and enhanced saltiness.* Food Hydrocolloids, **2017**. 69: p. 450-458.

15. Chiu, N., Hewson, L., Fisk, I., and Wolf, B., *Programmed emulsions for sodium reduction in emulsion based foods.* Food & Function, **2015**. 6(*5*): p. 1428-1434.

16. S., M. and M., K., *Rheological properties of W/O/W‐type multiple phase systems.*, in *Food texture and rheology*, P., S., Editor. **1979**, Academic Press: London. p. 437–452.

17. Serdaroğlu, M., Öztürk, B., and Urgu, M., *Emulsion characteristics, chemical and textural properties of meat systems produced with double emulsions as beef fat replacers.* Meat Science, **2016**. 117: p. 187-195.

22

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 phenomana 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 favour science. Flavour delivery from*
498   *the oral cavity to the nose.* Expression of multidisciplinary favour 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 β-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., *Tayloring*
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 carbogydrates.* 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 β-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.

23

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	5.4×10^{-4}	7.6×10^{-4}	6.6×10^{-4}
	3-pentanone	3.6×10^{-3}	1.5×10^{-3}	2×10^{-3}
+XG	diacetyl	5.4×10^{-4}	6.5×10^{-4}	6.1×10^{-4}
	3-pentanone	3.6×10^{-3}	2×10^{-3}	2.4×10^{-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[a]*	80.4±1.9[a]	80.4±1.9[a]
wT	82.8±1.4[ab]	80.6±3.1[a]	81.0±3.9[a]
wS	81.1±2.5[ab]	76.8±1.2[ab]	79.9±7.8[a]
owT	85.0±3.4[a]	77.9±3.5[ab]	70.3±3.9[b]
owS	84.7±1.9[a]	75.0±3.7[ab]	67.8±4.1[b]
wowT	78.9±3.1[b]	73.0±6.2[b]	66.0±5.9[b]
wowS	83.0±0.7[a]	75.9±2.4[ab]	68.5±1.7[b]

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

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

28

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	$58.0 \pm 1.7^{a*}$	48.6 ± 1.7^a	45.0 ± 1.7^b
wT	52.6 ± 2.5^{ab}	44.7 ± 3.5^{ab}	42.0 ± 4.7^b
wS	50.9 ± 1.4^b	40.2 ± 0.2^b	35.3 ± 0.4^a
owT	87.4 ± 0.8^d	78.6 ± 1.5^d	70.6 ± 1.3^d
owS	89.4 ± 7.9^d	77.1 ± 7.4^d	67.3 ± 6.5^d
wowT	73.1 ± 0.2^c	62.1 ± 2.7^c	53.0 ± 3.7^c
wowS	72.1 ± 2.2^c	59.7 ± 2.6^c	51.1 ± 2.4^{bc}

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[ab]*	79.5±1.2[a]	70.2±2.5[ab]
wT+XG	90.0±1.4[a]	79.8±3.4[a]	72.4±4.1[a]
wS+XG	79.5±1.9[cd]	73.8±3.8[ab]	68.2±6.5[ab]
owT+XG	80.1±4.2[cd]	69.4±5.2[b]	63.6±4.0[ab]
owS+XG	75.7±2.2[d]	68.4±3.3[b]	63.2±4.3[b]
wowT+XG	83.7±4.0[bc]	74.4±4.7[ab]	67.7±6.6[ab]
wowS+XG	79.4±5.7[cd]	73.5±4.0[ab]	68.5±6.0[ab]

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

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

30

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	$64.1\pm2.0^{ab*}$	49.7 ± 2.0^{ab}	39.1 ± 1.0^{ab}
wT+XG	60.6 ± 4.9^{ab}	49.9 ± 2.6^{ab}	38.8 ± 1.3^{ab}
wS+XG	61.4 ± 6.0^{ab}	47.7 ± 2.9^{a}	34.9 ± 2.1^{a}
owT+XG	67.1 ± 4.1^{a}	51.6 ± 4.8^{ab}	39.8 ± 4.0^{ab}
owS+XG	56.6 ± 6.0^{b}	44.8 ± 6.3^{a}	35.8 ± 4.7^{a}
wowT+XG	69.0 ± 6.3^{a}	56.4 ± 5.2^{b}	44.5 ± 2.8^{b}
wowS+XG	60.0 ± 6.9^{ab}	44.9 ± 3.3^{a}	38.7 ± 5.0^{ab}

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

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

563

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

32

Figure 1 Page 1

A)
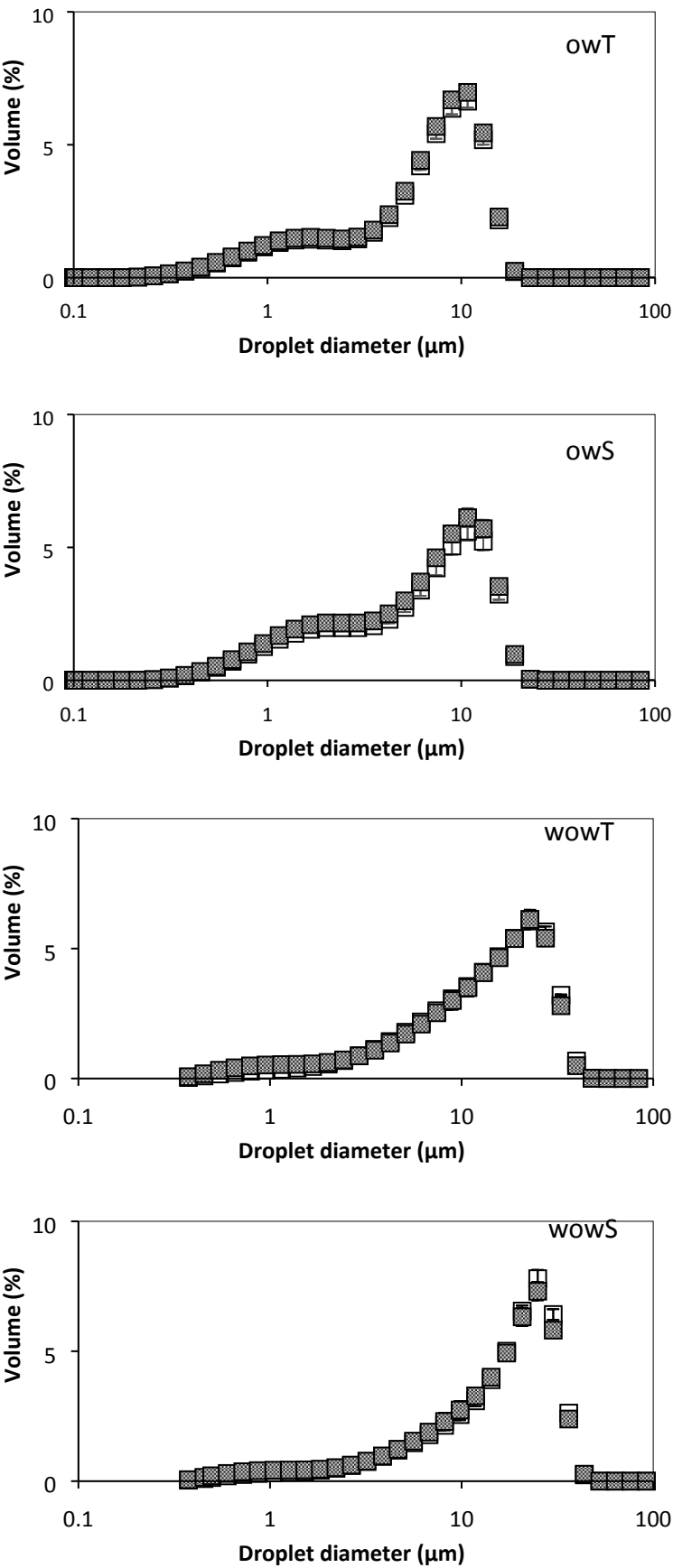
Figure 1 Page 2

B)
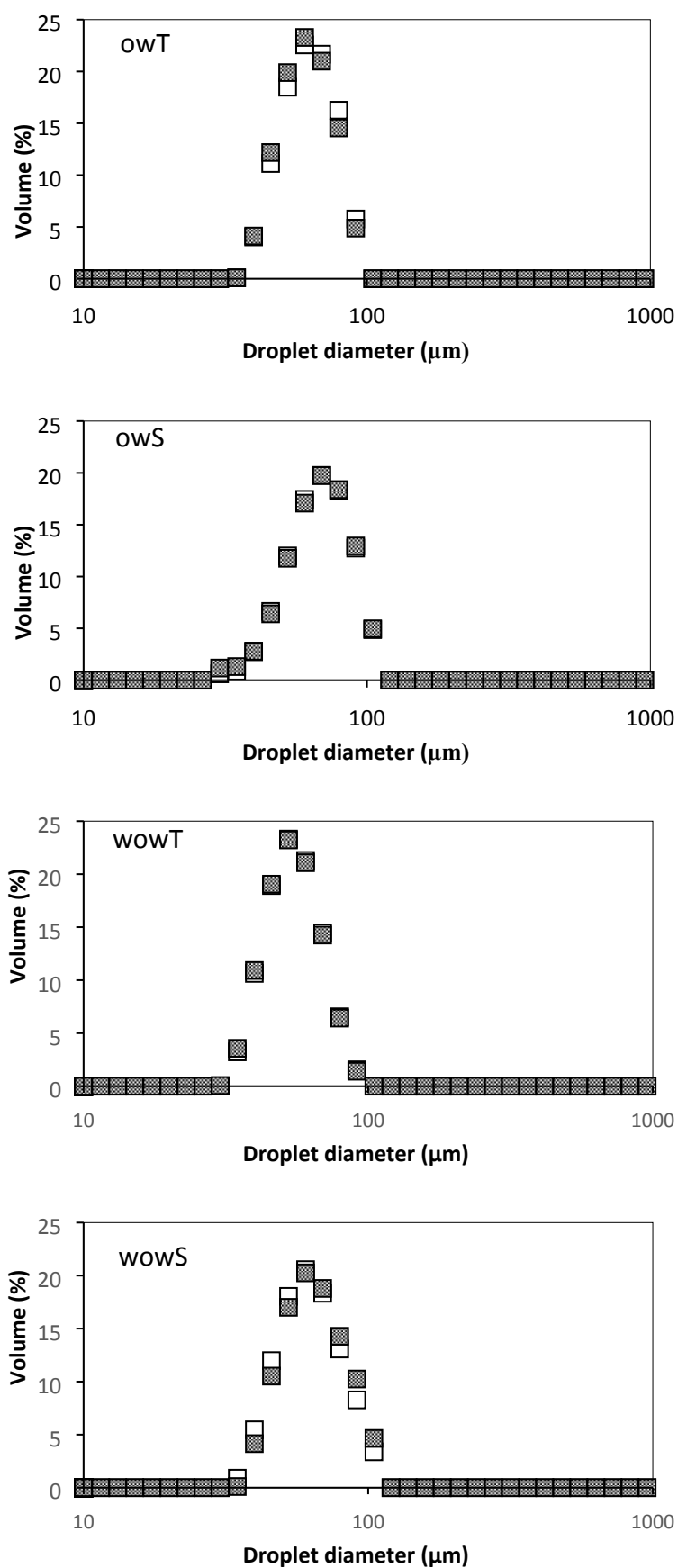
Figure 1 Page 3

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.
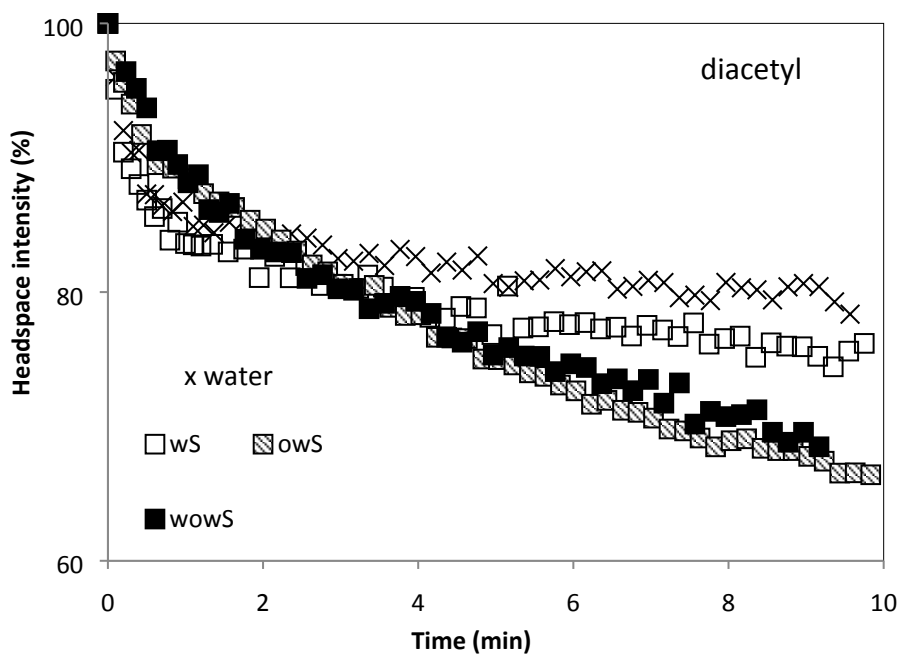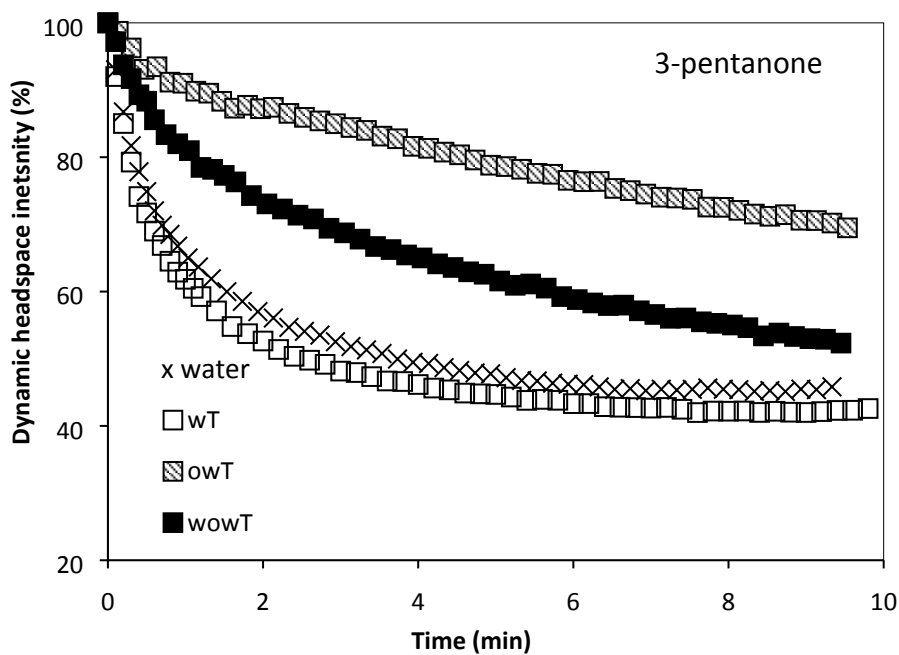
Figure 2 Page 1
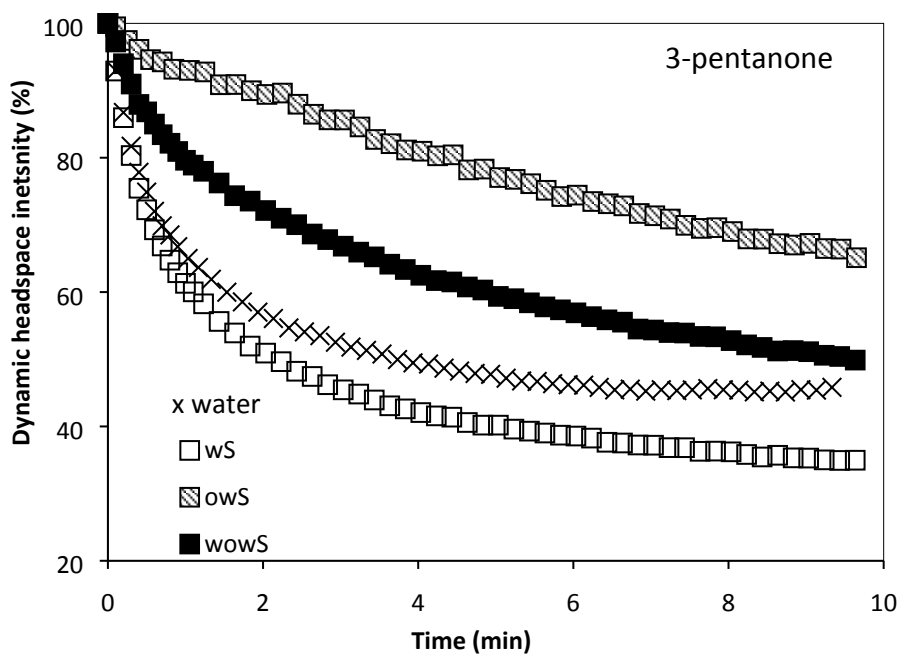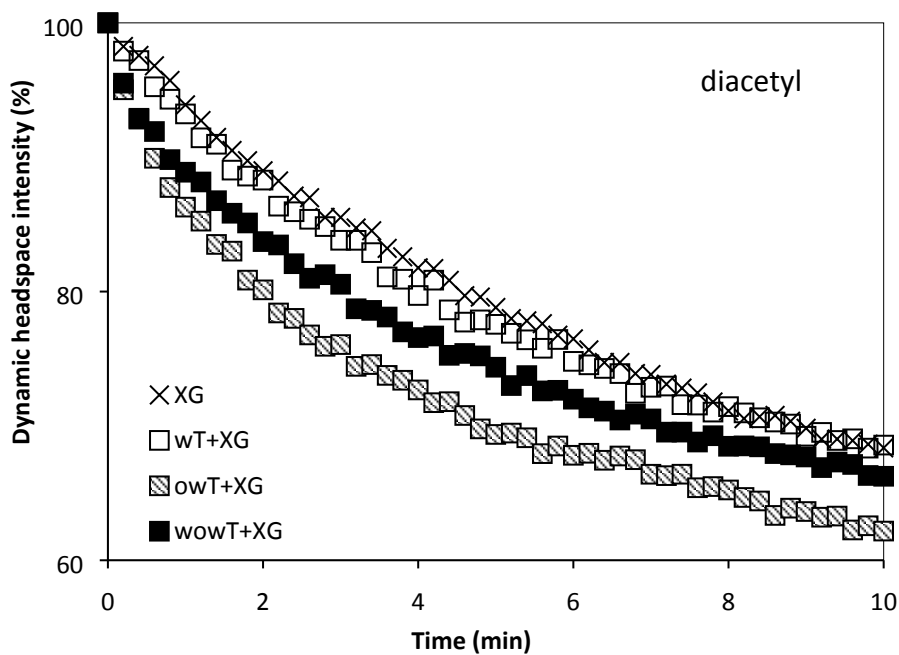
A)
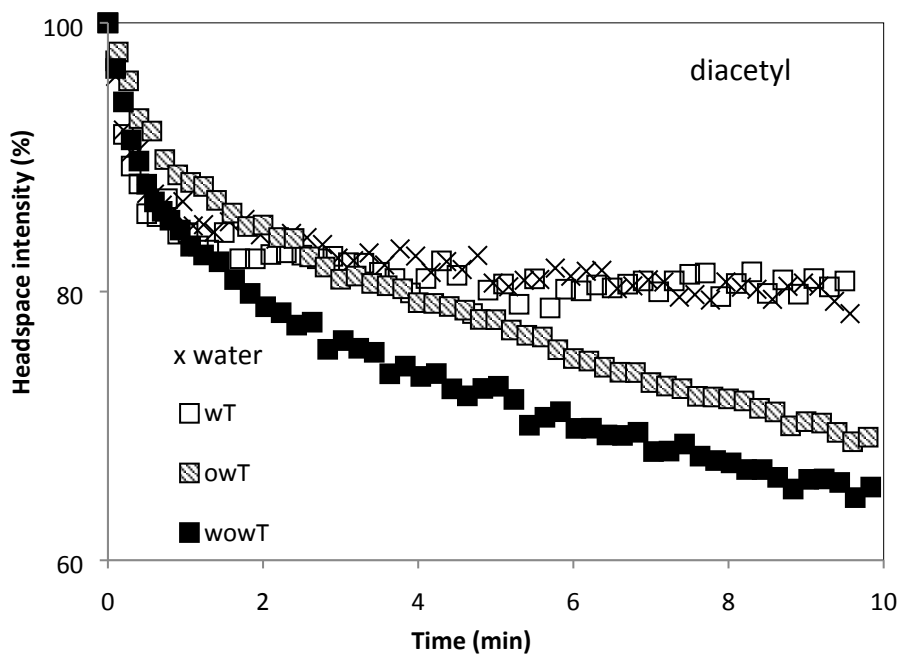
B)

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.
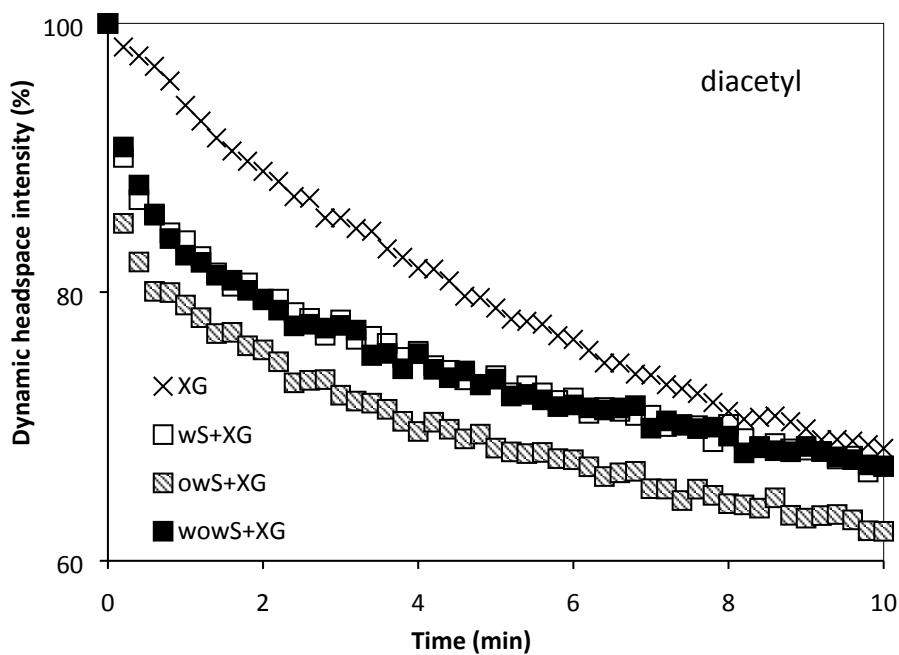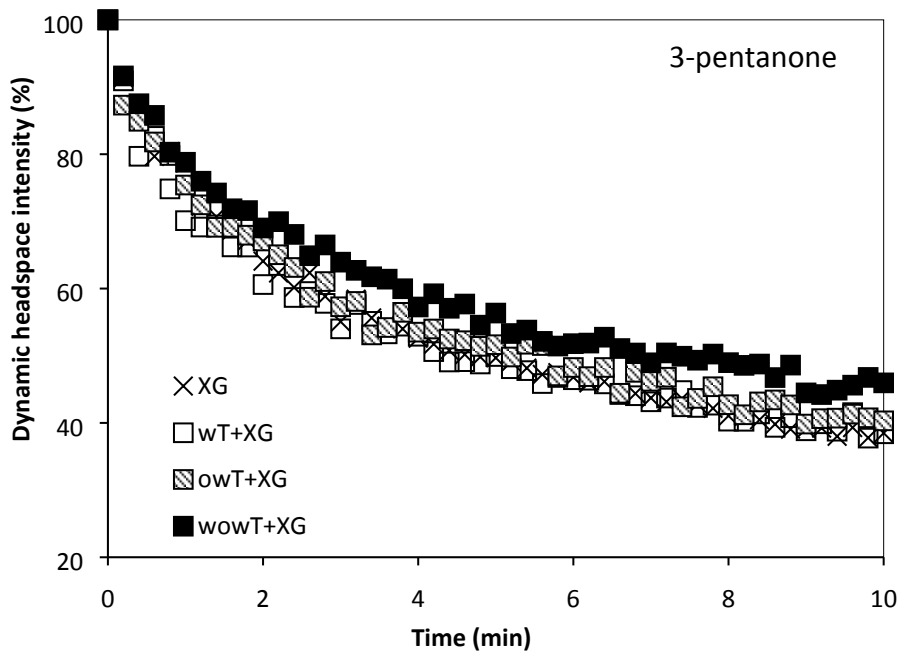
37

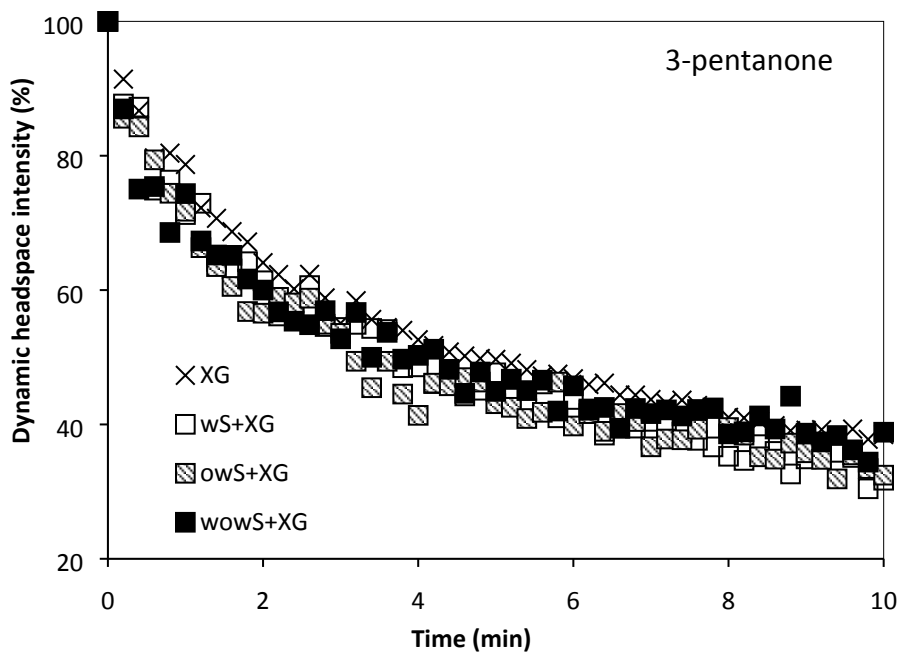Figure 3 Page 1

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,

39

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