

1 **Cheese whey valorisation: Production of valuable gaseous and liquid chemicals**
2 **from lactose by aqueous phase reforming**

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12 **ABSTRACT**

13 Cheese effluent management has become an important issue owing to its high
14 biochemical oxygen demand and chemical oxygen demand values. Given this scenario,
15 this work addresses the valorisation of lactose (the largest organic constituent of this
16 waste) by aqueous phase reforming, analysing the influence of the most important
17 operating variables (temperature, pressure, lactose concentration and mass of catalyst/
18 lactose mass flow rate ratio) as well as optimising the process for the production of
19 either gaseous or liquid value-added chemicals. The carbon converted into gas, liquid
20 and solid products varied as follows: 5-41%, 33-97% and 0-59%, respectively. The gas
21 phase was made up of a mixture of H₂ (8-58 vol.%), CO₂ (33-85 vol.%), CO (0-15
22 vol.%) and CH₄ (0-14 vol.%). The liquid phase consisted of a mixture of aldehydes: 0-
23 11%, carboxylic acids: 0-22%, monohydric alcohols: 0-23%, polyhydric-alcohols: 0-
24 48%, C₃-ketones: 4-100%, C₄-ketones: 0-18 %, cyclic-ketones: 0-15% and furans: 0-
25 85%. H₂ production is favoured at high pressure, elevated temperature, employing a
26 high amount of catalyst and a concentrated lactose solution. Liquid production is
27 preferential using diluted lactose solutions. At high pressure, the production of C₃-
28 ketones is preferential using a high temperature and a low amount of catalyst, while a
29 medium temperature and a high amount of catalyst favours the production of furans.
30 The production of alcohols is preferential using medium temperature and pressure and a
31 low amount of catalyst.

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33 **Keywords:** cheese whey, lactose, aqueous phase reforming, renewable hydrogen and
34 value-added liquids.

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50 **1. Introduction**

51 Cheese whey is a yellowish liquid resulting from the coprecipitation and removal of
52 milk casein in cheese making processes. On average, during the production of 1 kg of
53 cheese, 9 kg of cheese whey is produced as a by-product. This corresponds to 5 million
54 tons a year of whey worldwide [1-4]. The typical composition of this waste is as
55 follows: 4.5-6 wt.% lactose, 0.6-1.1 wt.% proteins, 0.8-1 wt.% minerals, 0.05-0.9 wt.%
56 lactic acid, 0.06-0.5 wt.% fats and 93-94 wt.% water [1-4]. It has biochemical oxygen
57 demand (BOD) and chemical oxygen demand (COD) values ranging from 27-60 kg/m³
58 and 50-102 kg/m³, respectively. Therefore, it should not be directly discharged into the
59 environment without appropriate treatment and/or valorisation [3] hence cheese whey
60 management has become an important issue [1-4].

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62 Two alternative methods of cheese whey management have traditionally been addressed
63 [3]. The first is the application of physicochemical treatments and filtration
64 technologies. Physicochemical treatments include thermal and isoelectric precipitation
65 [5, 6], as well as protein precipitation with coagulant/flocculant agents [7]. Filtration
66 technologies include the use of ultrafiltration membranes and reverse osmosis [2]. The
67 second option relies on the application of biological treatments without valorisation,
68 such as aerobic digestion, and with valorisation such as anaerobic digestion, lactose
69 hydrolysis and fermentation [3]. Aerobic digestion consists of the degradation of the
70 organic matter in the whey at room temperature using short hydraulic retention times
71 [8]. Anaerobic digestion is conducted to convert lactose into propionic acid, ethanol and
72 lactose acetates [9]. Lactose hydrolysis is a preliminary step for other processes [4].
73 Cheese whey fermentation includes the production of ethanol, lactic acid, and hydrogen

74 and many more [10]. The bioconversion of lactose to ethanol has a theoretical
75 maximum yield of 0.538 kg ethanol/kg of lactose [11, 12]. Anaerobic fermentation has
76 a theoretical yield of 4 mol H₂/mol lactose and produces a gas made up of a mixture of
77 H₂, CO₂ and CH₄.

78

79 Another interesting and very promising option for the treatment and valorisation of
80 cheese whey effluents is aqueous phase reforming (APR). APR is a catalytic process
81 carried out at quite low temperatures and moderate pressures that allows the
82 simultaneous production of different gases and liquids from an organic feedstock. The
83 gas phase consists of a gas with a high H₂ content, the liquid phase being a complex
84 mixture of different organic compounds in water such as alcohols, ketones, acids, esters,
85 aldehydes, furans, phenols and anhydro-sugars [13-16]. The product distribution
86 strongly depends on the operating conditions under which the process is conducted.
87 Therefore, APR can be customised either for the production of gases, helping to reduce
88 the BOD and COD values of the feed or for the production of valuable liquids. In
89 addition, the APR process dispenses with the need to vaporise the water and the organic
90 compounds of the feedstock, thus reducing the energy requirements [17]. To the best of
91 the authors' knowledge, there are no studies in the literature concerning the effect of the
92 operating conditions on the aqueous phase reforming of lactose or cheese whey.
93 Skoglund and Holles [18] developed different pseudomorphic overlayer catalysts
94 (Ni/Al₂O₃, Co/Al₂O₃, Pt/Al₂O₃, Ni/SiO₂-Al₂O₃, Co/SiO₂-Al₂O₃ and Pt/SiO₂-Al₂O₃) for
95 the aqueous phase reforming of lactose. Furthermore, works dealing with the aqueous
96 phase reforming of sugars are very scarce. Such studies that there are analyse the
97 aqueous phase reforming of xylitol, sorbitol and galactitol.

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99 Jiang et al. [19] studied the APR of xylitol for pentane production over Pt/HZSM-5 and
100 Ni/HZSM-5, analysing the effects of the reaction temperature, pressure and metal
101 loading on the xylitol conversion and pentane selectivity. Kirilin et al. [20] reported the
102 APR of xylitol in a continuous fixed bed reactor over three catalysts: Pt/Al₂O₃, Pt/TiO₂
103 and Pt-Re/TiO₂. Xi et al. [21] prepared different M/NbOPO₄ multifunctional catalysts
104 (M= Pt, Pd, Ru, Ir, Rh and Ni) for alkane production by the hydrodeoxygenation of
105 sorbitol in aqueous solution. Aiouache et al. [22] developed a lumped kinetic model for
106 the aqueous phase reforming of sorbitol. The model was tested at temperatures ranging
107 from 473 K to 523 K, using monometallic Ni and bimetallic Ni-Pd catalysts supported
108 on Al₂O₃, ZrO₂ and CeO₂. Kirilin et al. [23] investigated the APR of xylitol and sorbitol
109 using a Pt/Al₂O₃ catalyst. Godina et al. [24] analysed the APR of sorbitol and galactitol
110 using a Pt/Al₂O₃ catalyst in a continuous fixed-bed reactor at 225 °C.

111

112 Given this background, prior to deal with cheese whey, this work analyses the aqueous
113 phase reforming of a lactose solution, the major organic constituent of this waste, as a
114 possible option for the treatment and valorisation of cheese whey effluents and/or
115 lactose solutions recovered from whey. Specifically, the work addresses the effect of the
116 temperature, pressure, lactose concentration and W/m_{lactose} ratio on the APR of lactose
117 using a Ni-based catalyst. The effect of the operating conditions on the production and
118 selectivity to the different gas and liquid products has never been reported to date.
119 Therefore, the effect of the operating variables on gas, liquid and solid production and
120 on the compositions of the gas and liquid phases has been exhaustively analysed.
121 Furthermore, optimal values for the production of gas and liquid products have also
122 been sought for their selective production. Consequently, this work represents a

123 challenging and novel investigation not only for the management and valorisation of
124 cheese whey but also for the valorisation of sugars or sugar-based streams.

125

126 **2. Experimental**

127 *2.1 Materials*

128 The experiments were carried out in a small bench scale continuous unit for 3 hours
129 employing a Ni-La/Al₂O₃ catalyst. The catalyst was prepared by coprecipitation, having
130 28% (relative atomic percentage) of Ni expressed as Ni/(Ni+Al+La), an atomic La/Al
131 ratio of 0.035 and a Brunauer-Emmett-Teller (BET) surface area of 187 m²/g. The
132 lactose solutions were prepared dissolving D-lactose monohydrate (C₁₂H₂₂O₁₁·H₂O
133 Sigma Aldrich, CAS Number 64044-51-5, Bio-Ultra >99.5 % HPLC) in Milli-Q water.

134

135 *2.2 Experimental rig*

136 The experimental rig used in the experiments was a microactivity unit designed and
137 built by PID (Process Integral Development Eng & Tech, Spain). It consists of a
138 stainless steel tubular reactor with an inner diameter of 9 mm, heated up by means of an
139 electric furnace [25, 26]. The system pressure is reached with the aid of a micrometric
140 valve that automatically adapts its position with the help of a rotor. A pressure gauge
141 located at the exit of the reactor measures the pressure of the reaction section. A PDI
142 control system is used to keep the reactor pressure constant during the experiments. The
143 aqueous solutions of lactose are fed into the reactor by means of a high performance
144 liquid chromatography (HPLC) pump (Gilson, model 307). The reaction products (gas
145 and liquids) leave the reactor from its upper part, pass through the valve, where they are
146 depressurised, and arrive at the condensation system. This system consists of several

147 condensers where the liquid products are separated from the gas mixture at intervals of
148 1 h to analyse the evolution over time of the liquid phase. The gas mixture is made up of
149 N₂, used as an internal standard, and the different gaseous products formed during the
150 aqueous phase reforming reaction. An Agilent M3000 micro chromatograph equipped
151 with thermal conductivity detectors (TCD) was used for the online analysis of the gas
152 phase. The liquid fractions were collected and analysed offline with a gas
153 chromatograph (Agilent 7890 GC-system, model G3440A) equipped with Flame
154 Ionization (FID) and Mass Spectrometry (MS) detectors. A schematic diagram of the
155 experimental system is shown in Figure S1.

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157

158 *2.3 Operating conditions, response variables and statistical analyses*

159 The effect of the temperature (200-240 °C), pressure (38-50 bar), lactose concentration
160 (1-10 wt.%) and catalyst mass/lactose mass flow rate ratio ($W/m_{\text{lactose}} = 10-40$ g catalyst
161 min/g lactose) was experimentally analysed using a design of experiments (DOE) with
162 statistical analysis of the results carried out by means of an analysis of variance
163 (ANOVA). The effect of the operating conditions on the process was analysed for the
164 following response variables: global lactose conversion (X_{lactose} , %), carbon
165 conversion to gas, liquid and solid products (CC gas %, CC liq %, and CC sol %) as
166 well as the composition of the gas (N₂ and H₂O free, vol.%) and liquid (relative
167 chromatographic area free of water and un-reacted lactose, %). Table S1 summarises
168 the response variables and the analytical methods used for their calculation.

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172 The experiments, listed in Table S2, were designed using a 2^k factorial design, where k
173 indicates the number of factors studied (4 operating conditions) and 2^k represents the

174 number of runs (16). In addition, 5 replicates at the centre of the variation interval of
175 each factor were carried out in order to evaluate both the experimental error and the
176 curvature shown by the evolution of each variable. This factorial design minimises the
177 number of experiments needed to understand the effect on the process of the operating
178 variables and the interactions between them. As the response variables did not show a
179 linear trend, this design was increased with 8 axial runs following a Box-Wilson Central
180 Composite Face Centred (CCF, $\alpha: \pm 1$) design, enabling the operating variables and
181 interactions responsible for the curvature to be identified without modifying the range
182 of study initially considered for the operating variables. The lower and upper limits of
183 all the operating variables were normalised from -1 to 1 (codec factors) to identify their
184 influence in comparable terms.

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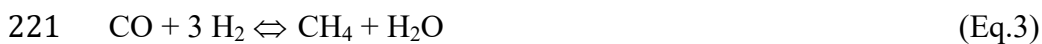
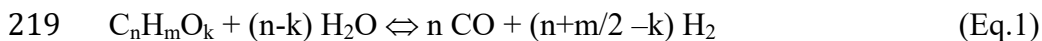
186 For the analysis of the results, firstly the evolution over time of the response variables
187 was studied. To do this, the results were divided into three intervals, each corresponding
188 to the average value of the studied response variables obtained during each one of the
189 three hours of experiment. All these values (three per experiment) have been compared
190 using a one-way analysis of variance (one-way ANOVA) and Fisher's least significant
191 difference (LSD) test, both with 95% confidence. The results of the ANOVA analyses
192 are provided as p-values. P-values lower than 0.05 indicate that at least two values are
193 significantly different. Furthermore, the LSD test was used to compare pairs of data, i.e.
194 either between two intervals of the same experiment or between two intervals of two
195 different experiments. The results of the LSD tests are presented graphically in the form
196 of LSD bars. To ensure significant differences between any pairs of data, their LSD bars
197 must not overlap. Secondly, the effect of the operating conditions was studied
198 considering the results corresponding to the first hour using a statistical analysis of

199 variance (one-way ANOVA) test with 95% confidence. This strategy allows not having
200 to include the effect of the variations with time of the different response variables in the
201 analysis. In addition, the cause-effect Pareto principle was used to calculate the relative
202 importance of the operating variables on each response variable.

203

204 *2.4 Possible reaction network for lactose aqueous phase reforming*

205 A plausible reaction pathway for the aqueous phase reforming of lactose is shown in
206 Figure 1. The reaction network includes the formation of gases and liquid products. The
207 formation of these compounds starts with an initial lactose decomposition by hydrolysis
208 into glucose and galactose [27], which can subsequently be decomposed into other
209 intermediate liquids. Three possible parallel routes explain the formation of
210 intermediate liquids from these monomers: glucose/galactose isomerisation to fructose
211 (A) [27-30] and/or retro-aldol fragmentation to erythrose and 2-hydroxyacetaldehyde
212 (B) [30] and/or dehydration to 5-hydroxymethyl-2-furancarboxaldehyde [21, 22, 27, 28,
213 31-33] (C). Gases, mainly H₂ and CO, are produced by the thermal decomposition
214 and/or reforming reactions of the lactose and all the liquid intermediates (Eq.1) as well
215 as by all the decarbonylation reactions that release CO. In addition, the WGS reaction
216 (Eq.2) and the methanation reaction (the inverse of methane steam reforming reactions)
217 (Eq.3-4) are also possible, explaining the presence of CO₂ and CH₄ in the gas phase [34,
218 35].



223

224 *2.4.1 Formation of products via fructose: route A*

225 2,3-dihydroxypropanal and/or 1,3-dihydroxypropan-2-one are produced from fructose
226 via retro-aldol fragmentation [27-30]. The latter can undergo hydrogenation to produce
227 glycerol and/or decarbonylation to form ethane-1,2-diol [29, 30]. On the one hand,
228 glycerol can be dehydrated to 1-hydroxypropan-2-one, which can then undergo
229 hydrogenation to produce propane-1,2-diol [13, 14, 36-38]. Propane-1,2-diol can
230 subsequently be dehydrated to form propan-2-one and/or propionaldehyde, which can
231 be hydrogenated to propan-2-ol and propan-1-ol, respectively [36]. Afterwards, these
232 two chemicals can be further transformed into butane and propane [14, 36-38]. Ethanol
233 might be formed from the hydrogenation of propan-2-ol [14]. On the other hand,
234 ethane-1,2-diol can evolve towards 2-hydroxyacetaldehyde formation via
235 dehydrogenation, which might lead to the formation of methanol by decarbonylation
236 [13, 14], or to the production of acetaldehyde and/or ethanol via dehydration and
237 dehydration/hydrogenation, respectively [13, 14, 37]. Acetaldehyde can subsequently be
238 transformed into acetic acid and/or methane, while ethene and ethane can be produced
239 from ethanol [13, 14, 37].

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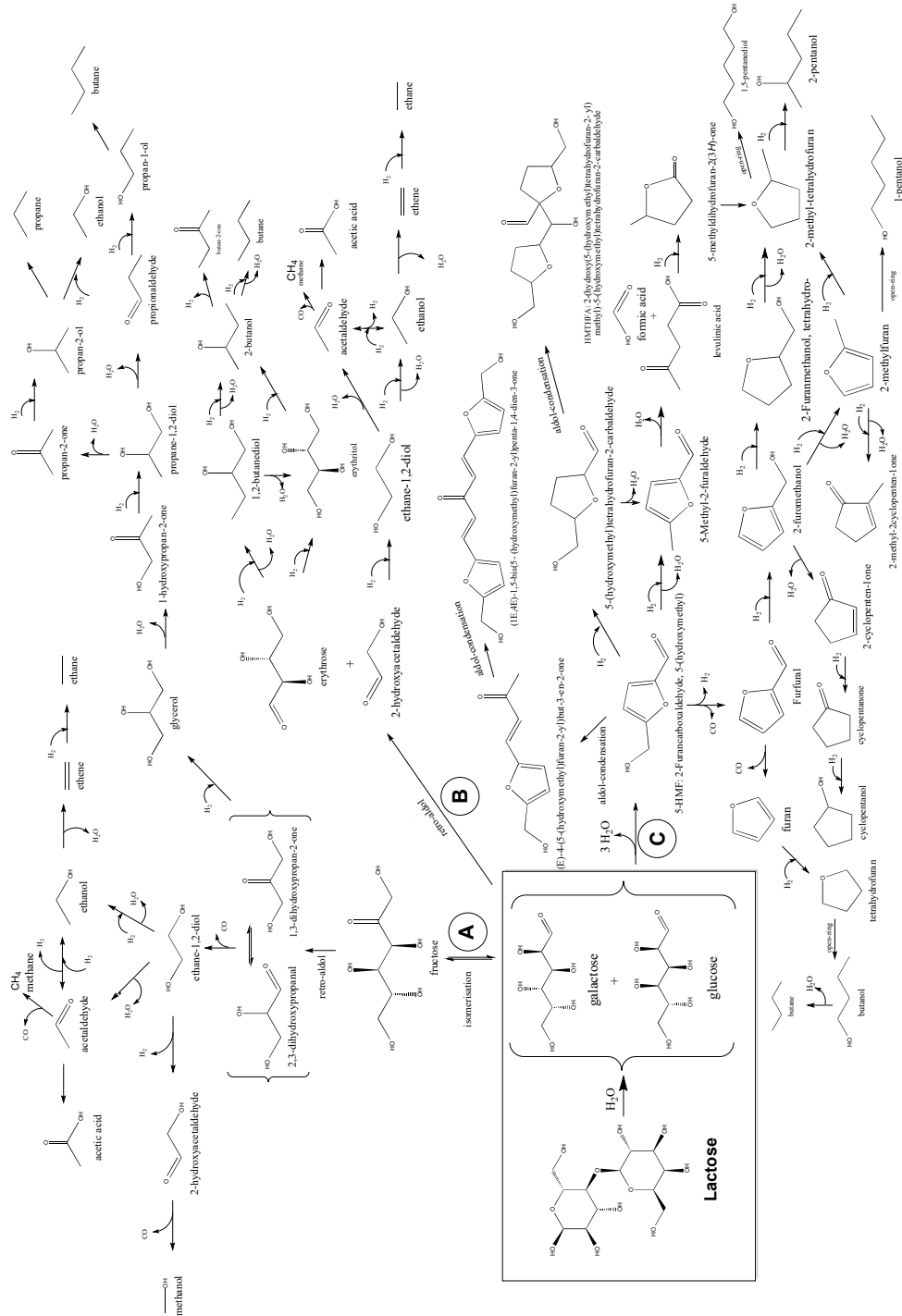
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259 Figure 1. Possible reaction pathways during the aqueous phase reforming of lactose.

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261 *2.4.2 Formation of products via erythrose and 2-hydroxyacetaldehyde: route B*

262 Erythrose can undergo further hydrogenation to erythritol and/or

263 hydrogenation/dehydration to 1,2-butane-diol. Subsequently, 2-butanol can be produced
264 via hydrogenation/dehydration [30]. Butan-2-one and butane can be produced from the
265 dehydrogenation and hydrogenation/dehydration of this latter compound. Ethane-1,2-
266 diol can be produced from the hydrogenation of 2-hydroxyacetaldehyde and can either
267 undergo further hydrogenation/dehydration to ethanol and/or dehydration to
268 acetaldehyde. Ethanol can subsequently be dehydrated to ethene and hydrogenated to
269 produce ethane, while acetaldehyde can subsequently be transformed into acetic acid
270 and/or methane [13, 14, 37].

271

272 *2.4.3 Formation of products via 5-hydroxymethyl-2-furancarboxaldehyde: route C*

273 5-hydroxymethyl-2-furancarboxaldehyde can be transformed into 5-methyl-2-
274 furaldehyde via hydrogenation/dehydration, and/or hydrogenated to 5-hydroxymethyl-
275 tetrahydrofuran-2-carbaldehyde and/or decarbonylated/dehydrogenated to produce
276 furfural and/or can evolve to (E)-4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one via
277 aldol-condensation [28, 31, 39, 40]. Subsequently, 5-methyl-2-furaldehyde can be
278 dehydrated giving formic acid and levulinic acid. This latter can be hydrogenated to 5-
279 methyl-dihydrofuran-2(3H)-one [33, 39, 40]. In addition, (1E,4E)-1,5-bis(5-
280 (hydroxymethyl)furan-2-yl)penta-1,4-dien-3-one and 2-(hydroxy(5-
281 (hydroxymethyl)tetrahydrofuran-2-yl)methyl)-5-(hydroxymethyl)tetrahydrofuran-2-
282 carbaldehyde can be produced from (E)-4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one
283 and 5-hydroxymethyl-tetrahydrofuran-2-carbaldehyde, respectively, via retro-aldol
284 condensation [28, 31, 39, 40]. Furthermore, furfural can undergo hydrogenation to 2-
285 furfuryl-methanol and/or decarbonylation to furan [32, 39, 41]. Furan can be hydrogenated
286 to tetrahydrofuran, which can firstly evolve to butanol through ring opening and

287 subsequently to butane via dehydration [42]. 2-furomethanol can undergo further
288 hydrogenation to 2- furanmethanol, tetrahydro- and/or hydrogenation/dehydration to 2-
289 methylfuran and/or dehydration to 2-cylcopenten-1one [39]. Subsequently, 2-
290 furanmethanol, tetrahydro can be hydrogenated/dehydrated to 2-methyl-tetrahydrofuran.
291 2-pentanol and 1,5-pentane-diol can be obtained from this latter chemical through
292 hydrogenation and ring opening, respectively [32]. 2-methylfuran can be hydrogenated
293 to 2-methyl-tetrahydrofuran and/or hydrogentated/dehydrated to 2methyl-2cyclopenten-
294 1one and/or evolve to 1-pentanol via ring opening. Cyclopentanone can be produced
295 from the hydrogenation of 2cyclopenten-1one. This latter can be hydrogenated to
296 cyclopentanol [32].

297

298 **3. Results and discussion**

299 *3.1 Global lactose conversion and carbon distribution: CC gas, CC liq and CC sol.*

300 A complete and steady global lactose conversion (X_{lactose}) was achieved in all the
301 experiments, indicating that all the lactose was converted into gas, liquid and solid
302 products. The C/O ratio close to 1 of lactose allows a complete conversion to be
303 achieved [34, 43]. Figure S2 shows the CC gas, CC liq and CC sol obtained for the
304 experiments, which vary as follows: 5-41%, 33-97% and 0-59%, respectively.

305 Increases and reductions in these variables over time are detected in some experiments.

306

307 The general trend for the CC gas is a steady evolution. However, decreases over time
308 occur for some experiments (2-4, 6, 8, 13-15, 23, 24, 27 and 29). These decreases are
309 particularly marked for experiments 8, 13, 15 and 29. One exception is experiment 8,
310 where a lower W/m_{lactose} ratio (10 g catalyst min/g lactose) was used. The drops for the

311 CC gas are more marked at operating conditions under which gas production is more
312 favoured [25]. The CC liq displays increases (experiments 1,9-13, 23-25, 27-29) and
313 decreases (experiments 6 and 8) over time. In particular, sharp increases are observed
314 for runs 1, 11 and 13. Most of the slight decreases observed for the CC gas take place
315 along with increases in the CC liq (experiments 13, 14, 23, 24, 27 and 29). This
316 evolution of the C product distribution is consistent with the work of Wawrzetz et al.
317 [37] and Remón et al. [25], who demonstrated that the formation of H₂ and CO₂ via
318 dehydrogenation followed by decarbonylation with the subsequent water gas shift is one
319 of the fastest reactions during aqueous phase reforming. In addition, gas production
320 decreases with catalyst deactivation, thus increasing the production of intermediate
321 liquid products.

322 Sharp increases in the CC sol are observed for experiments 6, 8 and 15, while decreases
323 take place for experiments 1 and 11. Most of the decreases in the CC sol occur along
324 with increases in the CC liq and vice versa (6 and 8-10). The decrease observed in the
325 CC gas for experiments 13 and 15 accounts for the increases in the CC liq and CC sol,
326 respectively, which might indicate a change in the product selectivity over time.

327 Experiments 6 and 8 were performed using the highest temperature (240 °C) and lactose
328 concentration (10 wt.%), along with the lowest W/m_{lactose} ratio used in this work. Sugar
329 molecules are unstable at the temperatures of this process and quickly decompose
330 through pyrolysis, leading to the formation of char particles and gases [35]. This solid
331 residue (char) can also be obtained from polymerised degradation products such as
332 humic acids and large organic compounds ranging from C₈ to C₁₅ [23, 27, 28, 31, 33,
333 39, 41]. The formation of these macromolecules can occur from furfural and 5-
334 hydroxymethyl-2-furancarboxaldehyde (route C). Furthermore, both lactose monomers
335 (glucose and galactose) can react with other liquid intermediates or with 5-

336 hydroxymethyl-2-furancarboxaldehyde by cross-polymerisation. These reactions are
337 favoured at high temperature and pressure [27, 28, 31, 33]. In addition, char obtained
338 from the pyrolysis of different biomass materials has been reported to have catalytic
339 activity for the reforming and cracking of different hydrocarbons [44-50], which
340 accounts for the decreases over time in the CC sol [34, 35] and the increases in the CC
341 liq observed in some experiments.

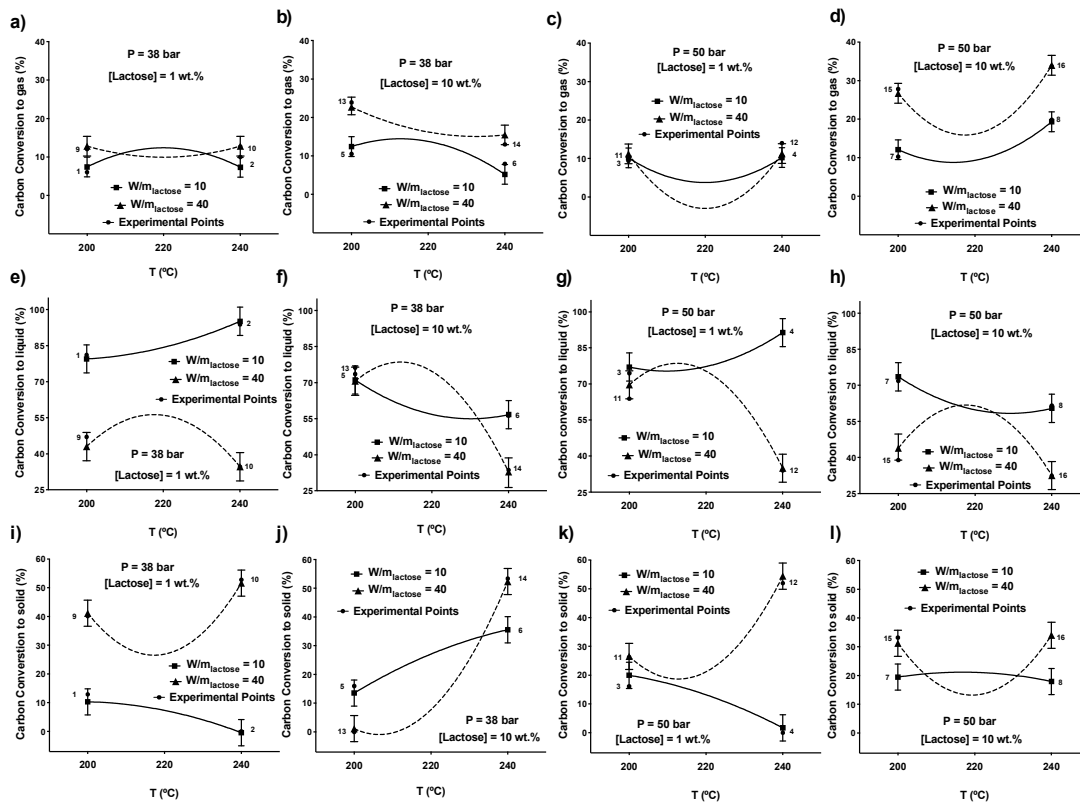
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343 The specific effect of the operating conditions as well as their possible interactions on
344 the process has been studied considering the results obtained during the first hour of
345 reaction. The models created in terms of codec factors considering the ANOVA analysis
346 and the relative importance of the operating variable taking into account the cause-
347 effect Pareto analysis are shown in Table S3. The CC gas is strongly affected by the
348 lactose concentration, both linear and quadratic terms, and the interaction between the
349 temperature and the W/m_{lactose} ratio (T^2W). An increase in the lactose concentration
350 increases the CC gas. The temperature and its interaction with the W/m_{lactose} (T^2W) are
351 the operating variables with the greatest effect on the CC liq and the CC sol. In addition,
352 significant interactions between the operating variables also influence the CC gas, CC
353 liq and CC sol.

354

355 Figure 2 illustrates the effect of the operating variables and the most important
356 interactions on the product distribution in carbon basis, according to the ANOVA
357 analysis. Specifically, Figures 2 a and b, e and f, and i and j show the effects on the CC
358 gas, CC liq and CC sol of the reaction temperature, employing a pressure of 38 bar for
359 W/m_{lactose} ratios of 10 and 40 g catalyst min/g lactose, when feeding 1 and 10 wt.%

360 lactose solutions, respectively. Figures 2 c and d, g and h, and k and l display the effect
 361 of the temperature for W/m_{lactose} ratios of 10 and 40 g catalyst min/g lactose employing
 362 a pressure of 50 bar when lactose solutions of 1 and 10 wt.%, respectively, were used.
 363



364
 365
 366 Figure 2. Interaction plots for the initial CC gas (a-d), CC liq (e-h) and CC sol conversion (i-l). Bars are
 367 LSD intervals with 95% confidence.
 368

369 3.1.1 Carbon conversion to gas: CC gas

370 The effect of the temperature on the CC gas depends on the pressure and concentration
 371 of lactose in the solution. At 38 bar, two trends are observed depending on the lactose
 372 concentration. When a 1 wt.% lactose solution is fed, the CC gas is low (8-14%) and
 373 neither the temperature nor the W/m_{lactose} exert a significant effect on the CC gas.
 374 Conversely, for a 10 wt.% lactose solution, the temperature has a greater influence on
 375 the CC gas and the effect of the temperature depends on the W/m_{lactose} ratio. For 10 g

376 catalyst min/g lactose, the CC gas remains low and steady (around 12%) between 200
377 and 220 °C and decreases slightly with a further increase in the temperature up to 240
378 °C. For a W/m_{lactose} ratio of 40 g catalyst min/g lactose an increase in the temperature
379 from 200 to 240 °C decreases the CC gas. In general, the CC gas is relatively low,
380 which indicates that gas formation is not favoured at low pressure [19, 23, 51]. In
381 addition, at 38 bar feeding a 10 wt.% lactose solution, the W/m_{lactose} ratio significantly
382 promotes gas production and an increase from 10 to 40 g catalyst min/g lactose
383 produces an increase in the CC gas due to its positive kinetic effect on cracking and
384 reforming reactions [25].

385

386 At 50 bar of pressure, the temperature exerts a greater effect on gas production than at
387 38 bar, and greater amounts of CC gas are obtained, especially for concentrated lactose
388 solutions and high W/m_{lactose} ratios. These conditions favour gas production from
389 lactose and its liquid intermediate due to the positive kinetic effect of the catalyst. An
390 increase in pressure favours gas formation [25] due to a increase in the rate of C-C bond
391 cleavage reactions [52]. An increase in the CC gas when increasing the total pressure of
392 the system has also been reported for the APR of xylitol [19] and other oxygenated
393 compounds [17, 53, 54].

394

395 Regardless of the lactose concentration, the gas production displays a minimum with
396 temperatures between 200 and 240 °C. Specifically, an increase in temperature from 200
397 to 220 °C decreases the CC gas, while a further increase from 220 to 240 increases the
398 CC gas regardless of the lactose concentration and W/m_{lactose} ratio. This evolution
399 depends on the W/m_{lactose} ratio. For 10 g catalyst min/g lactose the CC gas is relatively
400 low and the decrease and the subsequent increase in the CC gas observed with the

401 variation in temperature are not as marked as for 40 g catalyst min/ g lactose. For 40 g
402 catalyst min/g lactose a pronounced decay followed by a sharp increase in the CC gas
403 occurs. At low temperatures (200-220 °C) the positive kinetic effect helps to shift the
404 reaction towards the formation of intermediate liquids, increasing the CC liq.
405 Conversely, a further increase in temperature up to 240 °C favours the transformation of
406 these liquid products into gases, decreasing the CC liq [25]. As regards the W/m_{lactose}
407 ratio, an increase from 10 to 40 g catalyst min/g lactose does not greatly modify the CC
408 gas for a 1 wt.% lactose solution, while it increases the CC gas for a 10 wt.% lactose
409 solution within the whole temperature range considered. Gas production is kinetically
410 favoured at high pressure and using a concentrated lactose solution due to the positive
411 kinetic effect of these variables [25].

412

413 The effect of the lactose concentration can be gathered comparing Figures 2 a with b
414 and 2 c with d. This effect depends on the pressure and W/m_{lactose} ratio. For 10 g catalyst
415 min/g lactose, the effect of the lactose concentration is very weak regardless of the
416 pressure. Conversely, for 40 g catalyst min/g lactose the lactose concentration exerts a
417 greater influence. At 38 bar, the CC gas increases within the whole temperature range
418 considered, especially between 200 and 220 °C. At 50 bar, a great increase in the CC
419 gas takes place for 40 g catalyst min/g lactose regardless of the reaction temperature.

420

421 As regards the effect of the pressure, a comparison between Figures 2 a with 2 c and 2 b
422 with d shows the effect of this operating variable on the CC gas when 1 and 10 wt.%
423 lactose solution are used, respectively. For a 1 wt.% lactose solution, the effect of the
424 pressure is very weak. Conversely, for 40 g catalyst min/g lactose the decrease observed
425 in the CC gas is slightly greater. For a 10 wt.% lactose solution the CC gas does not

426 greatly vary when the pressure increases from 38 to 50 bar between 200 and 220 °C,
427 while a great increase in the CC gas takes places between 220 and 240 °C. The effect of
428 pressure is only significant when gas production is favoured [25]. The pressure exerts a
429 significant influence on the kinetics of the process, since an increase in the total
430 pressure of the system also increases the partial pressures of lactose and its
431 intermediates, increasing the reaction rates of lactose APR reactions and thus enhancing
432 gas production as reported in other works studying the APR of glycerol [17, 53, 54] and
433 sorbitol [19, 21].

434

435 *3.1.2 Carbon conversion to liquid and solid products: CC liq and CC sol*

436 The CC liq and CC sol show opposite tendencies, i.e. an increase in the former takes
437 place along with a decrease in the latter and vice versa. A statistically significant and
438 high relationship (p-value < 0.0001; $R^2 = 0.91$) was found between the CC liq and CC
439 sol by means of the Spearman's multivariate test.

440

441 The effect of the temperature on the CC liq and CC sol depends on the concentration of
442 lactose in the solution and the W/m_{lactose} ratio. For a 1 wt.% lactose solution and a
443 W/m_{lactose} ratio of 10 g catalyst min/g lactose, an increase in the reaction temperature
444 increases the CC liq and decreases the CC sol regardless of the pressure. Conversely,
445 when a W/m_{lactose} ratio of 40 g catalyst min/g lactose is used, the CC liq increases
446 between 200° and 220° and decreases with a further increase in the temperature up to
447 240 °C regardless of the lactose concentration. For a 10 wt.% lactose solution different
448 evolutions for the CC liq and CC sol are observed depending on the temperature,
449 pressure and W/m_{lactose} ratio. An increase in temperature decreases the CC liq and
450 increases the CC sol when a W/m_{lactose} ratio of 10 g catalyst min/g lactose is used. The

451 increase in the CC sol only occurs at low pressure (38 bar), while at high pressure (50
452 bar) the CC sol remains steady with the temperature and the decrease in the CC liq
453 occurs along with an increase in the CC gas. Conversely, for 40 g catalyst min/g lactose
454 the CC liq increases between 200 and 220 °C and decreases with a further increase in
455 temperature up to 240 °C.

456

457 The effect of the pressure on the CC liq/CC sol can be gathered comparing Figures 2 e/i
458 with g/k and 2 f/j with h/l for lactose concentrations of 1 and 10 wt.%, respectively.

459 The effect of the pressure is at its highest for 40 g catalyst min/g lactose, and an
460 increase from 38 to 50 bar between 200 and 230 °C increases the CC liq and reduces the
461 CC sol for a 1 wt.% lactose solution. For a 10 wt.% lactose solution an increase in the
462 pressure from 38 to 50 bar decreases the CC liq and increases the CC sol between 200
463 and 220 °C, while minor changes occur between 220 and 240 °C.

464

465 The effect of the W/m_{lactose} ratio depends on the lactose concentration and pressure. At
466 38 bar, an increase in the W/m_{lactose} ratio from 10 to 40 g catalyst min/g lactose
467 decreases the CC liq and increases the CC sol for a 1 wt.% lactose solution. For a 10
468 wt.% lactose solution, an increase in the W/m_{lactose} ratio from 10 to 40 g catalyst min/g
469 lactose increases the CC liq and decreases the CC sol between 210 and 230 °C. A
470 further increase in temperature up to 240 °C decreases the CC liq and increases the CC
471 sol. The analysis of the liquid product reveals that the concentration of furans in the
472 liquid increases when increasing the concentration of lactose in the solution for a low
473 W/m_{lactose} ratio at 38 bar. This suggests that polymerisation reactions might occur with a
474 lesser spread as the concentration of lactose increases. Therefore, for a diluted lactose
475 solution, an increase in the W/m_{lactose} ratio promotes polymerisation reactions, thus

476 increasing the CC sol. Conversely, for a concentrated lactose solution the thermal
477 decomposition of lactose might be responsible for char formation and an increase in the
478 W/m_{lactose} ratio mitigates char formation and/or helps its removal. At temperatures
479 between 230 °C and 240 °C this increase in the W/m_{lactose} ratio increases char
480 production, probably due to the higher spread of polymerisation reactions. At 50 bar, an
481 increase from 10 to 40 g catalyst min/g lactose does not significantly influence the CC
482 liq and CC sol between 200 and 220 °C for a 1 wt.% lactose solution. Conversely, for a
483 10 wt.% lactose solution, this increment in the W/m_{lactose} ratio decreases and increases
484 the CC liq and CC sol, respectively, from 200 to 210 °C. Between 220 and 240 °C, an
485 increase in the W/m_{lactose} ratio from 10 to 40 g catalyst min/g lactose decreases the CC
486 liq and increases the CC sol regardless of the pressure due to the greater spread of
487 condensation and cross-polymerisation reactions [27, 28, 31, 33].

488

489 The temperature exerts a positive kinetic effect on the process. When a low amount of
490 catalyst is used, an increase in the temperature helps to decrease solid formation.
491 However, an increase in the amount of catalyst in the bed also produces a greater spread
492 of polymerisation, cross-polymerisation and condensation reactions from furfural and 5-
493 hydroxymethyl-2-furancarboxaldehyde. These two latter compounds, found in some of
494 the liquid condensates, might lead to the formation of large molecules [23, 27, 28, 31,
495 33, 39, 41] that are insoluble in water and can promote char formation [27, 28, 31, 33].
496 These chemical reactions leading to the formation of polymers are favoured at high
497 temperature and pressure. Therefore, at temperatures between 220 and 240 °C the CC
498 liq decreases and the CC sol increases very sharply as high temperatures promote
499 polymerisation reactions [27, 28, 31, 33] and lactose decomposition through pyrolysis,
500 leading to the formation of char particles [35].

501

502 *3.2 Effect of the operating conditions on the volumetric composition of the gas*

503 Figure S3 shows the composition of the gas obtained for the experiments divided into
504 three intervals of 60 minutes each. The gas phase is made up of a mixture of H₂ (8-58
505 vol.%), CO₂ (33-90 vol.%), CO (0-18 vol.%) and CH₄ (0-14 vol.%). As regards the
506 evolution of the gas composition over time, H₂ and CO₂ display the greatest variations.
507 Statistically significant decreases are detected for the proportion of H₂, while increases
508 occur for the relative amount of CO₂ in the gas.

509

510 This H₂ depletion was also observed in the work of Kirilin et al. [23] during the APR of
511 xylitol and sorbitol. They reported that the oxygenated compounds formed during the
512 APR process might adsorb on the surface of the catalyst, thus hindering the catalyst
513 performance and leading to a decrease in the H₂ selectivity. This development is also
514 responsible for the increase in the proportion of CO₂ in the gas over time, as thermal
515 lactose decomposition might be more favoured over reforming with the progressive
516 deactivation of the catalyst. In addition, the decrease in the proportion of H₂ in the gas
517 may also be attributed to the structural changes of the alumina of the support [23]. The
518 alumina of the catalyst support can be transformed into boehmite by water [52, 55, 56].
519 This transformation was reported in a previous work where this catalyst was used for
520 the APR of crude glycerol [25].

521

522 The proportions of CO and CH₄ remain steady for the vast majority of the experiments.
523 In general, small variations are detected for the proportion of CO in the gas. One
524 exception is experiment 16, where a relatively high increase in the proportion of CO
525 over time takes place. The proportion of CH₄ shows small variations over time. In some

526 experiments an initial decrease in the proportion of CH₄ takes place between the first
527 and second hour of reaction, along with a posterior increase in its relative amount
528 between the second and third hour. However, these variations are not important from a
529 practical point of view due to the relatively low amount of CH₄ in the gas.

530

531 The specific effects of the operating conditions as well as their possible interactions on
532 the volumetric composition of the gas were studied considering the results obtained
533 during the first 60 minutes of reaction. Table S4 shows the results of the statistical
534 analyses performed. These analyses show that the temperature, the W/m_{lactose} ratio and
535 the interaction between these two operating variables are the variables with the greatest
536 influence on the proportion of H₂ in the gas. The temperature and the W/m_{lactose} are the
537 operating variables exerting the greatest influence on the proportion of CO₂. The
538 concentration of CO in the gas is mostly affected by the interactions between the
539 temperature and the concentration of lactose (TC and T²C). The concentration of lactose
540 substantially influences the relative amount of CH₄ in the gas.

541

542 Figure 3 illustrates the effect of these interactions according to the ANOVA analysis on
543 the composition of the gas. The effects of the reaction temperature, at 38 bar and 50 bar
544 for W/m_{lactose} ratios of 10 and 40 g catalyst min/g lactose, feeding a 1 wt.% lactose
545 solution, are shown in Figures 3 a and c, e and g, i and k, and m and o. Figures 3 b and
546 d, f and h, j and l, and n and p display the effect of the temperature and the W/m_{lactose}
547 ratio at 38 and 50 bar for a 10 wt.% lactose solution.

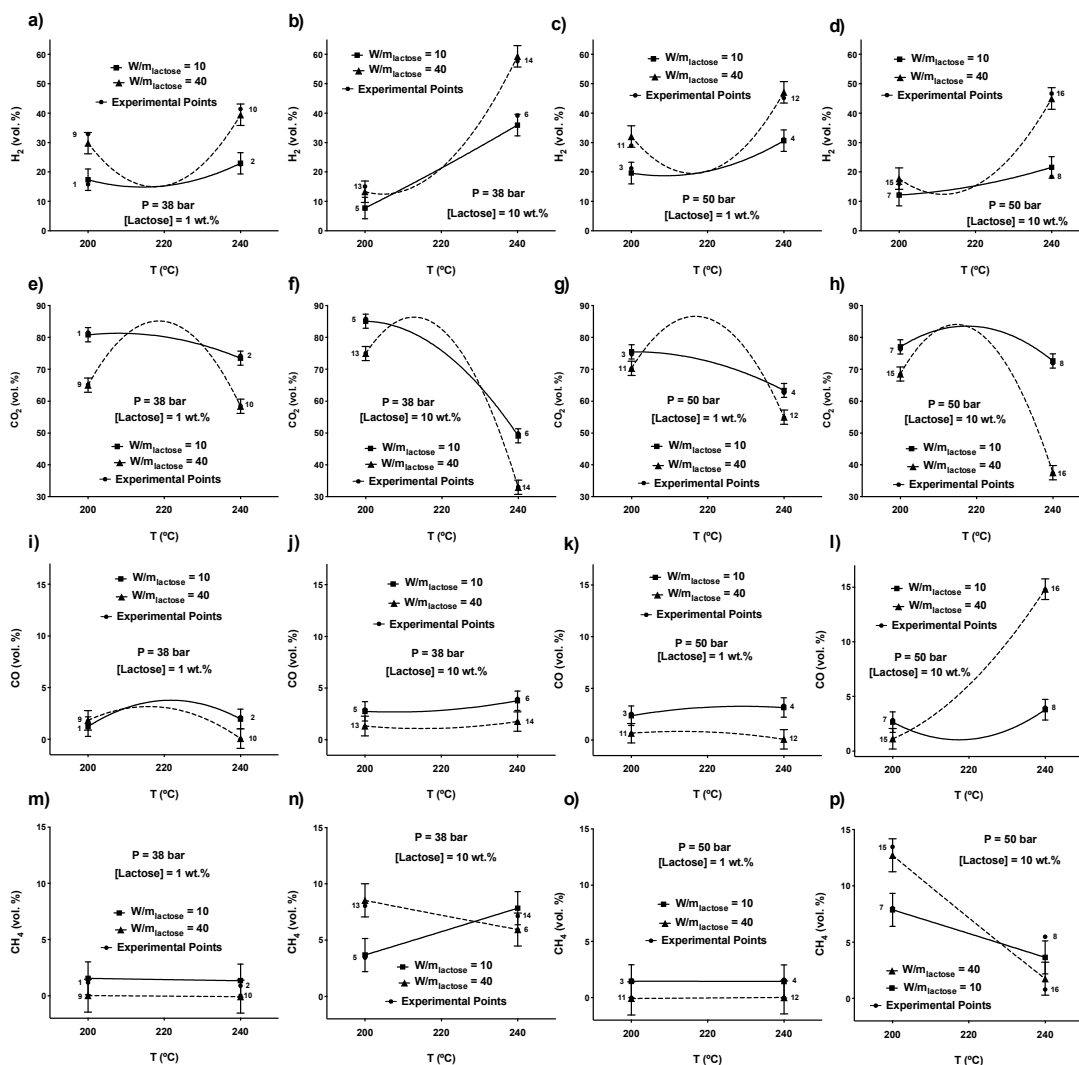
548 3.2.1 H_2 and CO_2

549 The reaction temperature exerts a great influence on the concentrations of H_2 and CO_2 .
550 An increase in the former gas occurs along with a decrease in the latter and vice versa,
551 as explained above. Therefore, the effect of the operating conditions is fully described
552 for the proportion of H_2 , the relative amount of CO_2 showing the opposite effect in most
553 cases. In general, two trends are observed for the evolution of H_2 and CO_2 depending on
554 the W/m_{lactose} ratio. For a low W/m_{lactose} ratio (10 g catalyst min/g lactose) an increase in
555 the temperature has little impact on the volumetric composition of these two gases
556 regardless of the lactose concentration and pressure. Exceptionally, for a 10 wt.%
557 lactose solution at low pressure (38 bar), a substantial increase in the proportion of H_2
558 occurs. The sharp increase in the CC sol obtained at 38 bar using a 10 wt.% lactose
559 might account for this development, as most of the carbon in the feed is transformed to
560 solid, which results in a gas with a higher H_2 content.

561

562 Conversely, for a W/m_{lactose} ratio of 40 g catalyst min/g lactose two trends are observed
563 depending on the lactose concentration. For a 1 wt.% lactose solution, an increase in the
564 temperature from 200 to 220 °C decreases the proportion of H_2 in the gas regardless of
565 the pressure. An increase in the W/m_{lactose} ratio increases H_2 generation by reforming.
566 Between 200 and 220 °C the proportions of monohydric and polyhydric alcohols in the
567 liquid increase dramatically, which is accounted for by a greater spread of H_2 reactions
568 which increase the consumption of H_2 [25]. Conversely, for a 10 wt.% solution this
569 same increase in temperature does not modify the proportion of H_2 in the gas, while the
570 increase observed in the proportion of CO_2 still takes place, although milder than that
571 occurring for a 1 wt.% lactose solution. Hydrogen solubility increases with pressure,
572 thus hydrogenation reactions in the liquid phase may be more favoured. The higher the

573 lactose concentration, the lower the amount of water and consequently the higher is the
 574 partial pressure of H₂ [25]. A further increase in the temperature from 220 to 240 °C
 575 results in a substantial increase in the H₂ concentration regardless of the lactose
 576 concentration and pressure. The H₂ solubility in the liquid phase decreases with the
 577 temperature, diminishing the extent of the hydrogenation reactions, thus augmenting the
 578 proportion of H₂ in the gas especially between 220 and 240 °C [37]. In addition, the
 579 reforming reactions are endothermic while the WGS reaction is exothermic, which also
 580 results in an increase in H₂ with the temperature [13, 17].



581
 582
 583
 584 Figure 3. Interaction plots for initial relative amounts (vol.%) of H₂ (a-d), CO₂ (e-h) CO (i-l) and CH₄ (m-
 585 p) in the gas. Bars are LSD intervals with 95% confidence.

586

587 The W/m_{lactose} ratio exerts a significant effect on the concentrations of H_2 and CO_2
588 between 200 and 215 °C and 225 to 240 °C. This effect depends on the concentration of
589 lactose in the feed. For a 1 wt.% lactose solution, an increase in the W/m_{lactose} ratio from
590 10 to 40 g catalyst min/g lactose results in an increase in the proportion of H_2 . An
591 increase in the W/m_{lactose} ratio favours reforming reactions, increasing H_2 production
592 [25]. For a 10 wt.% lactose solution, the effect of the W/m_{lactose} ratio is only significant
593 between 225 and 240 °C. Within this temperature range, an increase in the amount of
594 catalyst leads to an increase in the proportions of H_2 due to the positive kinetic effect of
595 the catalyst on the reforming reactions together with the decrease in the H_2 solubility
596 with temperature. At low temperature, the compensation between H_2 production and H_2
597 consumption in hydrogenation reactions accounts for the negligible effect of the
598 W/m_{lactose} ratio.

599

600 The effect of the concentration of lactose in the feed on the proportion of H_2/CO_2 in the
601 gas can be gathered comparing Figures 3 a/e with b/f at 38 bar and Figures 3 c/g with
602 d/h at 50 bar. This comparison reveals that the effect of the lactose concentration
603 depends on the temperature and pressure. Between 200 and 220 °C the concentration of
604 lactose exerts a weak impact on the proportions of these two gases. Conversely,
605 between 220 and 240 °C the concentration of lactose substantially influences the
606 proportions of H_2 and CO_2 in the gas. At 38 bar, a sharp increase in the proportion of H_2
607 takes place due to the increase in the partial pressure of the reagents inside the reactor
608 [25]. At 50 bar the effect of the lactose concentration depends on the W/m_{lactose} ratio.
609 For 10 g catalyst min/g lactose, an increase in the lactose content from 1 to 10 wt.%
610 very slightly decreases and increases the proportions of H_2 and CO_2 , respectively,
611 probably due to the increase in char formation. An increase in the W/m_{lactose} ratio lowers

612 the effect of the lactose concentration on the relative amount of H₂. As a result, the
613 effect of the lactose concentration on the proportion of H₂ for a W/m_{lactose} ratio of 40 g
614 catalyst min/g lactose is not significant, while the proportion of CO₂ decreases slightly
615 between 230 to 240 °C. Under these conditions the decrease in the proportion of CO₂ is
616 the consequence of the increase observed in the proportion of CO in the gas.

617

618 A comparison between Figures 3 a/e and b/f with 3 c/g and d/h shows the effect of the
619 total pressure on the proportion of H₂/CO₂ in the gas when lactose solutions of 1 and 10
620 wt.% are fed, respectively. This comparison reveals that the effect of the pressure
621 depends on the concentration of lactose. For a 1 wt.% lactose solution and 10 g catalyst
622 min/g lactose, an increase in the total pressure from 38 to 50 bar does not greatly
623 modify the proportions of H₂ and CO₂ in the gas. Conversely, for 40 g catalyst min/g
624 lactose, this increase in pressure slightly increases the proportion of CO₂ between 200
625 and 220 °C; the effect of the pressure being insignificant from 220 to 240 °C. For a 10
626 wt.% lactose solution the effect of the pressure depends on the reaction temperature.
627 The pressure does not exert a great impact between 200 and 220 °C, while the
628 proportions of these two gases are greatly modified with varying the system pressure
629 when a temperature between 220 and 240 °C is used. From 220 to 240 °C, an increase in
630 pressure from 38 to 50 bar leads to a decrease in the relative amount of H₂ when using a
631 W/m_{lactose} ratio of 10 g catalyst min/g lactose. In addition, these variations depend on the
632 W/m_{lactose} ratio; the lower the ratio, the greater are the variations in the proportions of H₂
633 and CO₂. An increase in pressure produces an increase in the partial pressure of the
634 reagents inside the reactor, which promotes their transformation into gases [25] due to
635 an increase in the rate of C-C bond cleavage reactions [52] favouring H₂ production.

636

637 3.2.2 CO and CH₄

638 The effect of the operating variables on the proportions of CO and CH₄ is weak and the
639 relative amounts of these two gases during the first hour of reaction are lower than 15
640 vol.%. Under the temperatures studied in this work, the water gas shift (WGS) reaction
641 is shifted towards H₂ and CO₂, which explains the low proportion of CO in the gas. The
642 effect of the temperature on the proportion of CO depends on the pressure and the
643 W/m_{lactose} ratio. In general the effect of the temperature on the proportion of CO in the
644 gas is very weak. At 38 bar, the temperature does not influence the proportion of CO in
645 the gas, which is lower than 4 vol.% regardless of the W/m_{lactose} ratio and the lactose
646 concentration. At 50 bar, the effect of the temperature is only significant when feeding a
647 10 wt.% lactose solution using a W/m_{lactose} ratio of 40 g catalyst min/g lactose. Under
648 these conditions an increase in temperature increases the proportion of CO in the gas
649 very sharply, which could indicate that decarbonylation reactions are intensified under
650 these operating conditions [25].

651

652 The effect of the W/m_{lactose} ratio on the proportion of CO depends on the pressure and
653 lactose concentration. At low pressure (38 bar), an increase from 10 to 40 g catalyst
654 min/g lactose does not modify the relative amount of CO in the gas. Conversely, at 50
655 bar, this same increase leads to a small decrease in the proportion of CO when feeding a
656 1 wt.% lactose solution, while a sharp increase is observed for a 10 wt.% lactose
657 solution as explained above. The effects of the pressure and the lactose concentration on
658 the proportion of CO in the gas are negligible, as CO formation is not
659 thermodynamically favoured at temperatures lower than 240 °C.

660

661 The effect of the temperature on the proportion of CH₄ in the gas depends on the
662 concentration of lactose, pressure and W/m_{lactose} ratio. Specifically, the temperature does
663 not significantly influence the proportion of CH₄ for a diluted lactose solution (1 wt.%),
664 while it exerts a moderate influence for a 10 wt.% lactose solution. For a 10 wt.%
665 solution the effect of the temperature depends on the pressure and the W/m_{lactose} ratio.
666 At 38 bar, an increase in the reaction temperature increases the proportion of CH₄ for a
667 low W/m_{lactose} ratio, while this increase in temperature decreases the relative amount of
668 CH₄ for a high W/m_{lactose} ratio. At 50 bar, an increase in temperature leads to a decrease
669 in the proportion of CH₄ in the gas regardless of the W/m_{lactose} ratio. The decreases in
670 the proportion of CH₄ in the gas are the consequence of the endothermic nature of the
671 methane reforming reaction [14] which is thermodynamically favoured at high
672 temperatures and kinetically promoted using a high W/m_{lactose} ratio.

673

674 As a result of the dependence of the effect of the temperature with the lactose
675 concentration and the W/m_{lactose} ratio, the effect of the W/m_{lactose} ratio is only significant
676 for a 10 wt.% lactose solution. The lower excess of water for a concentrated lactose
677 solution reduces the development of the methane reforming reactions, increasing the
678 proportion of CH₄ in the gas [57-61]. For a concentrated solution, an increase in this
679 ratio (from 10 to 40 g catalyst min/g lactose) increases the proportion of CH₄ in the gas
680 between 200 and 220 °C, as methanation is favoured within this temperature range [25].

681 The effect of the total pressure is only significant for a 10 wt.% lactose solution.

682 Between 200 and 220 °C an increase in pressure leads to an increase in the proportion of
683 CH₄ in the gas, while a further increase up to 240 °C reduces the relative amount of this
684 gas.

685

686 *3.3 Effect of the operating conditions on the composition of the liquid phase*

687 Figure S4 summarises the relative amount of each of the different families of liquid
688 compounds for the different experiments represented in 3 intervals of 60 minutes each.
689 The liquid phase is made up of a mixture of aldehydes, carboxylic acids, alcohols,
690 ketones and furans in water. Acetaldehyde is the most abundant compound for the
691 aldehydes, while the carboxylic acids are mainly made up of acetic and propionic acids
692 and, in a lower proportion, pentanoic acids. Alcohols include monohydric alcohols
693 (mainly methanol and ethanol, and in lower proportions 1-butanol, 2-butanol, 1-
694 pentanol and 2-pentanol), polyhydric alcohols (1,2-propanediol, 1,2-ethanediol, 2,3-
695 butanediol) and, in lower proportions, monohydric substituted (2-methyl-3-pentanol)
696 and alicyclic alcohols (2-furanmethanol). Ketones include C3-ketones such as 2-
697 propanone (acetone) and 2-propanone-1-hydroxy, C4-ketones (2-butanone-3-hydroxy
698 and 2-butanone-1-hydroxy, 2,3-butanedione and 2 butanone) and small amounts of
699 cyclic ketones (cyclopentanone and cyclohexanone) and furanic ketones (2-hydroxy-
700 gamma-butyrolactone). Furans comprise furfural, 5-hydroxymethyl-2-
701 furancaboxaldehyde and 5-methyl-2-furancaboxaldehyde. The presence of these
702 compounds in the condensates is consistent with the pathway proposed in Figure 1 and
703 those proposed by several authors studying the APR of polyols and sugar based
704 compounds [13, 14, 19-23, 27-33, 36-39, 41, 42, 54, 62, 63].

705

706 The statistical analysis reveals significant differences (p -values <0.005) in the relative
707 amounts of these compounds in the liquid phase. The results of the Fisher's LSD test
708 are plotted in Figure S4. The relative concentration for the most abundant compounds,
709 expressed as relative chromatographic area, varies as follows. Aldehydes: 0-11%,
710 carboxylic acids: 0-22%, monohydric alcohols: 0-23%, polyhydric-alcohols: 0-48%,

711 C3-ketones: 4-100%, C4-ketones: 0-18%, cyclic-ketones: 0-15% and furans: 0-85%.
712 Increases and decreases in the proportions of these families with time are detected.
713 Carboxylic acids, monohydric alcohols and C3 and C4 ketones display increases and
714 decreases over time. Aldehydes and cyclic ketones mostly show decreases, while
715 increases are mainly observed for furans. These variations have been analysed with the
716 multivariate Spearman's. The multivariate analysis reveals significant relationships for
717 the proportion of C3-ketones with the proportions of monohydric alcohols (p-value =
718 0.0001; $R^2 = 0.55$) and carboxylic acids (p-value = 0.0215; $R^2 = 0.24$); and between the
719 proportion of cyclic ketones and the proportions of C4-ketones (p-value = 0.0001; $R^2 =$
720 0.41) and aldehydes (p-value = 0.0001; $R^2 = 0.56$). In addition, the proportion of furans
721 depends on the proportion of carboxylic acids (p-value = 0.0001; $R^2 = 0.42$). These
722 relationships can explain most of the variations of the liquid phase composition and
723 confirm the pathway shown in Figure 1.

724

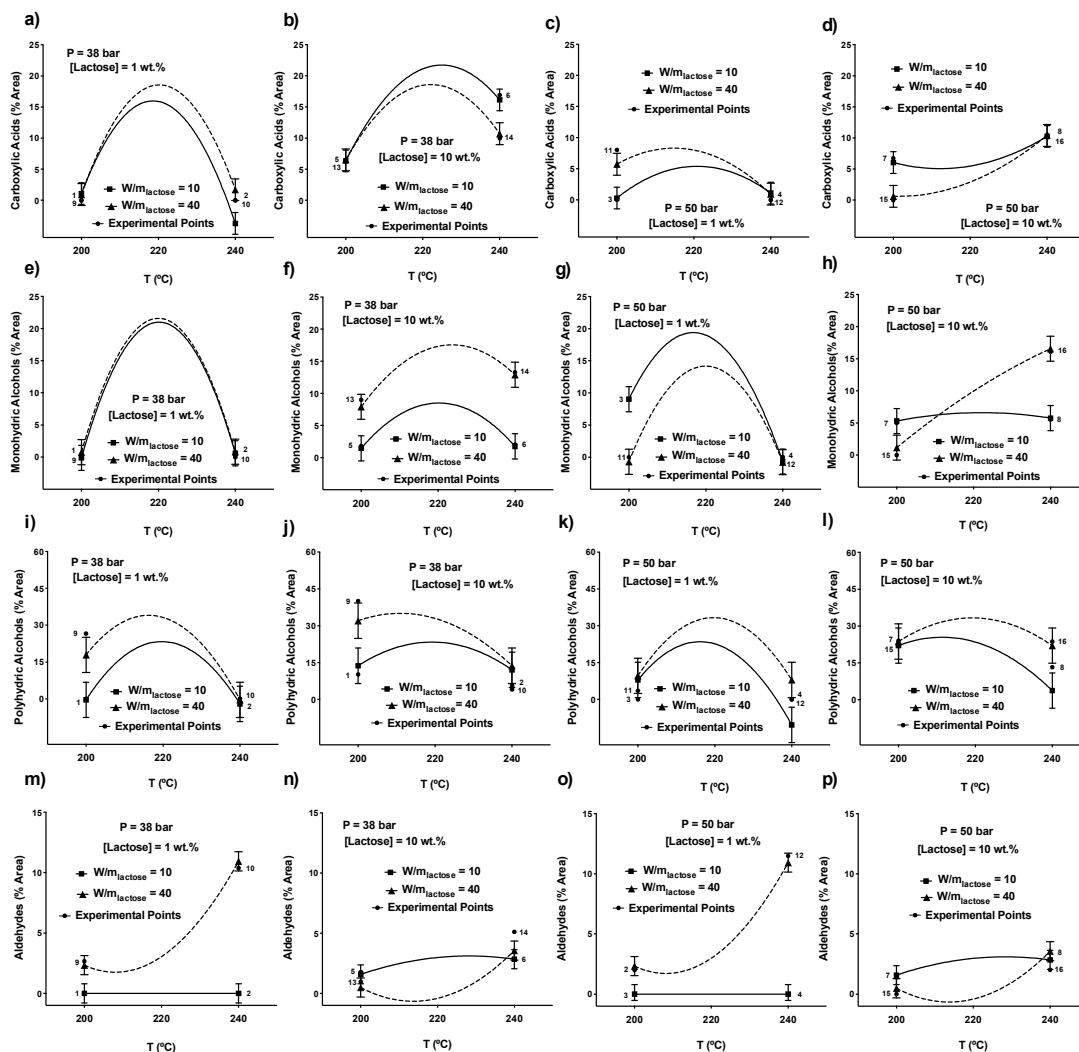
725 Table S4 shows the significant terms in the codec model and their relative influence in
726 the process according to the ANOVA analysis for the proportions of the most abundant
727 families of compounds present in the liquid phase during the first hour of reaction:
728 aldehydes, carboxylic acids, monohydric and polyhydric alcohols, ketones (C3, C4 and
729 cyclic) and furans. The interactions of the temperature with the W/m_{lactose} ratio and
730 lactose concentration with the W/m_{lactose} ratio greatly influence the composition of
731 aldehydes in the liquid. Carboxylic acids are influenced by the pressure and the
732 interactions of temperature with both the lactose concentration (T^2C) and the
733 pressure (T^2P). The interactions of the temperature with the lactose concentration (T^2C)
734 and with the system pressure (T^2P^2) are the major factors responsible for the evolution
735 of the proportions of monohydric and polyhydric alcohols. In addition, polyhydric

736 alcohols are greatly influenced by the temperature (T^2). The pressure (P^2) and the
737 interaction of the temperature with the lactose concentration (T^2C) have a high impact
738 on the proportion of C3-ketones, while C4-ketones mainly depend on the interactions
739 between the temperature, pressure, lactose concentration and W/m_{lactose} ratio (TPC and
740 TCW). Cyclic ketones are strongly influenced by the lactose concentration and its
741 interaction with the temperature and pressure (TPC). Many different interactions
742 between the operating variables influence the proportion of furans in the liquid.

743

744 Figures 4 and 5 illustrate the effect of these interactions according to the ANOVA
745 analysis for the relative amounts of the most abundant compounds present in the liquid
746 phase. Figure 4 displays these effects for the proportions of carboxylic acids,
747 monohydric and polyhydric alcohols, and aldehydes, while Figure 5 shows these effects
748 for the proportions of C3, C4 and cyclic ketones and furans. Specifically, the effects of
749 the reaction temperature, employing a pressure of 38 bar for W/m_{lactose} ratios of 10 and
750 40 g catalyst min/g lactose, feeding lactose concentrations of 1 and 10 wt.%, are shown
751 in Figures 4 and 5 a and b, e and f, i and j, and m and n. Figures 4 and 5 c and d, g and
752 h, k and l, and o and p display the effects of the temperature and the W/m_{lactose} ratio
753 employing a pressure of 50 bar when lactose solutions of 1 and 10 wt.% were used,
754 respectively.

755



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762

Figure 4. Interaction plots for the relative amounts in the liquid of carboxylic acids (a-d), monohydric alcohols (e-h), polyhydric alcohols (i-l) and aldehydes (m-p). Bars are LSD intervals with 95% confidence.

763 3.3.1 Carboxylic acids

764 Acetic and propionic acids are the most abundant carboxylic acids in the liquid phase.
765 Propionic acid formation occurs to a lesser extent due to the higher proportion of 1-
766 hydroxypropan-2-one hydrogenated compounds than dehydrated compounds in the
767 liquid. Acetic acid is mainly responsible for the variations observed in the proportion of
768 carboxylic acids during the first hour of reaction (Figures 4 a-d). Acetic acid is obtained
769 in the final steps of routes A and B. The temperature exhibits two different effects on

770 the proportion of carboxylic acids depending on the pressure. At 38 bar an increase in
771 the temperature leads to an initial increase in the proportion of carboxylic acids from
772 200 to 220 °C followed by a substantial decrease between 220 and 240 °C. In addition,
773 this latter depletion strongly depends on the concentration of lactose in the feed; the
774 lower the concentration of lactose, the sharper is the decrease observed. The
775 temperature exerts a positive catalytic effect on the process. Therefore, between 200 and
776 220 °C, an increase in temperature helps the formation of liquid end products. A further
777 increase in temperature might shift their decomposition to gases. In addition, high
778 temperatures can also partially hinder acetic acid formation as the solubility of H₂ in
779 water decreases with temperature. Conversely, at 50 bar the temperature exerts a weaker
780 effect on the relative amount of carboxylic acids. This increase in pressure kinetically
781 enhances the acetic acid decomposition rate [25]. This effect depends on the lactose
782 concentration. For a 1 wt.% lactose solution a mild increase with temperature occurs
783 between 200 and 220 °C, followed by a small decrease from 220 to 240 °C. However,
784 this evolution with temperature is not as pronounced as it is at 38 bar. For a 10 wt.%
785 lactose solution, the effect of the temperature is negligible between 200 and 220 °C,
786 while a small increase takes place with a further increase in the temperature up to 240
787 °C.

788

789 The effect of the W/m_{lactose} on the proportion of carboxylic acids depends on the
790 concentration of lactose, the temperature and the pressure. At 38 bar the W/m_{lactose} ratio
791 does not significantly influence the proportion of carboxylic acids between 200 and 220
792 °C regardless of the lactose concentration. Within this temperature range, the positive
793 kinetic effect of the temperature can mask the effect of the W/m_{lactose} ratio on the
794 process and the lowest W/m_{lactose} ratio used in this work (10 g catalyst min/g lactose)

795 might be sufficient to achieve high concentrations of acetic acid in the liquid. Between
796 220 and 240 °C an increase in the W/m_{lactose} ratio results in an increase in the proportion
797 of this family of compounds for a 1 wt.% lactose solution, while a decrease is observed
798 for 10 wt.%. An increase in the amount of catalyst promotes acetic acid production,
799 which accounts for the increase observed. However, an increase in the concentration of
800 lactose in the solution also increases the partial pressure of acetic acid inside the reactor,
801 which kinetically favours its decomposition to gases [25]. At 50 bar, the opposite effect
802 is observed. For a diluted lactose solution, an increase in the W/m_{lactose} ratio promotes
803 acetic acid formation, while for a concentrated solution it favours its decomposition due
804 to the increase in the partial pressure of the liquid intermediates [25]. In addition, the
805 increase observed in the proportion of carboxylic acids takes places along with a
806 decrease in C3-ketones, and vice versa. The greatest effect of the pressure on the
807 proportion of carboxylic acids takes place between 220 to 240 °C. An increase in the
808 pressure from 38 to 50 bar leads to a decrease in the proportion of carboxylic acids due
809 to the positive kinetic effect of this variable for acetic acid decomposition [25].

810

811 *3.3.2 Alcohols: monohydric and polyhydric alcohols*

812 The variations in the relative amount of monohydric alcohols basically correspond to
813 variations in methanol and ethanol, while the variations observed for polyhydric
814 alcohols are accounted for by variations in the proportions of 1,2-propane-diol and 1,2-
815 ethane-diol. The temperature has different influences on the proportion of monohydric
816 and polyhydric alcohols depending on the lactose concentration, pressure and W/m_{lactose}
817 ratio, due to the large number of interactions detected between these variables.

818

819 For a diluted lactose solution (1 wt.%), an initial increase in the temperature from 200 to
820 220 °C leads to an initial increase in the proportion of monohydric and polyhydric
821 alcohols. The proportions of both families of alcohols decrease when the temperature is
822 further increased up to 240 °C regardless of the pressure and W/m_{lactose} ratio. In
823 addition, the increase and the decrease observed for the proportion of monohydric
824 alcohols are sharper than for polyhydric alcohols. The temperature exerts a positive
825 kinetic effect on lactose decomposition, which favours the production of liquid end
826 products [25]. These results suggest that routes A and B are prevalent over route C
827 between 200 and 220 °C. This is in good agreement with the results from other works
828 that report that sugar dehydration to produce furanic compounds is preferential at high
829 temperatures [27, 28, 31, 33]. A further increase in the temperature from 220 to 240 °C
830 helps the transformation of monohydric and polyhydric alcohols to gases [37, 52, 54,
831 64, 65]. In addition, high temperatures also potentiate dehydration reactions from
832 lactose [27, 28, 31, 33]. This leads to the formation of furan compounds, which favours
833 route C over A and B.

834

835 For a 10 wt.% lactose solution, the effect of the temperature depends on the pressure
836 and W/m_{lactose} ratio. At 38 bar, an increase in temperature between 200 and 220 °C
837 increases the proportion of monohydric alcohols without significantly modifying the
838 relative amount of polyhydric alcohols in the liquid regardless of the W/m_{lactose} ratio. A
839 further increase up to 240 °C results in a decrease in the proportion of monohydric
840 alcohols irrespective of the W/m_{lactose} ratio and in a decrease in the relative amount of
841 polyhydric alcohols only when the highest W/m_{lactose} ratio is used. An increase in the
842 lactose concentration favours the advancement of the reactions in the liquid phase [25].
843 As a result, a lower temperature is required to achieve the highest proportion of

844 polyhydric alcohols when the highest W/m_{lactose} is used for a 10 wt.% than for a 1 wt.%
845 lactose solution. In addition, an increase in the concentration of lactose produces a
846 greater spread of sugar dehydration reactions towards furanic compounds [28]. This
847 development produces a competition between routes A and B and route C. Therefore, a
848 greater amount of catalyst is needed to produce the end products obtained from routes A
849 and B.

850

851 At 50 bar two different trends are observed depending on the W/m_{lactose} ratio for a 10
852 wt.% lactose solution. When using a W/m_{lactose} ratio of 10 g catalyst min/g lactose, an
853 increase in the temperature does not significantly modify the proportion of monohydric
854 alcohols but slightly decreases the proportion of polyhydric alcohols. High temperature
855 and pressure favours dehydration reactions from sugars [27, 28, 31, 33], and therefore a
856 low proportion of liquid end products obtained via routes A and B is achieved.

857 Conversely, for 40 g catalyst min/g lactose, this increment in the temperature produces a
858 sharp increase in the proportion of monohydric alcohols, without greatly modifying the
859 proportion of polyhydric alcohols. This might account for the increase in the
860 concentration of end products obtained from routes A and B.

861

862 The pressure exerts a weaker effect on the proportions of monohydric and polyhydric
863 alcohols than the temperature. The variations observed for the proportion of
864 monohydric alcohols are relatively low when the system pressure increases from 38 to
865 50 bar, while variations in polyhydric alcohols are not important from a practical point
866 of view. The variations observed for monohydric alcohols depend on the lactose
867 concentration. On the one hand, when a diluted lactose solution (1 wt.%) is fed, an
868 increase in pressure from 38 to 50 bar slightly increases the proportion of monohydric

869 alcohols between 200 and 215 °C when a W/m_{lactose} ratio of 10 g catalyst min/g lactose
870 is used. Within this range, an increase in pressure increases the development of the
871 reaction leading to the formation of liquid end products. This effect is only significant
872 for a low W/m_{lactose} ratio, as the positive kinetic effect of the catalyst can compensate for
873 the lower amount of catalyst used, thus masking the effect of the pressure for high
874 W/m_{lactose} ratios. Conversely, for 40 g catalyst min/g lactose, this increase in pressure
875 decreases the proportion of monohydric alcohols between 210 and 230 °C. This
876 increase in pressure kinetically enhances the decomposition of monohydric alcohols
877 when a high amount of catalyst is used [25]. On the other hand, for a 10 wt.% lactose
878 solution, the effect of the pressure is relatively weak for 10 g catalyst min/g lactose,
879 while a moderate decrease in the proportion of monohydric alcohols is observed for 40
880 g catalyst min/g lactose between 200 and 230 °C.

881

882 The effect of the W/m_{lactose} ratio is relatively weak and depends on the pressure and
883 lactose concentration. At 38 bar, an increase in the W/m_{lactose} ratio from 10 to 40 g
884 catalyst min/g lactose does not modify the proportion of monohydric alcohols when a
885 diluted solution is used (1wt.%). Conversely, an increase in the lactose concentration
886 makes the effect of the W/m_{lactose} ratio significant, increasing the proportions of
887 monohydric alcohols in the liquid. An increase in the lactose concentration makes route
888 C prevalent over A and B, as explained above. This increase in the W/m_{lactose} ratio
889 increases the proportion of polyhydric alcohols between 200 and 220 °C regardless of
890 the lactose concentration due to the positive kinetic effect of the catalyst, which favours
891 lactose decomposition. At 50 bar an increase in the W/m_{lactose} ratio decreases the
892 proportion of monohydric alcohols between 200 and 220 °C for a 1 wt.% lactose
893 solution. This depletion occurs along with an increase in the proportions of aldehydes

894 and carboxylic acids in the liquid. Increases in the proportion of acetaldehyde and acetic
895 acid are accounted for by these variations. The positive catalytic effect of the pressure
896 and W/m_{lactose} ratio helps shift the decomposition of monohydric alcohols to end liquids
897 and gases [25]. Conversely, an increase in this family of compounds occurs between
898 220 and 240 °C when a 10 wt.% lactose solution is fed. Dehydration reactions are
899 favoured at high temperature, pressure and using a concentrated lactose solution, which
900 makes route C prevalent over routes A and B. Therefore, at these operating conditions
901 under which routes A and B are not predominant, it might be necessary to use a high
902 W/m_{lactose} ratio to produce a greater spread of the reactions leading to the formation of
903 end products obtained via routes A and B. In addition, the proportion of polyhydric
904 alcohols increases between 220 and 240 °C regardless of the lactose concentration due
905 to the positive kinetic effect of the catalyst.

906

907 *3.3.3 Aldehydes*

908 The relative amount of this compound in the liquid phase is low (0-12%), probably
909 because it is one of the end products of lactose aqueous phase reforming and/or it can
910 easily be transformed into gas in the final steps of the process [25]. The relative amount
911 of aldehydes strongly depends on the W/m_{lactose} ratio and the concentration of lactose in
912 the solution. Very interestingly, the pressure (between 38 and 50 bar) does not
913 significantly influence the proportion of aldehydes in the liquid. This was also reported
914 in a previous work analysing the effect of the pressure on the proportion of this family
915 of compounds during the APR of crude glycerol [25].

916

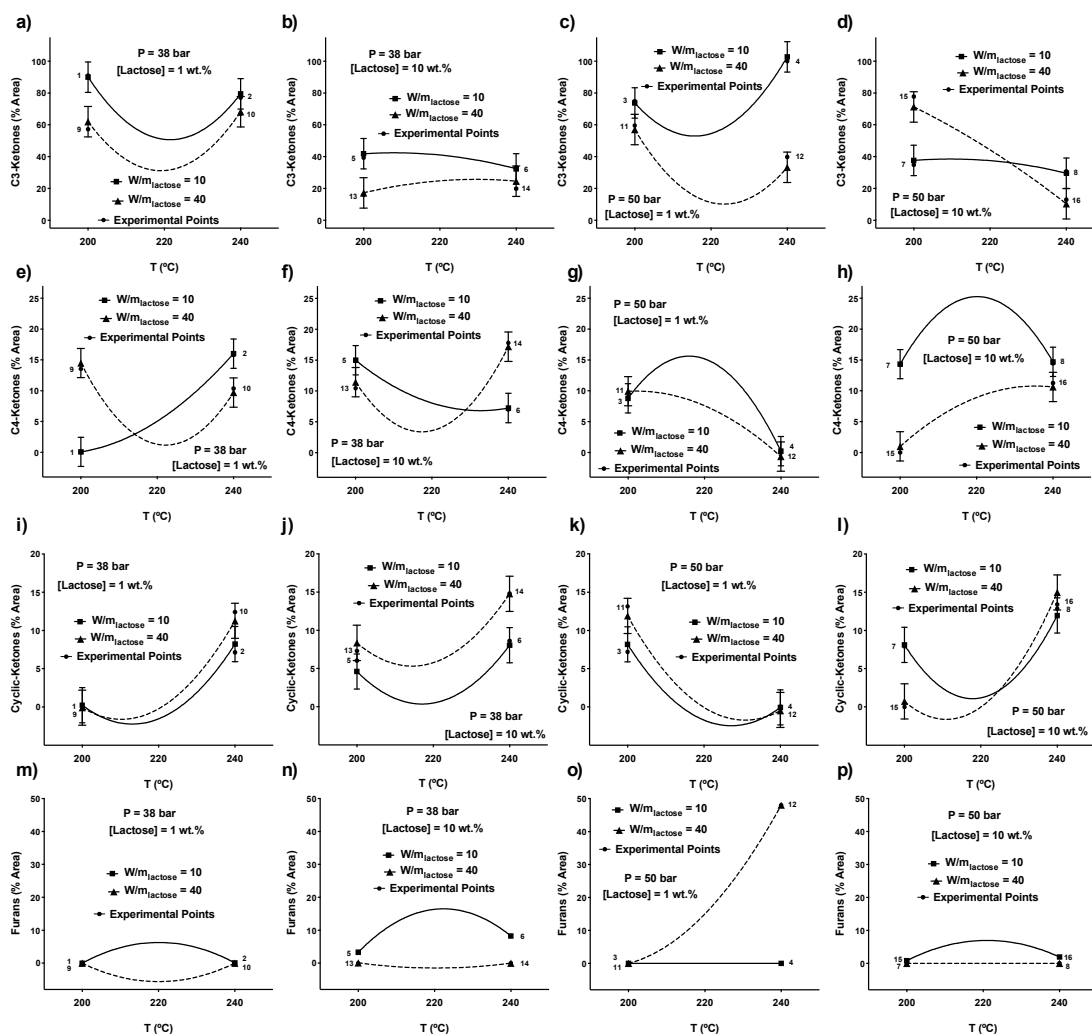
917 When a 1 wt.% lactose solution is fed, the liquid product has a negligible concentration
918 of aldehydes for a W/m_{lactose} ratio of 10 g catalyst min/g lactose, regardless of the
919 pressure. Conversely, a sharp increase in the proportion of aldehydes occurs when
920 increasing the temperature, especially between 220 and 240 °C, for 40 g catalyst min/g
921 lactose within the whole interval of pressure considered (38-50 bar). This increase in the
922 proportion of aldehydes accounts for the decrease observed in the relative amount of
923 monohydric alcohols. This development indicates that the dehydration of ethane 1,2-
924 diol to acetaldehyde is more likely to occur than its hydrogenation to ethanol since at
925 high temperatures H_2 solubility decreases with temperature. In addition, high
926 temperatures and W/m_{lactose} ratios favour the advancement of the reaction in the liquid
927 phase towards the formation of liquid products. Therefore, when a diluted lactose
928 solution is fed, an increase in the W/m_{lactose} ratio from 10 to 40 g catalyst min/g lactose
929 leads to a substantial increase in the proportion of aldehydes in the liquid.

930

931 *3.3.4 Ketones: C3-ketones, C4-ketones and cyclic ketones*

932 The ketonic fraction is made up of ketones of three and four carbon atoms (C3-ketones
933 and C4-ketones) together with cyclic ketones and, in lower proportions, furanic ketones.
934 C3-ketones, mainly obtained from dehydration reactions, are the most abundant ketones
935 in the liquid phase.

936



937
938
939
940
941

Figure 5. Interaction plots for the relative amounts in the liquid of C3-ketones (a-d), C4-ketones (e-h), cyclic ketones (i-l) and furans (m-p). Bars are LSD intervals with 95% confidence.

942 The effect of the temperature depends on the lactose concentration and pressure. For a 1
943 wt.% lactose solution, the proportion of C3-ketones decreases from 200 to 220 °C and
944 increases with a further increase in the temperature up to 240 °C, regardless of the
945 pressure and the W/m_{lactose} ratio. Between 200 and 220 °C an increase in temperature
946 kinetically produces a greater spread of hydrogenation reactions in the liquid. However,
947 the H₂ solubility in water decreases with a further increase in temperature up to 240 °C,
948 thus hindering the hydrogenation of ketones to alcohols. This accounts for the increase
949 observed in ketones and the decreases observed in the proportions of monohydric and

950 polyhydric alcohols [25]. For this diluted lactose solution, an increase in the W/m_{lactose}
951 ratio from 10 to 40 g catalyst/min g lactose leads to a decrease in the proportion of C3-
952 ketones. This drop occurs between 200 and 230 °C at 38 bar and between 210 to 240 °C
953 at 50 bar. These depletions account for a greater advancement of the reaction in the
954 liquid phase towards the formation of liquid products [25].

955

956 For a 10 wt.% lactose solution the effect of the temperature strongly depends on the
957 pressure. At 38 bar, the temperature does not significantly affect the proportion of C3
958 ketones in the liquid, and the W/m_{lactose} ratio is only significant between 200 and 215 °C,
959 where an increase from 10 to 40 g catalyst min/g lactose slightly decreases the relative
960 amount of C3-ketones. It is believed that the non-significant effect of the temperature is
961 the consequence of two developments. On the one hand, between 200 and 220 °C an
962 increase in the lactose concentration increases the partial pressure of C3-ketones in the
963 liquid, favouring their transformation towards liquid end products, thus decreasing their
964 relative amount in the liquid. On the other hand, between 220 and 240 °C the formation
965 of furanic compounds from the dehydration of glucose and galactose through route C is
966 favoured, decreasing the proportion of C3-ketones in the liquid. At 50 bar, the effect of
967 the temperature is not significant for a low W/m_{lactose} ratio. However, an increase in the
968 W/m_{lactose} ratio up to 40 g catalyst min/g lactose increases the proportion of C3-ketones
969 at low temperatures very sharply. This increase is accounted for by the decrease in the
970 proportion of monohydric alcohols in the liquid. For this W/m_{lactose} ratio, an increase in
971 the temperature results in a substantial reduction in the proportion of this family of
972 compounds in the liquid, which accounts for the increase observed in the proportion of
973 monohydric alcohols.

974

975 The effect of the pressure on the relative amount of C3-ketones strongly depends on the
976 temperature and lactose concentration. The effect of the pressure is minimal between
977 200 and 220 °C, while significant variations occur between 220 and 240 °C. When a 1
978 wt.% lactose solution is used, an increase in pressure from 38 to 50 bar results in an
979 increase and a decrease in the proportion of C3-ketones for W/m_{lactose} ratios of 10 and
980 40 g catalyst min/g lactose, respectively, between 220 and 240 °C. An increase in the
981 total pressure raises the solubility of H_2 in the liquid, which can compensate for the
982 decrease in the solubility of this gas with the temperature when a high amount of
983 catalyst is employed.

984

985 For a 10 wt.% lactose solution, the effect of the pressure depends on the W/m_{lactose} ratio.
986 For 10 g catalyst min/g lactose, an increase in the pressure from 38 to 50 bar does not
987 significantly modify the proportion of C3-ketones in the liquid. Conversely, for 40 g
988 catalyst min/g lactose, this increase in pressure increases the proportion of C3-ketones
989 in the liquid very sharply between 200 and 230 °C. The chemical analysis of the liquid
990 reveals that this increase is accounted for by a sharp increase in 1-hydroxypropan-2-one.
991 For concentrated lactose solutions, route C is favoured over route A and B. However, an
992 increase in the W/m_{lactose} ratio can promote the isomerisation of glucose and galactose to
993 fructose and the posterior retro-aldol reaction [27, 29], thus increasing the presence in
994 the liquid of initial products obtained from route A. In addition, a high W/m_{lactose} ratio
995 produces a greater spread of condensation and cross-polymerisation reactions from the
996 furan compounds obtained via route C [27, 28, 31, 33].

997

998 The proportion of C4-ketones and cyclic-ketones in the liquid phase is lower than the

999 relative amount of C3-ketones. 2-butanone-3-hydroxy, 1-hydroxy-2-butanone and 2,3-
1000 butanedione, which are obtained from the dehydration/hydrogenation of erythritol
1001 (route B), are the most abundant C4-ketones in the liquid. The effect of the temperature
1002 on the relative amount of C4 ketones depends on the pressure and the concentration of
1003 lactose. At 38 bar, the effect of the temperature depends on the concentration of lactose
1004 and the W/m_{lactose} ratio. For a 1wt.% lactose solution and using 10 g catalyst min/g
1005 lactose, the proportion of C4 ketones at low temperatures is negligible, and an increase
1006 in temperature from 200 to 240 °C leads to a substantial increase in the proportion of
1007 C4-ketones. The decrease in the H_2 solubility with temperature, decreasing the
1008 proliferation of hydrogenation reactions [25] of C4-ketones to alcohols, might be
1009 responsible for this increase in the proportion of C4-ketones. Conversely, an increase in
1010 the W/m_{lactose} ratio up to 40 g catalyst min/g lactose increases the proportion of C4-
1011 ketones at low temperature very sharply as the presence of a catalyst favours retro-aldol
1012 reactions [30]; thus increasing the presence of liquid products obtained via route B in
1013 the liquid. For this latter ratio, an increase in temperature decreases the proportion of
1014 C4-ketones between 200 and 220 °C. A further increase in temperature up to 240 °C
1015 leads to a substantial increase in the proportion of C4-ketones. At low temperature, an
1016 increase in the temperature kinetically favours hydrogenation reactions, while a further
1017 increase in temperature decreases the H_2 solubility in water, thus hindering
1018 hydrogenation reactions [25]. Between 220 and 240 °C an increase in the W/m_{lactose} ratio
1019 from 10 to 40 g catalyst min/g lactose reduces the relative amount of C4-ketones in the
1020 liquid.

1021

1022 At 50 bar and using a W/m_{lactose} ratio of 10 g catalyst min/g lactose, the effect of the
1023 temperature on the relative amount of C4-ketones in the liquid has a similar evolution

1024 regardless of the lactose concentration. The proportion of C4-ketones increases when
1025 increasing the temperature from 200 to 220 °C, while a further increase in temperature
1026 up to 240 °C results in a decrease in the proportion of C4-ketones. High pressure
1027 promotes retro-aldol reactions in hot compressed water [66]. Therefore at 50 bar, an
1028 increase in temperature increases the proportion of C4-ketones in the liquid, which are
1029 obtained through route B due to the greater spread of glucose/galactose decomposition
1030 via reatro-aldol reactions at high pressure. Conversely, for 40 g catalyst min/g lactose
1031 the effect of the temperature depends on the concentration of lactose. When feeding a 1
1032 wt.% lactose solution, the concentration of C4-ketones decreases with temperature,
1033 while for a 10 wt.% solution, an increase takes places as the temperature increases from
1034 200 to 240 °C. For a low lactose concentration the catalyst favours hydrogenation
1035 reactions [25], which leads to a decrease in the proportion of C4-ketones. Conversely,
1036 for a concentrated lactose solution, route C prevails over routes A and B [27, 28, 31,
1037 33]. Therefore, an increase in temperature might shift the retro-aldol reactions [66],
1038 which results in a liquid with a higher concentration of initial products obtained via
1039 route B. At this pressure (50 bar), an increase in the W/m_{lactose} ratio from 10 to 40 g
1040 catalyst/min leads to a decrease in the proportion of C4-ketones regardless of the lactose
1041 concentration, as the catalyst favours the advancement of route B towards liquid end
1042 products.

1043

1044 An increase in the pressure for a 1 wt.% lactose solution has two different effects
1045 depending on the W/m_{lactose} ratio. When a low amount of catalyst is used, an increase in
1046 pressure from 38 to 50 bar increases and decreases the proportion of C4-ketones
1047 between 200 and 230 °C and between 230 and 240 °C, respectively. This is the
1048 consequence of two developments. High pressure promotes retro-aldol reactions in hot

1049 compressed water [66]. In addition, their subsequent transformation to end liquids is not
1050 favoured due to the low amount of catalyst, which globally results in an increase in the
1051 amount of C4-ketones in the liquid. For a W/m_{lactose} ratio of 40 g catalyst min/g lactose,
1052 the same increase in pressure does not provoke great differences in the proportion of
1053 C4-ketones; the proportion slightly decreases between 200 and 240 °C. For a 10 wt.%
1054 lactose solution, this increase in pressure leads to a decrease in the proportion of C4-
1055 ketones between 200-215 °C and 225-240 °C; the effect of the pressure being negligible
1056 from 215 to 225 °C. For a 10 wt.% lactose solution, route C is favoured over routes A
1057 and B [27, 28, 31, 33], which can explain the decay observed between 225 and 240 °C.

1058

1059 Cyclopentanone, 2-hydroxy-3-methyl-2-cyclopenten-1-one and 2-methyl-2-
1060 cyclopenten-1-one are responsible for the variations observed in the proportion of cyclic
1061 ketones during the first hour of reaction. These ketones are obtained from the
1062 hydrogenation of different liquid intermediates obtained through the decomposition of
1063 5-hydroxymethyl-2-furancarboxaldehyde, which is obtained from glucose/galactose
1064 dehydration (route C). The effect of the temperature depends on the pressure. On the
1065 one hand, at 38 bar and regardless of the W/m_{lactose} ratio and lactose concentration, the
1066 temperature does not significantly influence the proportion of cyclic ketones between
1067 200 and 220 °C, while an increase in the relative amount of this family of ketones
1068 occurs as the temperature increases from 220 to 240 °C. The decrease in the H_2
1069 solubility with temperature might be responsible for the increase observed in this family
1070 of compounds, as this H_2 limitation stops the advancement of the reaction in the liquid
1071 phase towards end products obtained through route C. In addition, high temperatures
1072 favour route C over routes A and B [27, 28, 31, 33], which accounts for the increase in
1073 this family of compounds and the decreases observed in the proportions of carboxylic

1074 acids and monohydric alcohols. At this pressure (38 bar), an increase in the W/m_{lactose}
1075 ratio from 10 to 40 g catalyst min/g lactose increases the concentration of cyclic ketones
1076 in the liquid. The W/m_{lactose} ratio does not significantly modify the proportion of cyclic
1077 ketones in the liquid for a diluted lactose solution. However, the higher the lactose
1078 concentration, the greater is the impact of the W/m_{lactose} ratio on the proportion of this
1079 family of ketones.

1080

1081 On the other hand, at 50 bar the effect of the temperature depends on the W/m_{lactose} ratio
1082 and lactose concentration. For a 1 wt.% lactose solution, the proportion of cyclic
1083 ketones sharply decreases when increasing the temperature from 200 to 220 °C and a
1084 liquid free of cyclic ketones is obtained between 220 and 240 °C. For a low W/m_{lactose}
1085 ratio this decrease accounts for the increase in the proportion of C3-ketones, while for a
1086 high W/m_{lactose} ratio the sharp increase in the relative amount of furans in the liquid is
1087 responsible for the decrease in the proportion of cyclic ketones. For a 10 wt.% lactose
1088 solution two different trends are observed depending on the W/m_{lactose} ratio. Between
1089 200 and 220 °C, the proportion of cyclic ketones drops when increasing the temperature
1090 for 10 g catalyst min/g lactose. Within this temperature interval the proportion of cyclic
1091 ketones is negligible for a W/m_{lactose} ratio of 40 g catalyst min/g lactose. Between 220
1092 and 240 °C, the W/m_{lactose} ratio does not influence the proportion of cyclic ketones, and
1093 an increase in the relative amount of cyclic ketones occurs as the reaction temperature
1094 increases regardless of the W/m_{lactose} ratio. The increase observed in the CC gas between
1095 220 and 240 °C might be responsible for this development. An increase in temperature
1096 favours the evolution of the intermediate liquid compounds obtained from route A and
1097 B towards gases [25], thus increasing the proportion of liquids obtained from route C.
1098 This transformation is favoured at high pressure [25]. In addition, the decrease in the H_2

1099 solubility with temperature might be responsible for the increase observed in this family
1100 of compounds.

1101

1102 The effect of the pressure depends on the concentration of lactose, the temperature and
1103 the W/m_{lactose} ratio. When a diluted lactose solution (1 wt.%) is fed, an increase in
1104 pressure from 38 to 50 bar increases the proportion of cyclic ketones between 200 and
1105 220 °C and reduces their relative amount between 220 and 240 °C, regardless of the
1106 W/m_{lactose} ratio. At low temperatures route C is not favoured, and an increase in the
1107 pressure increases the partial pressure of H_2 , which promotes hydrogenation reactions to
1108 produce cyclic ketones. Conversely, between 220 and 240 °C an increase in pressure
1109 favours the formation of C3-ketones and furans. When a 10 wt.% lactose solution is fed,
1110 the effect of the pressure is only significant between 200 and 220 °C, an interval under
1111 which two different evolutions are observed depending on the W/m_{lactose} ratio. For 10 g
1112 catalyst min/g lactose, the pressure does not greatly influence the proportion of cyclic
1113 ketones in the liquid, while for 40 g catalyst min/g lactose this increase in pressure
1114 results in a decrease in the proportion of this family of ketones in the liquid product.

1115

1116 *3.3.5 Furans*

1117 Furanic compounds, mainly 5-hydroxymethyl-2-furancarboxaldehyde, 5-methyl-2-
1118 furancarboxaldehyde and furfural, are obtained from the dehydration of glucose and
1119 galactose via route C. The proportion of this family of compounds in the liquid is
1120 relatively low. Exceptionally, the proportion of furans in the liquid dramatically
1121 increases with temperature at high pressure and employing a high W/m_{lactose} ratio for a
1122 diluted lactose solution.

1123 The effect of the temperature on the relative amount of furans strongly depends on the
1124 pressure. At 38 bar, the proportion of furans in the liquid is very low. For 10 g catalyst
1125 min/g lactose, an increase in the temperature from 200 to 220 °C slightly increases their
1126 proportion in the liquid, while a further increase in the temperature up to 240 °C leads to
1127 a decrease in the relative amount of this family of compounds. Between 220 and 240 °C
1128 the CC liq decreases and the CC sol increases very sharply as high temperatures
1129 promote the polymerisation and aldol-condensation reactions of furans [27, 28, 31, 33].
1130 At this pressure an increase from 10 to 40 g catalyst min/g lactose reduces the
1131 proportion of furans regardless of the lactose concentration for the whole temperature
1132 interval considered, probably due to the greater spread of polymerisation and
1133 condensation reactions from furans [27, 28, 31, 33] which might help the advancement
1134 of the reactions occurring via route C.

1135

1136 At 50 bar, the concentration of furans in the liquid depends on the lactose concentration
1137 and the W/m_{lactose} ratio. When a low amount of catalyst is used, the proportion of furans
1138 in the liquid is very low and the effect of the temperature is very weak. Conversely, an
1139 increase in the W/m_{lactose} ratio has a great impact on the proportion of furans when
1140 diluted lactose solutions are used. Specifically, for a 1 wt.% lactose solution and 40 g
1141 catalyst min/g lactose, an increase in temperature from 200 to 240 °C increases the
1142 proportion of furans very sharply. This increase in the temperature also increases the
1143 CC sol as described above, suggesting that under these operating conditions the glucose
1144 and galactose dehydration is favoured, thus increasing the amount of liquids produced
1145 via route C. An increase in the concentration of lactose in the solution can potentiate the
1146 condensation and polymerisation of furans, thus decreasing their relative amount in the
1147 liquid [27, 28, 31, 33]. As a result, a negligible concentration of furans is obtained with

1148 a 10 wt.% lactose solution using 40 g catalyst min/g lactose.

1149

1150 The effect of the pressure depends on the lactose concentration and W/m_{lactose} ratio.

1151 When a W/m_{lactose} ratio of 10 g catalyst min/g lactose is used, an increase in pressure

1152 from 38 to 50 bar reduces the proportion of furans regardless of the lactose

1153 concentration. An increase in the system pressure favours the advancement of the

1154 reactions leading to the formation of end products [25]. Conversely, an increase in the

1155 W/m_{lactose} ratio modifies the effect of the pressure. The proportion of furans augments

1156 when the W/m_{lactose} ratio increases and decreases when increasing the concentration of

1157 lactose in the solution.

1158

1159 *3.4 Prediction of optimal operating conditions within the range of study*

1160 Optimal conditions for gas and liquid production were sought for this process, making

1161 use of the experimental models developed. The predicted R^2 of all the models is higher

1162 than 0.90, allowing their use for prediction purposes. Four different optimisations were

1163 carried out. The first aims at the production of a gas with a high H_2 content, and

1164 therefore comprises the maximisation of the CC gas and the relative amount of H_2 in the

1165 gas. The second, third and fourth seek to maximise the production of alcohols

1166 (monohydric and polyhydric alcohols), ketones and furans, respectively. Therefore, the

1167 CC liq and the proportion of each family of liquids were maximised. In addition, the CC

1168 sol was minimised for all the optimisations. To meet these objectives, a solution that

1169 strikes a compromise between the optimum values for all the response variables was

1170 sought. To do this, a relative importance (from 1 to 5) was given to each of the

1171 objectives in order to come up with the solution that satisfies all the criteria. To globally

1172 maximise gas and liquid production, a relative importance of 5 was assigned to the CC
 1173 gas and CC liq, while a relative importance of 3 was given to the properties of the gas or
 1174 liquid (vol. H₂ and relative amount of each family of compound) and to the
 1175 minimisation of the CC sol in all cases. Table 1 lists the optimisation results.
 1176

1177 Table 1. Theoretical optimisation: Objectives, optimum values for the operating
 1178 variables and optimised values for some responses

Opt	Variable/s maximised	T (°C)	P (bar)	[Lactose] (wt.%)	W/m _{lactose} (g _{cat} min/g _{lactose})	CC gas (%)	CC liq (%)	CC sol (%)	H ₂ (vol.%)	Alcohols (%)	C3-ketones (%)	Furans (%)
1	CC gas, H ₂ (vol.%)	240	50	10	40	32	36	31	44	48	6	0
2	CC liq, (Alcohols %)	230	43	1	13	10	93	0	19	43	44	1
3	CC liq (C3-ketones)	240	50	1	10	10	93	0	29	1	98	0
4	CC liq, (Furans %)	224	48	1	40	18	74	4	24	48	7	16

1179

1180 Taking these restrictions into account, optimisation 1 predicts a possible optimum for
 1181 H₂ production at the highest values of the temperature, pressure, lactose concentration
 1182 and W/m_{lactose} ratio used in this work. Under these conditions 4 mol H₂/mol lactose is
 1183 produced. This H₂ yield is similar to that obtained in anaerobic fermentation (4 mol
 1184 H₂/mol lactose) and anaerobic fermentation plus photo-fermentation with L-malic acid
 1185 (2-10 mol H₂/mol lactose), but lower than the H₂ yield obtained during the catalytic
 1186 steam reforming of lactose (16 mol H₂/mol lactose) [67]. The production of value-added
 1187 liquids (optimisations 2, 3 and 4) is favoured when feeding a diluted lactose solution (1
 1188 wt.%). Specifically, optimisation 2 indicates that the production of alcohols is
 1189 preferential at medium temperature and medium pressure, using a low W/m_{lactose} ratio.
 1190 Under these conditions the proportions of monohydric and polyhydric alcohols in the
 1191 liquid are 26 and 17%, respectively. Optimisation 3 predicts a selective production of
 1192 C3-ketones at high temperature and pressure, using a low amount of catalyst. Under
 1193 these conditions, the hydrogen solubility in the liquid is relatively low. This hinders

1194 hydrogenation reactions, thus increasing the proportion of C3-ketones in the liquid.
1195 Optimisation 4 predicts a maximum for the proportion of furans at medium temperature
1196 and high pressure using a high W/m_{lactose} ratio.

1197

1198 **4. Conclusions**

1199 Aqueous phase reforming turned out to be a highly customisable process for the
1200 valorisation of lactose, the major organic constituent of cheese whey, for the production
1201 of either gas or liquid value-added chemicals. The operating variables exert a significant
1202 influence on the global results of the aqueous phase reforming (carbon converted into
1203 gas, liquid and solid products) as well as on the composition of the gas and liquid
1204 phases. The gas phase is composed of H_2 , CO_2 , CO and CH_4 . The liquid phase consisted
1205 of a mixture of aldehydes, carboxylic acids, monohydric alcohols, polyhydric-alcohols,
1206 C3, C4 and cyclic-ketones and furans. The optimisation of the process revealed that an
1207 elevated temperature and a high pressure favour gas production when using a high
1208 W/m_{lactose} ratio and a concentrated lactose solution. Liquid production is favoured at
1209 high temperature using a diluted lactose solution and a low W/m_{lactose} ratio. An elevated
1210 temperature and a high W/m_{lactose} ratio favour solid production due to the proliferation
1211 of condensation and polymerisation reactions.

1212

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1219

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1406

SUPPLEMENTARY MATERIAL

FIGURES

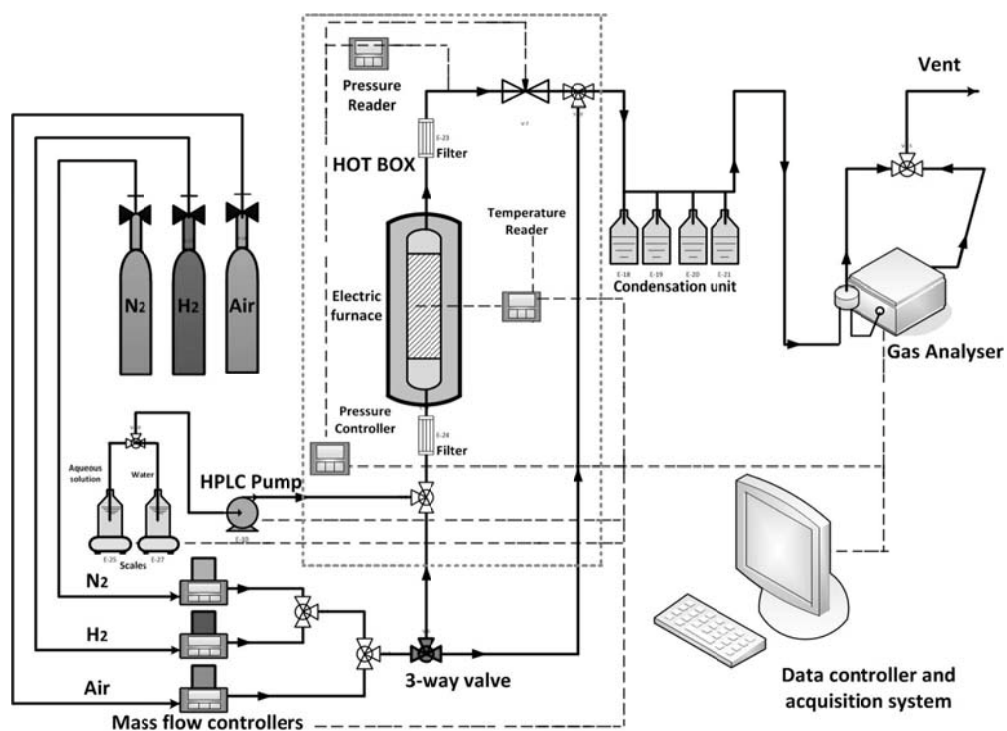


Figure S1. Schematic diagram of the aqueous phase reforming experimental rig.

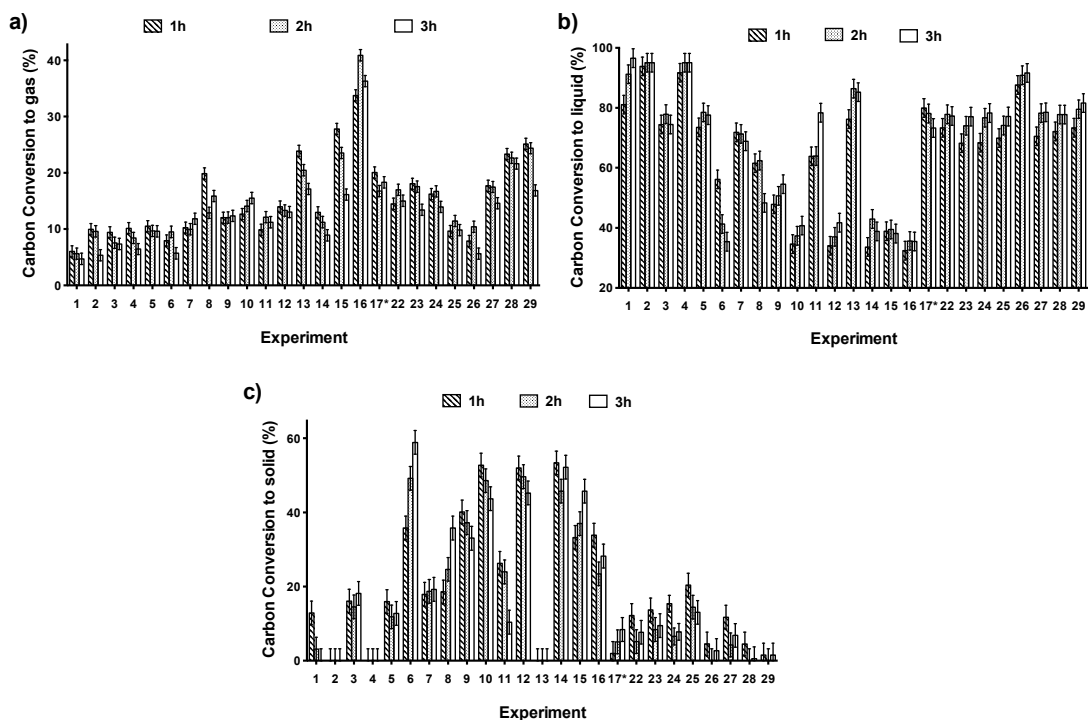


Figure S2. Carbon conversion to gas (a), liquid (b) and solid (c) obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean \pm 0.5 Fisher LSD intervals with 95% confidence.

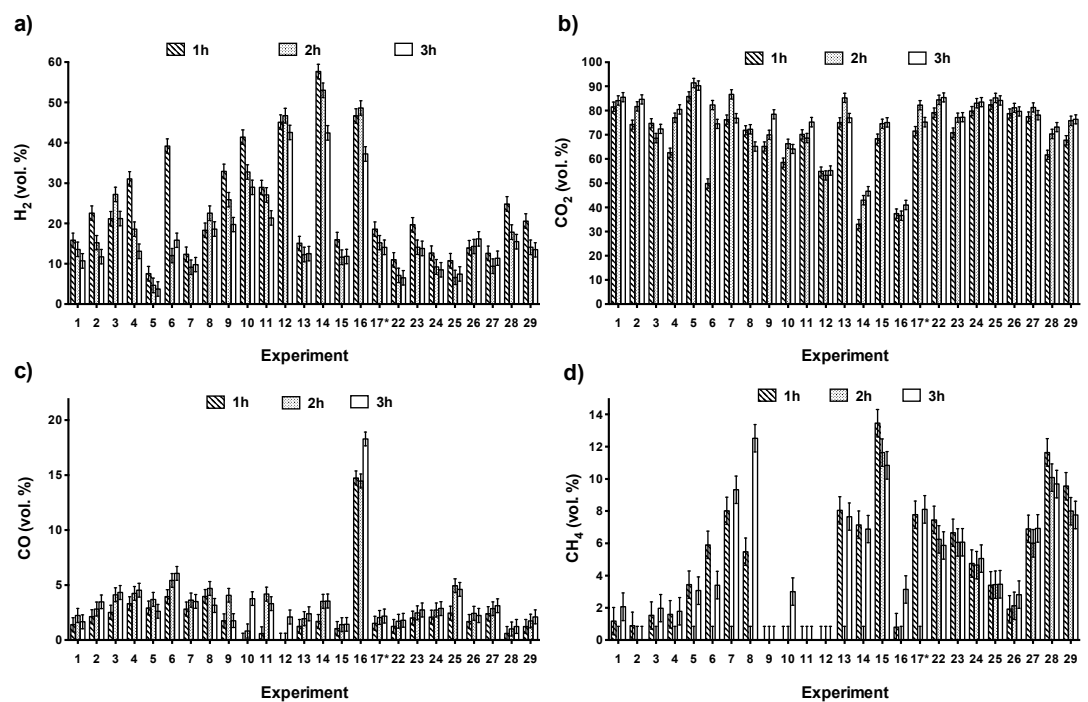


Figure S3. Relative amounts (vol.%) of H₂ (a), CO₂ (b) CO (c) and CH₄ (d) in the gas obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean \pm 0.5 Fisher LSD intervals with 95% confidence.

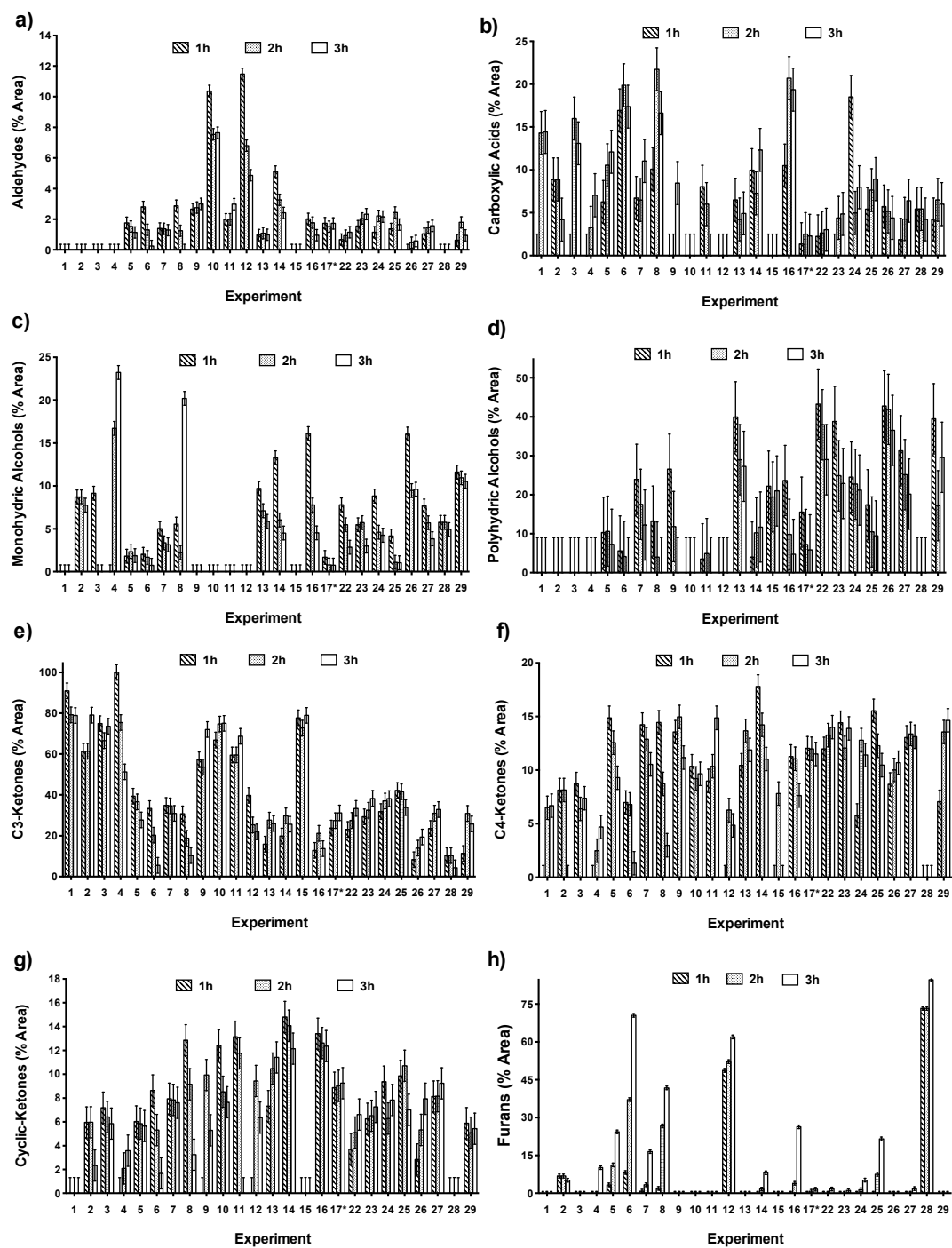


Figure S4. Proportions (% chromatographic area) of aldehydes (a), carboxylic acids (b), monohydric alcohols (c), polyhydric alcohols (d), C3-ketones (e), C4-ketones (f), cyclic ketones (g) and furans (h) in the liquid obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean \pm 0.5 Fisher LSD intervals with 95% confidence.

TABLES

Table S1. Response variables. Definitions and analytical techniques used in their determination.

Product	Response variable	Analytical method
Gas	$CC\ gas\ (\%) = \frac{C\ in\ the\ gas\ (g)}{C\ fed\ (g)} 100$	Micro Gas Chromatograph (Micro GC). N ₂ as internal standard Online analyses
	$Composition\ (vol.\ \%) = \frac{mol\ of\ each\ gas}{total\ mol\ of\ gas} 100$	
Liquid	$CC\ liq\ (\%) = \frac{C\ in\ the\ liquid\ products\ (g)}{C\ fed\ (g)} 100$	Total Organic Carbon (TOC).
	$Composition\ (area\ \%) = \frac{area\ of\ each\ compound}{total\ area} 100$	GC-MS (Gas Chromatography-Mass Spectrometry)
	$X\ lactose\ (\%) = \frac{lactose\ fed\ (g) - lactose\ in\ the\ liquid\ (g)}{lactose\ fed\ (g)} 100$	HPLC (High Performance Liquid Chromatography) Offline analyses
Solid	$CC\ sol\ (\%) = 100 - CC\ gas\ (\%) - CC\ liq^*\ (\%)$	

$CC\ liq$ = Carbon conversion to liquid products (unreacted lactose free).

$CC\ liq^*$ = Carbon conversion to liquids including unreacted lactose

Table S2. Operating conditions employed in the experiments

Run	Lactose (wt.%)		Pressure (bar)		Temperature (°C)		W _{catalyst} /m _{lactose} (g cat min/g lactose)	
	Actual	codec	actual	codec	actual	codec	Actual	codec
1	1	-1	38	-1	200	-1	10	-1
2	1	-1	38	-1	240	1	10	-1
3	1	-1	50	1	200	-1	10	-1
4	1	-1	50	1	240	1	10	-1
5	10	1	38	-1	200	-1	10	-1
6	10	1	38	-1	240	1	10	-1
7	10	1	50	1	200	-1	10	-1
8	10	1	50	1	240	1	10	-1
9	1	-1	38	-1	200	-1	40	1
10	1	-1	38	-1	240	1	40	1
11	1	-1	50	1	200	-1	40	1
12	1	-1	50	1	240	1	40	1
13	10	1	38	-1	200	-1	40	1
14	10	1	38	-1	240	1	40	1
15	10	1	50	1	200	-1	40	1
16	10	1	50	1	240	1	40	1
17* (17,18,19, 20, 21)	5.5	0	44	0	220	0	25	0
22	5.5	0	44	0	200	-1	25	0
23	5.5	0	44	0	240	1	25	0
24	5.5	0	38	-1	220	0	25	0
25	5.5	0	50	1	220	0	25	0
26	1	-1	44	0	220	0	25	0
27	10	1	44	0	220	0	25	0
28	5.5	0	44	0	220	0	10	-1
29	5.5	0	44	0	220	0	40	1

Table S3. *Relative influence of the operating conditions on the CC gas, CC liq and CC sol according to the ANOVA analysis for the first hour of reaction.*

	R ²	Indep.	T	P	C	W	TP	TC	TW	PC	PW	CW	T ²	P ²	C ²	W ²	TPC	TPW	TCW	PCW	T ² P	T ² C	T ² W	TP ²	T ² P ²	TPCW
CC gas (%)	0.95	20.07	n.s	-3.28 (6)	4.04 (14)	n.s	1.83 (6)	n.s	n.s	2.10 (7)	n.s	2.30 (8)	-3.79 (2)	-7.12 (7)	-7.29 (10)	4.17 (6)	1.90 (6)	n.s	n.s	1.09 (4)	5.72 (6)	n.s	3.93 (13)	n.s	8.40 (4)	n.s
CC liq (%)	0.97	78.28	n.s	n.s	-5.23 (8)	n.s	n.s	-3.97 (6)	-5.91 (8)	-2.60 (4)	n.s	4.92 (7)	-8.12 (14)	-9.73 (6)	n.s	n.s	3.45 (6)	n.s	3.22 (4)	-4.15 (6)	n.s	n.s	-15.17 (21)	-5.61 (8)	n.s	3.13 (4)
CC sol (%)	0.97	3.74	n.s	n.s	n.s	n.s	-3.88 (6)	4.07 (6)	6.3 (9)	n.s	n.s	-6.87 (10)	8.48 (17)	13.42 (9)	n.s	n.s	-5.12 (7)	n.s	-2-12 (3)	2.93 (4)	n.s	n.s	10.90 (16)	5.24 (8)	n.s	-3.12 (5)

n.s: Non significant with 95% confidence

Response = Indep. + Coefficient T·T + Coefficient P·P + Coefficient C·C + Coefficient W·W + Coefficient TC·T·C + Coefficient TW·T·W + Coefficient PC·P·C + Coefficient PW·P·W + Coefficient CW·C·W + Coefficient T²·T² + Coefficient P²·P² + Coefficient C²·C² + Coefficient W²·W² + Coefficient TPC·T·P·C + Coefficient TPW·T·P·W + Coefficient TCW·T·C·W + Coefficient PCW·P·C·W + Coefficient T²P·T²·P + Coefficient T²C·T²·C + Coefficient T²W·T²·W + Coefficient TP²·T·P² + Coefficient TPCW·T·P·C·W.

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

Table S4. Relative influence of the operating conditions on the volumetric composition of the gas according to the ANOVA analysis for the first hour of reaction.

	R ²	Ind.	T	P	C	W	TP	TC	TW	PC	PW	CW	T ²	P ²	C ²	W ²	TPC	TPW	TCW	PCW	T ² P	T ² C	T ² W	TP ²	T ² P ²	TPCW	
H ₂ (vol.%)	0.95	16.69	4.34 (20)	n.s.	n.s.	n.s.	-1.67 (4)	4.35 (9)	2.73 (6)	-2.48 (5)	n.s.	n.s.	n.s.	-4.98 (1)	n.s.	6.03 (17)	-3.03 (7)	n.s.	1.72 (4)	n.s.	n.s.	-1.64 (4)	7.23 (16)	5.17 (4)	10.5 (5)	n.s.	
CO ₂ (vol.%)	1	71.51	-4.13 (16)	n.s.	n.s.	3.01 (11)	1.82 (3)	-4.50 (7)	-2.20 (n.s.)	1.70 (3)	n.s.	-1.59 (3)	3.53 (8)	9.60 (3)	6.64 (2)	-6.77 (8)	n.s.	-1.53 (6)	-1.88 (3)	-2.16 (4)	n.s.	-2.76 (5)	-5.54 (6)	-5.54 (3)	-19.52 (4)	1.04 (2)	
CO (vol.%)	0.97	1.54	n.s.	n.s.	n.s.	n.s.	0.91 (7)	1.07 (9)	0.50 (4)	0.73 (6)	0.59 (6)	0.76 (6)	n.s.	1.17 (6)	n.s.	n.s.	0.76 (6)	0.89 (7)	0.99 (8)	1.03 (8)	0.87 (7)	1.29 (11)	n.s.	0.97 (8)	n.s.	0.75 (6)	
CH ₄ (vol.%)	0.93	7.62	n.s.	n.s.	2.89 (22)	n.s.	-1.03 (7)	-0.84 (6)	-0.83 (6)	n.s.	n.s.	0.74 (5)	n.s.	-3.62 (8)	-3.29 (18)	2.90 (9)	-1.07 (8)	n.s.	-0.86 (6)	n.s.	n.s.	n.s.	n.s.	-0.87 (6)	n.s.	n.s.	
Aldehydes (%)	0.94	1.27	n.s.	n.s.	n.s.	n.s.	n.s.	-0.53 (7)	1.30 (17)	n.s.	n.s.	-1.70 (23)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	-0.85 (11)	n.s.	n.s.	-0.60 (8)	1.61 (21)	1.62 (13)	1.45 (13)	n.s.	
Carboxylic Acids (%)	0.93	4.23	n.s.	-6.54 (5)	n.s.	n.s.	n.s.	2.25 (12)	n.s.	-1.27 (7)	n.s.	-1.32 (7)	-3.11 (14)	7.74 (14)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	6.27 (11)	3.69 (20)	n.s.	1.25 (7)	-4.18 (5)	1.40 (7)
Mono-OH (%)	0.96	7.44	n.s.	-2.32 (1)	-4.19 (9)	0.97 (5)	n.s.	1.88 (8)	1.79 (8)	n.s.	-1.37 (6)	2.06 (9)	n.s.	n.s.	4.42 (9)	2.92 (6)	1.32 (6)	1.28 (6)	0.67 (6)	n.s.	2.92 (3)	6.93 (10)	n.s.	0.76 (11)	-10.92 (11)	n.s.	
Poly-OH (%)	0.75	28.31	n.s.	n.s.	n.s.	4.99 (13)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	12.71 (23)	n.s.	n.s.	n.s.	n.s.	4.16 (10)	n.s.	n.s.	n.s.	7.04 (17)	n.s.	-4.99 (12)	-30.22 (25)	n.s.	
C3-Ketones (%)	0.95	23.28	n.s.	n.s.	n.s.	-8.97 (10)	-3.58 (4)	-4.50 (5)	-4.50 (5)	4.11 (4)	n.s.	6.73 (7)	n.s.	13.7 (18)	n.s.	n.s.	-4.78 (5)	-8.70 (9)	n.s.	5.85 (6)	n.s.	-18.9 (19)	n.s.	-4.38 (4)	14.95 (5)	n.s.	
C4-ketones (%)	0.95	11.86	n.s.	4.88 (5)	2.06	-4.02 (3)	-1.14 (5)	1.0 (4)	n.s.	0.74 (3)	-1.98 (8)	-1.21 (5)	n.s.	-2.48 (7)	n.s.	n.s.	2.65 (11)	0.91 (4)	2.85 (12)	-1.0 (4)	-6.89 (9)	n.s.	3.85 (5)	n.s.	n.s.	-1.43 (6)	
Cyclic Ketones (%)	0.93	9.08	1.68 (9)	n.s.	2.02 (11)	0.76 (4)	-1.98 (10)	1.82 (10)	0.79 (4)	n.s.	-0.89 (5)	n.s.	-4.1 (2)	n.s.	-3.60 (3)	4.40 (2)	3.01 (16)	0.88 (5)	n.s.	-0.97 (5)	n.s.	n.s.	n.s.	n.s.	9.94 (9)	0.93 (5)	
Furans (%)	1	0	n.s.	n.s.	n.s.	-3.86 (3)	2.76 (6)	-2.62 (5)	2.62 (5)	-3.55 (7)	3.55 (7)	-3.90 (8)	n.s.	n.s.	n.s.	3.86 (5)	-3.24 (7)	-3.24 (7)	-3.38 (7)	-2.45 (5)	2.45 (5)	-2.10 (4)	5.96 (4)	3.38 (7)	0.036 (1)	-2.76 (6)	

n.s.: Non significant with 95% confidence

Response = Ind. + Coefficient T·T + Coefficient P·P + Coefficient C·C + Coefficient W·W + Coefficient TC·T·C + Coefficient TW·T·W + Coefficient PC·P·C + Coefficient PW·P·W + Coefficient CW·C·W + Coefficient T²·T² + Coefficient P²·P² + Coefficient C²·C² + Coefficient W²·W² + Coefficient TPC·T·P·C + Coefficient TPW·T·P·W + Coefficient TCW·T·C·W + Coefficient PCW·P·C·W + Coefficient T²P·T²·P + Coefficient T²C·T²·C + Coefficient T²·W·T²·W + Coefficient T·P²·T·P² + Coefficient TPCW·T·P·C·W.

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.