

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

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**ABSTRACT**

Cheese effluent management has become an important issue owing to its high biochemical oxygen demand and chemical oxygen demand values. Given this scenario, this work addresses the valorisation of lactose (the largest organic constituent of this waste) by aqueous phase reforming, analysing the influence of the most important operating variables (temperature, pressure, lactose concentration and mass of catalyst/lactose mass flow rate ratio) as well as optimising the process for the production of either gaseous or liquid value-added chemicals. The carbon converted into gas, liquid and solid products varied as follows: 5-41%, 33-97% and 0-59%, respectively. The gas phase was made up of a mixture of H<sub>2</sub> (8-58 vol.%), CO<sub>2</sub> (33-85 vol.%), CO (0-15 vol.%) and CH<sub>4</sub> (0-14 vol.%). The liquid phase consisted of a mixture of aldehydes: 0-11%, carboxylic acids: 0-22%, monohydric alcohols: 0-23%, polyhydric-alcohols: 0-48%, C3-ketones: 4-100%, C4-ketones: 0-18 %, cyclic-ketones: 0-15% and furans: 0-85%. H<sub>2</sub> production is favoured at high pressure, elevated temperature, employing a high amount of catalyst and a concentrated lactose solution. Liquid production is preferential using diluted lactose solutions. At high pressure, the production of C3-ketones is preferential using a high temperature and a low amount of catalyst, while a medium temperature and a high amount of catalyst favours the production of furans. The production of alcohols is preferential using medium temperature and pressure and a 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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## 1. Introduction

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

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

and many more [10]. The bioconversion of lactose to ethanol has a theoretical maximum yield of 0.538 kg ethanol/kg of lactose [11, 12]. Anaerobic fermentation has a theoretical yield of 4 mol H<sub>2</sub>/mol lactose and produces a gas made up of a mixture of H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>.

Another interesting and very promising option for the treatment and valorisation of cheese whey effluents is aqueous phase reforming (APR). APR is a catalytic process carried out at quite low temperatures and moderate pressures that allows the simultaneous production of different gases and liquids from an organic feedstock. The gas phase consists of a gas with a high H<sub>2</sub> content, the liquid phase being a complex mixture of different organic compounds in water such as alcohols, ketones, acids, esters, aldehydes, furans, phenols and anhydro-sugars [13-16]. The product distribution strongly depends on the operating conditions under which the process is conducted. Therefore, APR can be customised either for the production of gases, helping to reduce the BOD and COD values of the feed or for the production of valuable liquids. In addition, the APR process dispenses with the need to vaporise the water and the organic compounds of the feedstock, thus reducing the energy requirements [17]. To the best of the authors' knowledge, there are no studies in the literature concerning the effect of the operating conditions on the aqueous phase reforming of lactose or cheese whey. Skoglund and Holles [18] developed different pseudomorphic overlayer catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) for the aqueous phase reforming of lactose. Furthermore, works dealing with the aqueous phase reforming of sugars are very scarce. Such studies that there are analyse the 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/Al<sub>2</sub>O<sub>3</sub>, Pt/TiO<sub>2</sub>  
103 and Pt-Re/TiO<sub>2</sub>. Xi et al. [21] prepared different M/NbOPO<sub>4</sub> 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 Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>. Kirilin et al. [23] investigated the APR of xylitol and sorbitol  
109 using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Godina et al. [24] analysed the APR of sorbitol and galactitol  
110 using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in a continuous fixed-bed reactor at 225 °C.

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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  $W/m_{\text{lactose}}$  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

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

## **2. Experimental**

### *2.1 Materials*

The experiments were carried out in a small bench scale continuous unit for 3 hours employing a Ni-La/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was prepared by coprecipitation, having 28% (relative atomic percentage) of Ni expressed as Ni/(Ni+Al+La), an atomic La/Al ratio of 0.035 and a Brunauer-Emmett-Teller (BET) surface area of 187 m<sup>2</sup>/g. The lactose solutions were prepared dissolving D-lactose monohydrate (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>·H<sub>2</sub>O Sigma Aldrich, CAS Number 64044-51-5, Bio-Ultra >99.5 % HPLC) in Milli-Q water.

### *2.2 Experimental rig*

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

condensers where the liquid products are separated from the gas mixture at intervals of 1 h to analyse the evolution over time of the liquid phase. The gas mixture is made up of  $N_2$ , used as an internal standard, and the different gaseous products formed during the aqueous phase reforming reaction. An Agilent M3000 micro chromatograph equipped with thermal conductivity detectors (TCD) was used for the online analysis of the gas phase. The liquid fractions were collected and analysed offline with a gas chromatograph (Agilent 7890 GC-system, model G3440A) equipped with Flame Ionization (FID) and Mass Spectrometry (MS) detectors. A schematic diagram of the experimental system is shown in Figure S1.

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

The effect of the temperature (200-240 °C), pressure (38-50 bar), lactose concentration (1-10 wt.%) and catalyst mass/lactose mass flow rate ratio ( $W/m_{\text{lactose}} = 10-40$  g catalyst min/g lactose) was experimentally analysed using a design of experiments (DOE) with statistical analysis of the results carried out by means of an analysis of variance (ANOVA). The effect of the operating conditions on the process was analysed for the following response variables: global lactose conversion (X lactose, %), carbon conversion to gas, liquid and solid products (CC gas %, CC liq %, and CC sol %) as well as the composition of the gas ( $N_2$  and  $H_2O$  free, vol.%) and liquid (relative chromatographic area free of water and un-reacted lactose, %). Table S1 summarises the response variables and the analytical methods used for their calculation.

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

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

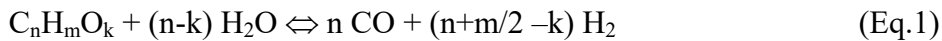
For the analysis of the results, firstly the evolution over time of the response variables was studied. To do this, the results were divided into three intervals, each corresponding to the average value of the studied response variables obtained during each one of the three hours of experiment. All these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



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

#### 2.4 Possible reaction network for lactose aqueous phase reforming

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



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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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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].

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#### 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 methylidihydrofuran-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 furomethanol 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

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

### 3. Results and discussion

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

A complete and steady global lactose conversion (X lactose) was achieved in all the experiments, indicating that all the lactose was converted into gas, liquid and solid products. The C/O ratio close to 1 of lactose allows a complete conversion to be achieved [34, 43]. Figure S2 shows the CC gas, CC liq and CC sol obtained for the experiments, which vary as follows: 5-41%, 33-97% and 0-59%, respectively. Increases and reductions in these variables over time are detected in some experiments.

The general trend for the CC gas is a steady evolution. However, decreases over time occur for some experiments (2-4, 6, 8, 13-15, 23, 24, 27 and 29). These decreases are particularly marked for experiments 8, 13, 15 and 29. One exception is experiment 8, where a lower  $W/m_{\text{lactose}}$  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 H<sub>2</sub> and CO<sub>2</sub> 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<sub>lactose</sub> 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 C<sub>8</sub> to C<sub>15</sub> [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-

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

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

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

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

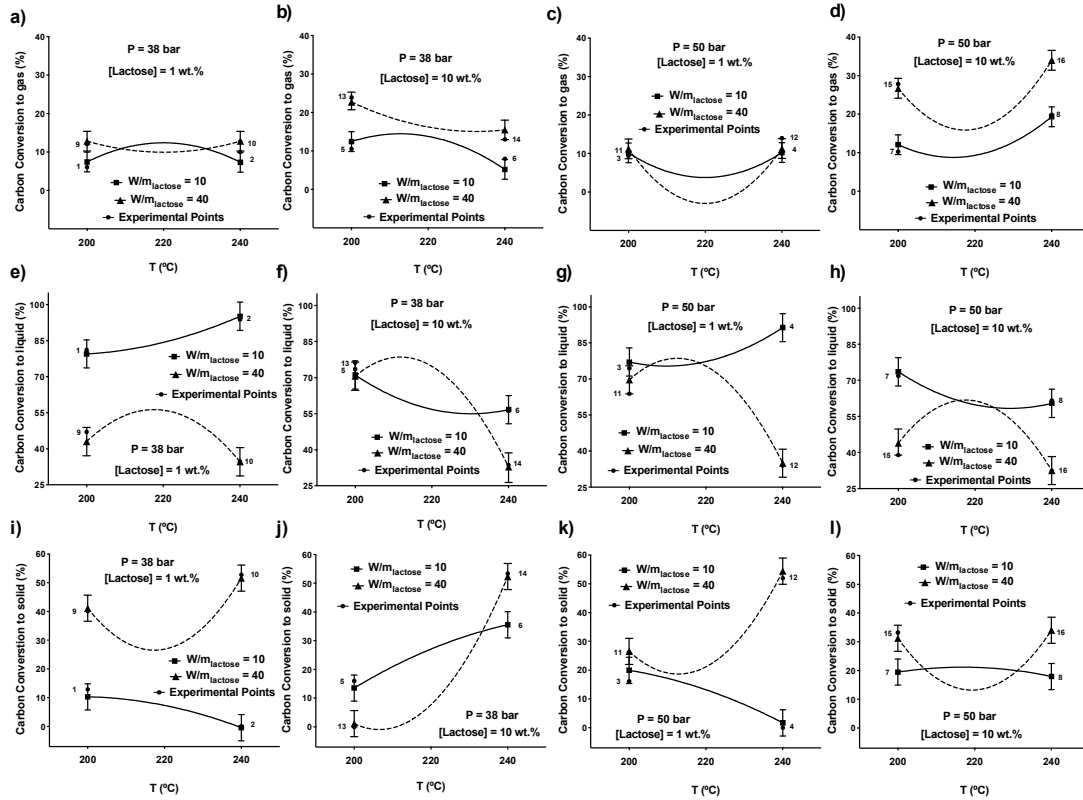


Figure 2. Interaction plots for the initial CC gas (a-d), CC liq (e-h) and CC sol conversion (i-l). Bars are LSD intervals with 95% confidence.

### 3.1.1 Carbon conversion to gas: CC gas

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



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

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

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

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

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

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

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

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

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

The effect of the temperature on the CC liq and CC sol depends on the concentration of lactose in the solution and the  $W/m_{\text{lactose}}$  ratio. For a 1 wt.% lactose solution and a  $W/m_{\text{lactose}}$  ratio of 10 g catalyst min/g lactose, an increase in the reaction temperature increases the CC liq and decreases the CC sol regardless of the pressure. Conversely, when a  $W/m_{\text{lactose}}$  ratio of 40 g catalyst min/g lactose is used, the CC liq increases between 200° and 220° and decreases with a further increase in the temperature up to 240 °C regardless of the lactose concentration. For a 10 wt.% lactose solution different evolutions for the CC liq and CC sol are observed depending on the temperature, pressure and  $W/m_{\text{lactose}}$  ratio. An increase in temperature decreases the CC liq and increases the CC sol when a  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  ratio depends on the lactose concentration and pressure. At  
466 38 bar, an increase in the  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  ratio mitigates char formation and/or helps its removal. At temperatures  
479 between 230 °C and 240 °C this increase in the  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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].

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

Figure S3 shows the composition of the gas obtained for the experiments divided into three intervals of 60 minutes each. The gas phase is made up of a mixture of H<sub>2</sub> (8-58 vol.%), CO<sub>2</sub> (33-90 vol.%), CO (0-18 vol.%) and CH<sub>4</sub> (0-14 vol.%). As regards the evolution of the gas composition over time, H<sub>2</sub> and CO<sub>2</sub> display the greatest variations. Statistically significant decreases are detected for the proportion of H<sub>2</sub>, while increases occur for the relative amount of CO<sub>2</sub> in the gas.

This H<sub>2</sub> depletion was also observed in the work of Kirilin et al. [23] during the APR of xylitol and sorbitol. They reported that the oxygenated compounds formed during the APR process might adsorb on the surface of the catalyst, thus hindering the catalyst performance and leading to a decrease in the H<sub>2</sub> selectivity. This development is also responsible for the increase in the proportion of CO<sub>2</sub> in the gas over time, as thermal lactose decomposition might be more favoured over reforming with the progressive deactivation of the catalyst. In addition, the decrease in the proportion of H<sub>2</sub> in the gas may also be attributed to the structural changes of the alumina of the support [23]. The alumina of the catalyst support can be transformed into boehmite by water [52, 55, 56]. This transformation was reported in a previous work where this catalyst was used for the APR of crude glycerol [25].

The proportions of CO and CH<sub>4</sub> remain steady for the vast majority of the experiments. In general, small variations are detected for the proportion of CO in the gas. One exception is experiment 16, where a relatively high increase in the proportion of CO over time takes place. The proportion of CH<sub>4</sub> shows small variations over time. In some

experiments an initial decrease in the proportion of CH<sub>4</sub> takes place between the first and second hour of reaction, along with a posterior increase in its relative amount between the second and third hour. However, these variations are not important from a practical point of view due to the relatively low amount of CH<sub>4</sub> in the gas.

The specific effects of the operating conditions as well as their possible interactions on the volumetric composition of the gas were studied considering the results obtained during the first 60 minutes of reaction. Table S4 shows the results of the statistical analyses performed. These analyses show that the temperature, the W/m<sub>lactose</sub> ratio and the interaction between these two operating variables are the variables with the greatest influence on the proportion of H<sub>2</sub> in the gas. The temperature and the W/m<sub>lactose</sub> are the operating variables exerting the greatest influence on the proportion of CO<sub>2</sub>. The concentration of CO in the gas is mostly affected by the interactions between the temperature and the concentration of lactose (TC and T<sup>2</sup>C). The concentration of lactose substantially influences the relative amount of CH<sub>4</sub> in the gas.

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



lactose concentration, the lower the amount of water and consequently the higher is the partial pressure of  $H_2$  [25]. A further increase in the temperature from 220 to 240 °C results in a substantial increase in the  $H_2$  concentration regardless of the lactose concentration and pressure. The  $H_2$  solubility in the liquid phase decreases with the temperature, diminishing the extent of the hydrogenation reactions, thus augmenting the proportion of  $H_2$  in the gas especially between 220 and 240 °C [37]. In addition, the reforming reactions are endothermic while the WGS reaction is exothermic, which also results in an increase in  $H_2$  with the temperature [13, 17].

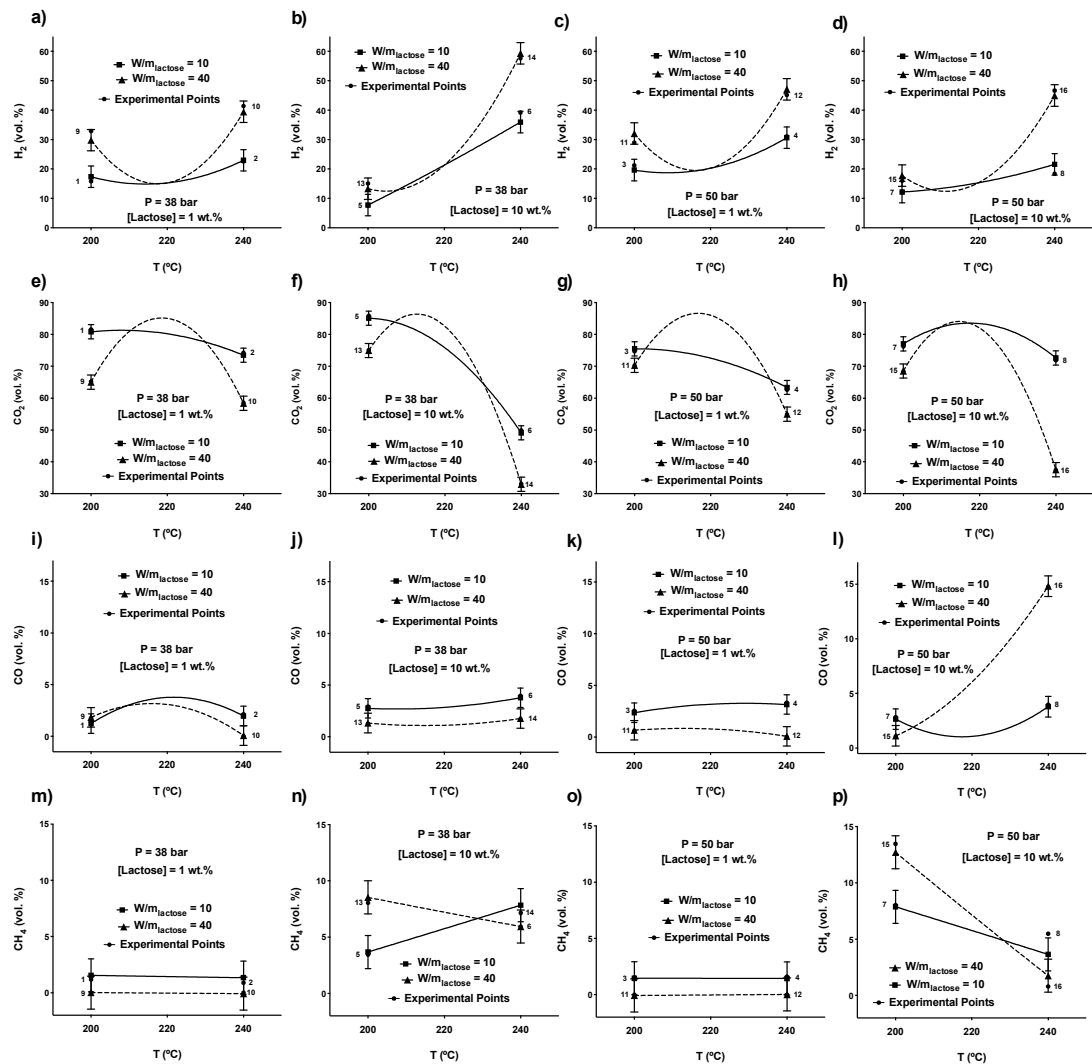


Figure 3. Interaction plots for initial relative amounts (vol.%) of  $H_2$  (a-d),  $CO_2$  (e-h)  $CO$  (i-l) and  $CH_4$  (m-p) in the gas. Bars are LSD intervals with 95% confidence.

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

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

the effect of the lactose concentration on the relative amount of  $H_2$ . As a result, the effect of the lactose concentration on the proportion of  $H_2$  for a  $W/m_{\text{lactose}}$  ratio of 40 g catalyst min/g lactose is not significant, while the proportion of  $CO_2$  decreases slightly between 230 to 240 °C. Under these conditions the decrease in the proportion of  $CO_2$  is the consequence of the increase observed in the proportion of CO in the gas.

A comparison between Figures 3 a/e and b/f with 3 c/g and d/h shows the effect of the total pressure on the proportion of  $H_2/CO_2$  in the gas when lactose solutions of 1 and 10 wt.% are fed, respectively. This comparison reveals that the effect of the pressure depends on the concentration of lactose. For a 1 wt.% lactose solution and 10 g catalyst min/g lactose, an increase in the total pressure from 38 to 50 bar does not greatly modify the proportions of  $H_2$  and  $CO_2$  in the gas. Conversely, for 40 g catalyst min/g lactose, this increase in pressure slightly increases the proportion of  $CO_2$  between 200 and 220 °C; the effect of the pressure being insignificant from 220 to 240 °C. For a 10 wt.% lactose solution the effect of the pressure depends on the reaction temperature. The pressure does not exert a great impact between 200 and 220 °C, while the proportions of these two gases are greatly modified with varying the system pressure when a temperature between 220 and 240 °C is used. From 220 to 240 °C, an increase in pressure from 38 to 50 bar leads to a decrease in the relative amount of  $H_2$  when using a  $W/m_{\text{lactose}}$  ratio of 10 g catalyst min/g lactose. In addition, these variations depend on the  $W/m_{\text{lactose}}$  ratio; the lower the ratio, the greater are the variations in the proportions of  $H_2$  and  $CO_2$ . An increase in pressure produces an increase in the partial pressure of the reagents inside the reactor, which promotes their transformation into gases [25] due to an increase in the rate of C-C bond cleavage reactions [52] favouring  $H_2$  production.

### 637 3.2.2 CO and CH<sub>4</sub>

638 The effect of the operating variables on the proportions of CO and CH<sub>4</sub> 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 H<sub>2</sub> and CO<sub>2</sub>, 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<sub>lactose</sub> 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<sub>lactose</sub> 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<sub>lactose</sub> 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<sub>lactose</sub> 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

The effect of the temperature on the proportion of CH<sub>4</sub> in the gas depends on the concentration of lactose, pressure and W/m<sub>lactose</sub> ratio. Specifically, the temperature does not significantly influence the proportion of CH<sub>4</sub> for a diluted lactose solution (1 wt.%), while it exerts a moderate influence for a 10 wt.% lactose solution. For a 10 wt.% solution the effect of the temperature depends on the pressure and the W/m<sub>lactose</sub> ratio. At 38 bar, an increase in the reaction temperature increases the proportion of CH<sub>4</sub> for a low W/m<sub>lactose</sub> ratio, while this increase in temperature decreases the relative amount of CH<sub>4</sub> for a high W/m<sub>lactose</sub> ratio. At 50 bar, an increase in temperature leads to a decrease in the proportion of CH<sub>4</sub> in the gas regardless of the W/m<sub>lactose</sub> ratio. The decreases in the proportion of CH<sub>4</sub> in the gas are the consequence of the endothermic nature of the methane reforming reaction [14] which is thermodynamically favoured at high temperatures and kinetically promoted using a high W/m<sub>lactose</sub> ratio.

As a result of the dependence of the effect of the temperature with the lactose concentration and the W/m<sub>lactose</sub> ratio, the effect of the W/m<sub>lactose</sub> ratio is only significant for a 10 wt.% lactose solution. The lower excess of water for a concentrated lactose solution reduces the development of the methane reforming reactions, increasing the proportion of CH<sub>4</sub> in the gas [57-61]. For a concentrated solution, an increase in this ratio (from 10 to 40 g catalyst min/g lactose) increases the proportion of CH<sub>4</sub> in the gas between 200 and 220 °C, as methanation is favoured within this temperature range [25].

The effect of the total pressure is only significant for a 10 wt.% lactose solution. Between 200 and 220 °C an increase in pressure leads to an increase in the proportion of CH<sub>4</sub> in the gas, while a further increase up to 240 °C reduces the relative amount of this gas.

### 3.3 Effect of the operating conditions on the composition of the liquid phase

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

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

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

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

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

Figures 4 and 5 illustrate the effect of these interactions according to the ANOVA analysis for the relative amounts of the most abundant compounds present in the liquid phase. Figure 4 displays these effects for the proportions of carboxylic acids, monohydric and polyhydric alcohols, and aldehydes, while Figure 5 shows these effects for the proportions of C3, C4 and cyclic ketones and furans. Specifically, the effects of the reaction temperature, employing a pressure of 38 bar for  $W/m_{\text{lactose}}$  ratios of 10 and 40 g catalyst min/g lactose, feeding lactose concentrations of 1 and 10 wt.%, are shown 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 h, k and l, and o and p display the effects of the temperature and the  $W/m_{\text{lactose}}$  ratio employing a pressure of 50 bar when lactose solutions of 1 and 10 wt.% were used, respectively.



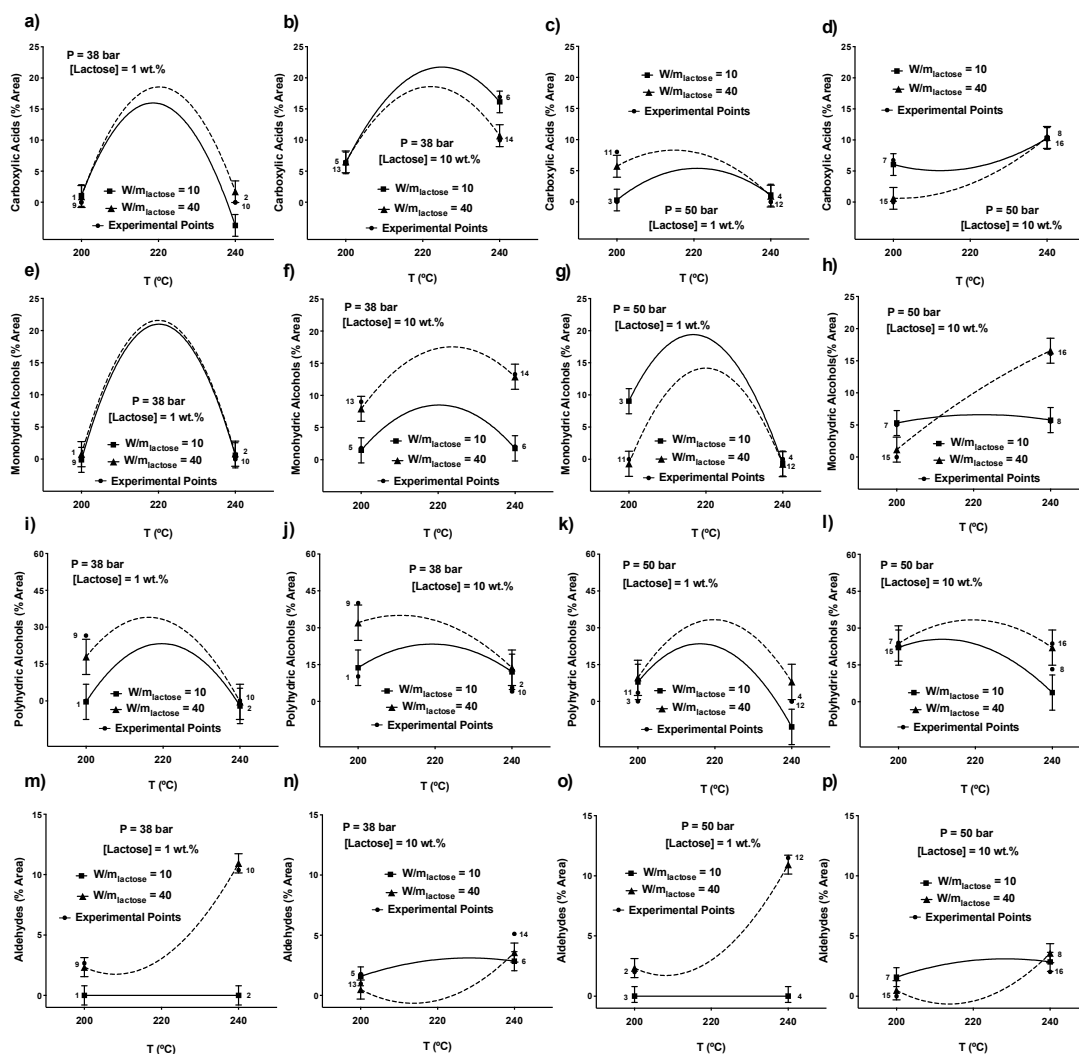


Figure 4. Interaction plots for the relative amounts in the liquid of carboxylic acids (a-d), monohydric alcohols (e-h), polyhydric alcohols (i-l) and aldehydes (m-p). Bars are LSD intervals with 95% confidence.

### 3.3.1 Carboxylic acids

Acetic and propionic acids are the most abundant carboxylic acids in the liquid phase.

Propionic acid formation occurs to a lesser extent due to the higher proportion of 1-

hydroxypropan-2-one hydrogenated compounds than dehydrated compounds in the

liquid. Acetic acid is mainly responsible for the variations observed in the proportion of

carboxylic acids during the first hour of reaction (Figures 4 a-d). Acetic acid is obtained

in the final steps of routes A and B. The temperature exhibits two different effects on

the proportion of carboxylic acids depending on the pressure. At 38 bar an increase in the temperature leads to an initial increase in the proportion of carboxylic acids from 200 to 220 °C followed by a substantial decrease between 220 and 240 °C. In addition, this latter depletion strongly depends on the concentration of lactose in the feed; the lower the concentration of lactose, the sharper is the decrease observed. The temperature exerts a positive catalytic effect on the process. Therefore, between 200 and 220 °C, an increase in temperature helps the formation of liquid end products. A further increase in temperature might shift their decomposition to gases. In addition, high temperatures can also partially hinder acetic acid formation as the solubility of H<sub>2</sub> in water decreases with temperature. Conversely, at 50 bar the temperature exerts a weaker effect on the relative amount of carboxylic acids. This increase in pressure kinetically enhances the acetic acid decomposition rate [25]. This effect depends on the lactose concentration. For a 1 wt.% lactose solution a mild increase with temperature occurs between 200 and 220 °C, followed by a small decrease from 220 to 240 °C. However, this evolution with temperature is not as pronounced as it is at 38 bar. For a 10 wt.% lactose solution, the effect of the temperature is negligible between 200 and 220 °C, while a small increase takes place with a further increase in the temperature up to 240 °C.

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

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

### *3.3.2 Alcohols: monohydric and polyhydric alcohols*

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

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

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

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

At 50 bar two different trends are observed depending on the  $W/m_{\text{lactose}}$  ratio for a 10 wt.% lactose solution. When using a  $W/m_{\text{lactose}}$  ratio of 10 g catalyst min/g lactose, an increase in the temperature does not significantly modify the proportion of monohydric alcohols but slightly decreases the proportion of polyhydric alcohols. High temperature and pressure favours dehydration reactions from sugars [27, 28, 31, 33], and therefore a low proportion of liquid end products obtained via routes A and B is achieved. Conversely, for 40 g catalyst min/g lactose, this increment in the temperature produces a sharp increase in the proportion of monohydric alcohols, without greatly modifying the proportion of polyhydric alcohols. This might account for the increase in the concentration of end products obtained from routes A and B.

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

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

881

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

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

### 3.3.3 Aldehydes

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

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

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

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



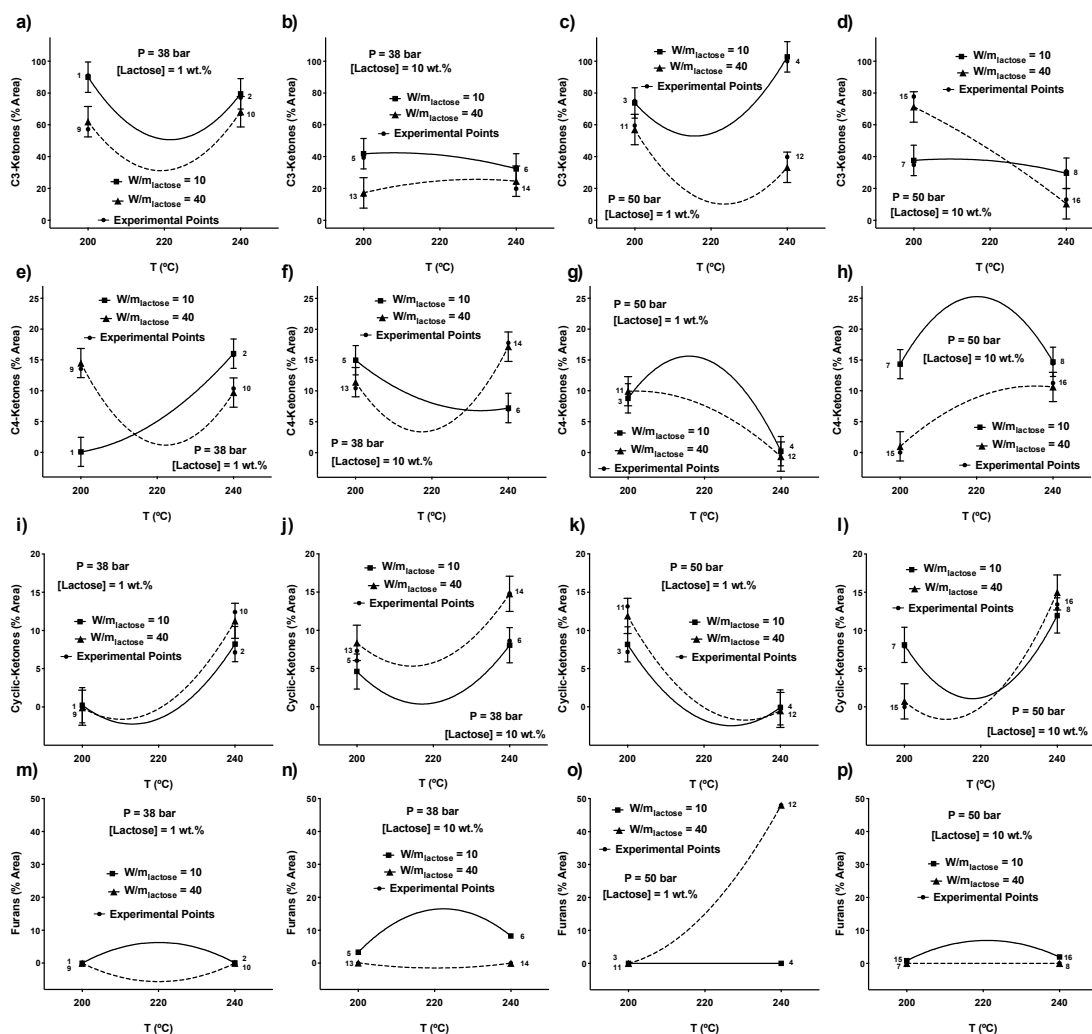


Figure 5. Interaction plots for the relative amounts in the liquid of C3-ketones (a-d), C4-ketones (e-h), cyclic ketones (i-l) and furans (m-p). Bars are LSD intervals with 95% confidence.

The effect of the temperature depends on the lactose concentration and pressure. For a 1 wt.% lactose solution, the proportion of C3-ketones decreases from 200 to 220 °C and increases with a further increase in the temperature up to 240 °C, regardless of the pressure and the  $W/m_{\text{lactose}}$  ratio. Between 200 and 220 °C an increase in temperature kinetically produces a greater spread of hydrogenation reactions in the liquid. However, the  $H_2$  solubility in water decreases with a further increase in temperature up to 240 °C, thus hindering the hydrogenation of ketones to alcohols. This accounts for the increase observed in ketones and the decreases observed in the proportions of monohydric and

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

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

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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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

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

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

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

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

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

Cyclopentanone, 2-hydroxy-3-methyl-2-cyclopenten-1-one and 2-methyl-2-cyclopenten-1-one are responsible for the variations observed in the proportion of cyclic ketones during the first hour of reaction. These ketones are obtained from the hydrogenation of different liquid intermediates obtained through the decomposition of 5-hydroxymethyl-2-furancarboxaldehyde, which is obtained from glucose/galactose dehydration (route C). The effect of the temperature depends on the pressure. On the one hand, at 38 bar and regardless of the  $W/m_{\text{lactose}}$  ratio and lactose concentration, the temperature does not significantly influence the proportion of cyclic ketones between 200 and 220 °C, while an increase in the relative amount of this family of ketones occurs as the temperature increases from 220 to 240 °C. The decrease in the  $H_2$  solubility with temperature might be responsible for the increase observed in this family of compounds, as this  $H_2$  limitation stops the advancement of the reaction in the liquid phase towards end products obtained through route C. In addition, high temperatures favour route C over routes A and B [27, 28, 31, 33], which accounts for the increase in 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  $W/m_{\text{lactose}}$   
1075 ratio from 10 to 40 g catalyst min/g lactose increases the concentration of cyclic ketones  
1076 in the liquid. The  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$   
1085 ratio this decrease accounts for the increase in the proportion of C3-ketones, while for a  
1086 high  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  ratio of 40 g catalyst min/g lactose. Between 220  
1092 and 240 °C, the  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  ratio.

1151 When a  $W/m_{\text{lactose}}$  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  $W/m_{\text{lactose}}$  ratio modifies the effect of the pressure. The proportion of furans augments

1156 when the  $W/m_{\text{lactose}}$  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. H<sub>2</sub> 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 <sub>lactose</sub> (g <sub>cat</sub> min/g <sub>lactose</sub> )	CC gas (%)	CC liq (%)	CC sol (%)	H <sub>2</sub> (vol.%)	Alcohols (%)	C3-ketones (%)	Furans (%)
1	CC gas, H <sub>2</sub> (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 H<sub>2</sub> production at the highest values of the temperature, pressure, lactose concentration  
 1182 and W/m<sub>lactose</sub> ratio used in this work. Under these conditions 4 mol H<sub>2</sub>/mol lactose is  
 1183 produced. This H<sub>2</sub> yield is similar to that obtained in anaerobic fermentation (4 mol  
 1184 H<sub>2</sub>/mol lactose) and anaerobic fermentation plus photo-fermentation with L-malic acid  
 1185 (2-10 mol H<sub>2</sub>/mol lactose), but lower than the H<sub>2</sub> yield obtained during the catalytic  
 1186 steam reforming of lactose (16 mol H<sub>2</sub>/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<sub>lactose</sub> 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

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

#### **4. Conclusions**

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

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## SUPPLEMENTARY MATERIAL

### FIGURES

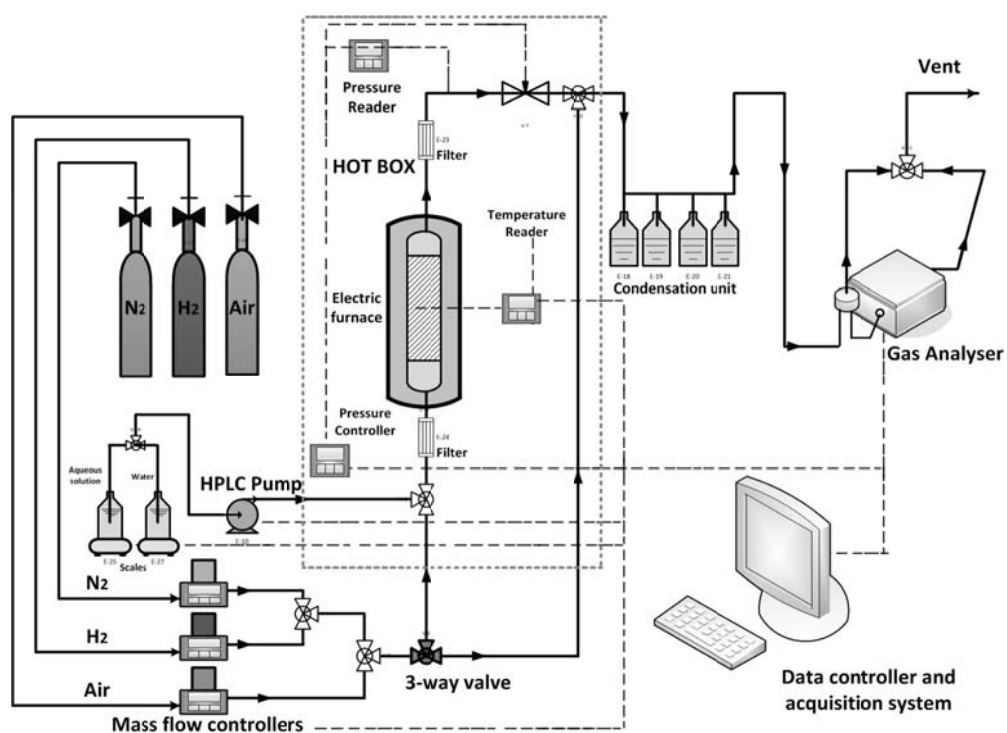


Figure S1. Schematic diagram of the aqueous phase reforming experimental rig.

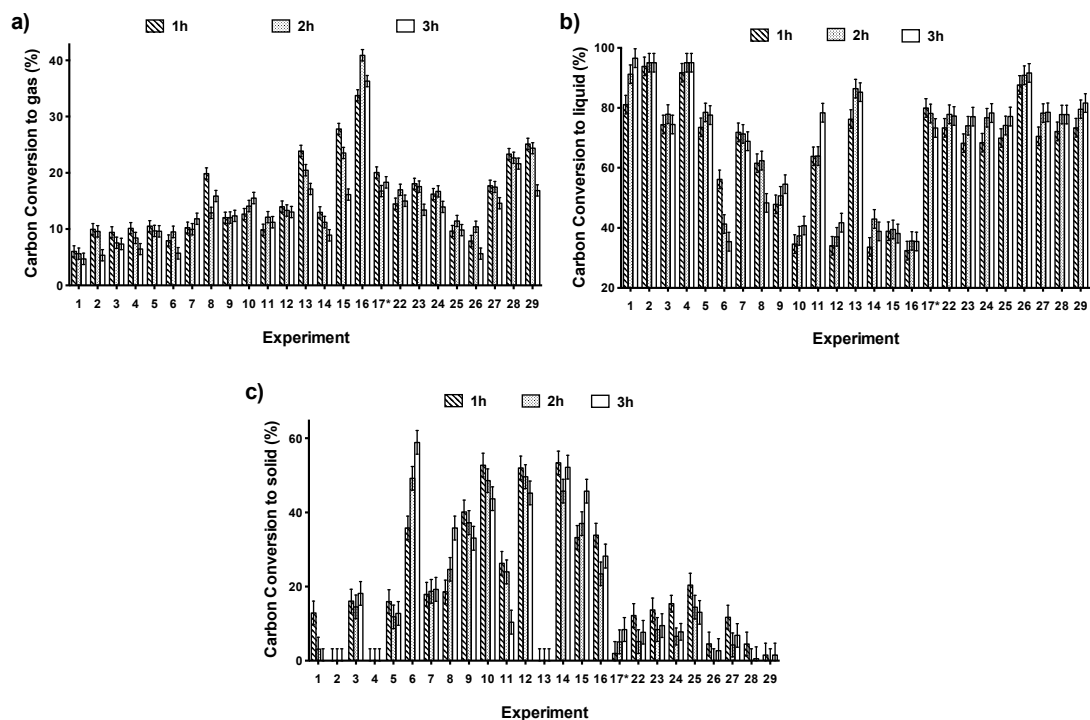


Figure S2. Carbon conversion to gas (a), liquid (b) and solid (c) obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean  $\pm 0.5$  Fisher LSD intervals with 95% confidence.

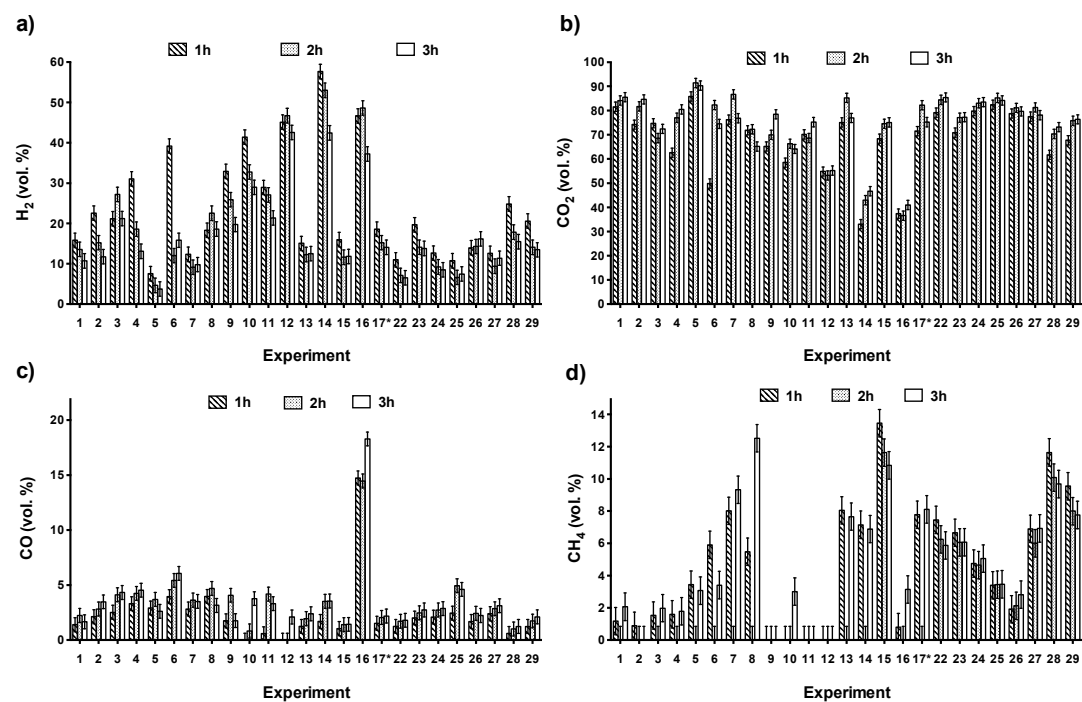


Figure S3. Relative amounts (vol.%) of H<sub>2</sub> (a), CO<sub>2</sub> (b) CO (c) and CH<sub>4</sub> (d) in the gas obtained during the APR experiments. Results are presented as the overall values obtained every 60 minutes and expressed as mean  $\pm 0.5$  Fisher LSD intervals with 95% confidence.

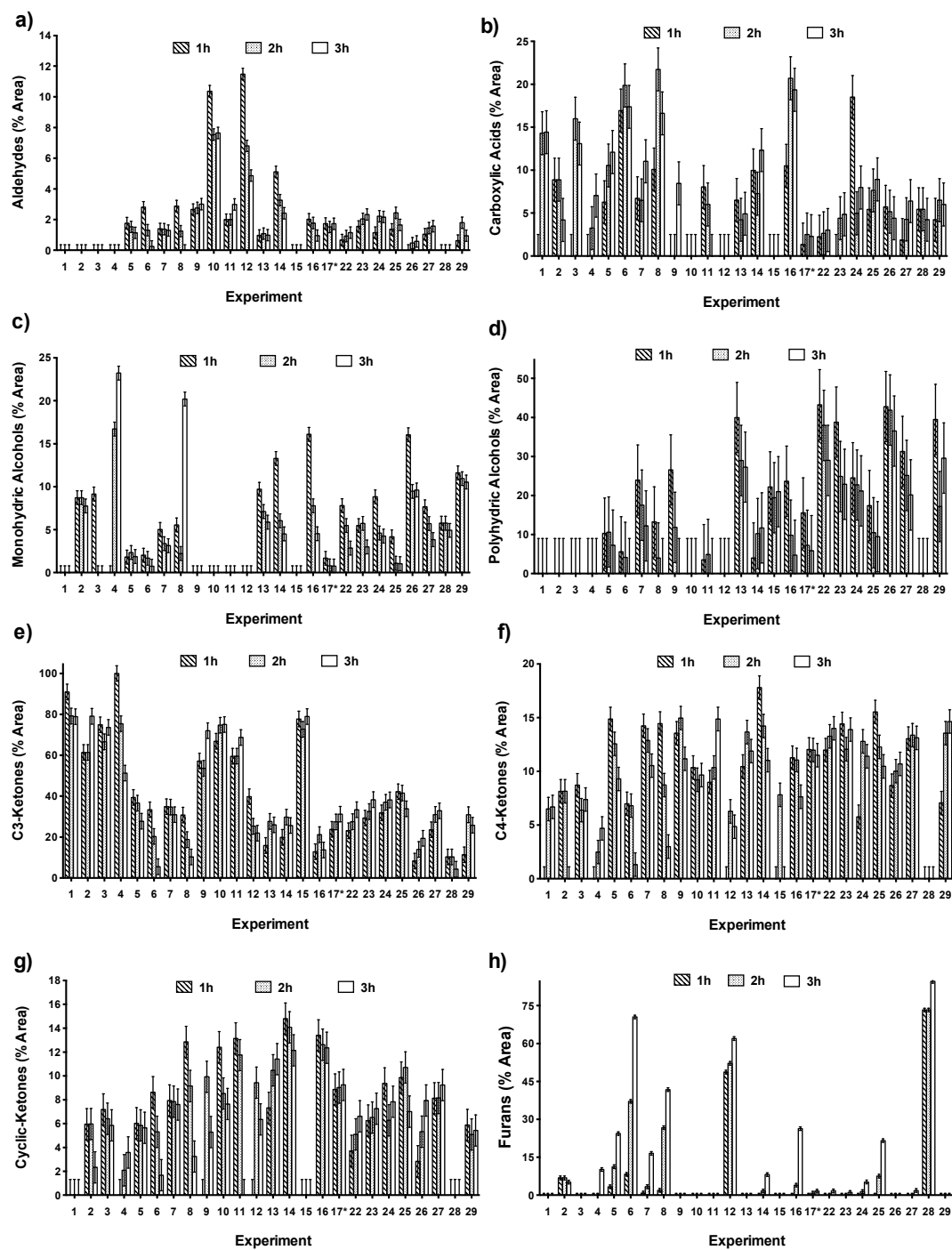


Figure S4. Proportions (% chromatographic area) of aldehydes (a), carboxylic acids (b), monohydric alcohols (c), polyhydric alcohols (d), C3-ketones (e), C4-ketones (f), cyclic ketones (g) and furans (h) in the liquid obtained during the APR experiments. Results are presented as the overall values obtained 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 <sub>2</sub> as internal standard
	$Composition\ (vol.\ \%) = \frac{mol\ of\ each\ gas}{total\ mol\ of\ gas} 100$	Online analyses
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)		Wcatalyst/m <sub>lactose</sub> (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 <sup>2</sup>	Indep.	T	P	C	W	TP	TC	TW	PC	PW	CW	T <sup>2</sup>	P <sup>2</sup>	C <sup>2</sup>	W <sup>2</sup>	TPC	TPW	TCW	PCW	T <sup>2</sup> P	T <sup>2</sup> C	T <sup>2</sup> W	TP <sup>2</sup>	T <sup>2</sup> P <sup>2</sup>	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 T<sup>2</sup>·T<sup>2</sup> + Coefficient P<sup>2</sup>·P<sup>2</sup> + Coefficient C<sup>2</sup>·C<sup>2</sup> + Coefficient W<sup>2</sup>·W<sup>2</sup> + Coefficient TPC·T·P·C + Coefficient TPW·T·P·W + Coefficient TCW·T·C·W + Coefficient PCW·P·C·W + Coefficient T<sup>2</sup>P·T<sup>2</sup>·P + Coefficient T<sup>2</sup>C·T<sup>2</sup>·C + Coefficient T<sup>2</sup>W·T<sup>2</sup>·W + Coefficient TP<sup>2</sup>·T·P<sup>2</sup> + 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 <sup>2</sup>	Ind.	T	P	C	W	TP	TC	TW	PC	PW	CW	T <sup>2</sup>	P <sup>2</sup>	C <sup>2</sup>	W <sup>2</sup>	TPC	TPW	TCW	PCW	T <sup>2</sup> P	T <sup>2</sup> C	T <sup>2</sup> W	TP <sup>2</sup>	T <sup>2</sup> P <sup>2</sup>	TPCW
H <sub>2</sub> (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 <sub>2</sub> (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 (3)	-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	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 (6)	
CH <sub>4</sub> (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	
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	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	7.74 (14)	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	n.s	2.92 (3)	6.93 (10)	n.s	0.76	-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 (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 T<sup>2</sup>·T<sup>2</sup> + Coefficient P<sup>2</sup>·P<sup>2</sup> + Coefficient C<sup>2</sup>·C<sup>2</sup> + Coefficient W<sup>2</sup>·W<sup>2</sup> + Coefficient TPC·T·P·C + Coefficient TPW·T·P·W + Coefficient TCW·T·C·W + Coefficient PCW·P·C·W + Coefficient T<sup>2</sup>P·T<sup>2</sup>·P + Coefficient T<sup>2</sup>C·T<sup>2</sup>·C + Coefficient T<sup>2</sup>·W·T<sup>2</sup>·W + Coefficient T·P<sup>2</sup>·T·P<sup>2</sup> + 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.