

1 **Hydrogen production from cheese whey by catalytic steam reforming: Preliminary**  
2 **study using lactose as a model compound**

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12 **ABSTRACT**

13 Cheese whey is a yellowish liquid by-product of the cheese making process. Owing to  
14 its high BOD and COD values, this feedstock should not be directly discharged into the  
15 environment without appropriate treatment. Before dealing with real cheese whey, this  
16 work addresses the production of a rich hydrogen gas from lactose (the largest organic  
17 constituent of this waste) by catalytic steam reforming. This reforming process has been  
18 theoretically and experimentally studied. The theoretical study examines the effect of  
19 the temperature (300-600 °C), lactose concentration (1-10 wt.%) and N<sub>2</sub> (0-80 cm<sup>3</sup>  
20 STP/min) and liquid flow (0.1-0.5 mL/min) rates on the thermodynamic composition of  
21 the gas. The results show that the temperature and lactose concentration exerted the  
22 greatest influence on the thermodynamics. The experimental study, conducted in a fixed  
23 bed reactor using a Ni-based catalyst, considers the effect of the temperature (300-600  
24 °C), lactose concentration (1-10 wt.%) and spatial time (4-16 g catalyst min/ g lactose)  
25 on the global lactose conversion, product distribution on a carbon basis (gas, liquid and  
26 solid) and the compositions of the gas and liquid phases. Complete lactose conversion  
27 was achieved under all the experimental conditions. The carbon converted into gas,  
28 liquid and solid was 2-97%, 0-66% and 0-94%, respectively. The gas phase was made  
29 up of a mixture of H<sub>2</sub> (0-70 vol.%), CO<sub>2</sub> (20-70 vol.%), CO (2-34 vol.%) and CH<sub>4</sub> (0-3  
30 vol.%). The liquid phase consisted of a mixture of aldehydes, ketones, carboxylic acids,  
31 sugars, furans, alcohols and phenols. Optimal conditions for cheese whey valorisation

1 were sought considering the energetic aspects of the process. Using a lactose  
2 concentration similar to that of cheese whey (5.5 wt.%), maxima for the CC gas (88%)  
3 and the proportion of H<sub>2</sub> (67 vol.%) in the gas together with a carbon-free liquid stream  
4 can be achieved at 586 °C using a spatial time of 16 g catalyst min/g lactose.  
5 Theoretically, the combustion of 20% of this gas provides the energy necessary for the  
6 process enabling the transformation of 68% of the carbon present in the initial effluent  
7 into a H<sub>2</sub> rich gas (67 vol.%) with a global H<sub>2</sub> yield of 16 mol H<sub>2</sub>/mol lactose. In a real  
8 case it would be necessary to increase the amount of gas combusted to compensate for  
9 heat losses.

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11 **Keywords:** cheese whey, lactose, catalytic steam reforming, hydrogen production

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## 1 **1. Introduction**

2 Cheese whey is a yellowish liquid resulting from the coprecipitation and removal of  
3 milk casein in cheese making processes. On average, for the production of 1 kg of  
4 cheese 10 kg of milk are used, which produces 9 kg of cheese whey as a by-product.  
5 This is equivalent to 5 million tons a year of whey worldwide. Some of the most  
6 important components of whey are lactose and soluble proteins. Typically, cheese whey  
7 contains 4.5-6 wt.% lactose, 0.6-1.1 wt.% proteins, 0.8-1 wt.% minerals, 0.05-0.9 wt.%  
8 lactic acid, 0.06-0.5 wt.% fats and 93-94 wt.% of water [1-4]. This effluent produced by  
9 the cheese industry has BOD and COD values ranging from 27-60 kg/m<sup>3</sup> and 50-102  
10 kg/m<sup>3</sup>, respectively. Therefore, it should not be directly discharged into the environment  
11 without appropriate treatment and/or valorisation [3]. In the past, most cheese factories  
12 released their effluents onto land or discharged them into rivers, lakes and/or oceans  
13 without any pre-treatment. However, as a result of environmental concerns and stricter  
14 regulations, cheese effluent management has become an important issue [1-4].

15

16 In this context, two different options for cheese whey management have normally been  
17 considered [3]. The first is the application of filtration technologies and  
18 physicochemical treatments such as coagulation-flocculation. These technologies aim to  
19 recover the most valuable compounds from cheese whey such as proteins and lactose.  
20 Filtration technologies can be used to separate lactose and proteins from whey [3].  
21 Ultrafiltration membranes can be used to separate proteins and reverse osmosis to  
22 increase the lactose concentration in order to facilitate the evaporation of water and the  
23 crystallisation of lactose [2]. Physicochemical treatments include thermal and isoelectric  
24 precipitation [5, 6], as well as protein precipitation with coagulant/ flocculant agents [7].

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2 The second option relies on the application of biological treatments without  
3 valorisation, such as aerobic digestion, and with valorisation such as anaerobic  
4 digestion, lactose hydrolysis and fermentation for hydrogen and methane production  
5 [3]. Aerobic digestion consists of the degradation of the organic matter of whey at room  
6 temperature using short hydraulic retention times. However, the high organic content of  
7 cheese whey makes this technique inappropriate [8]. Anaerobic digestion takes place  
8 under mesophilic conditions (35-37 °C) where lactose can be converted into propionic  
9 acid, ethanol and lactose acetates [9]. Lactose hydrolysis constitutes a preliminary step  
10 for other biological processes, as the number of microorganisms able to metabolise  
11 glucose and galactose are significantly higher than those that directly metabolise lactose  
12 [4].

13

14 Cheese whey fermentation includes the production of ethanol, lactic acid, and hydrogen.  
15 The bioconversion of lactose to ethanol has a theoretical maximum yield of 0.538 kg  
16 ethanol/kg of lactose [10, 11]. However, cheese whey fermentation is hardly  
17 economically competitive if compared to other feedstocks, particularly when using  
18 diluted cheese whey solutions [3]. To improve the economy of the process, the  
19 anaerobic fermentation of the permeate solution obtained after subjecting cheese whey  
20 to an ultrafiltration process has been considered, increasing the concentration of the  
21 ethanol produced by up to 12% [11]. The production of lactic acid has usually been  
22 carried out using the concentrated cheese whey coming from ultrafiltration [12-16]. The  
23 greatest limitation for the production of lactic acid from cheese whey is the low yield of  
24 the process (3.8-12 kg/m<sup>3</sup>).

1 Anaerobic fermentation processes have been conducted for hydrogen production from  
2 different cheese whey effluents: the original cheese whey [17, 18], diluted cheese whey  
3 solutions [19-21], concentrated whey powder [22-24] and permeates resulting from  
4 different filtration processes [25]. The anaerobic fermentation has a theoretical yield of  
5 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>.  
6 Different clostridium species [21] and facultative anaerobic species [24] have been used  
7 employing CSTR, batch, and UASB reactors [3]. COD reductions of around 80-90 %  
8 and lactose consumption between 87 and 97% have been reported [17-19, 21, 24, 25].  
9 However, the residual liquid feed is still unsuitable for disposal as it contains different  
10 organics such as acetic, propionic and butyric acids and ethanol together with unreacted  
11 lactose.

12

13 The presence of these compounds in the residual stream has led other authors [17, 18] to  
14 consider this residual effluent from H<sub>2</sub> production for CH<sub>4</sub> generation in anaerobic  
15 continuous bioreactors. A COD removal of 95.3% has been achieved, with 2.2 kg/m<sup>3</sup> of  
16 COD remaining after the two anaerobic processes. Azbar and Dokgoz [19] treated this  
17 effluent by photo-fermentation with *Rhodospseudomonas palustris* in a two-step  
18 biological process. The authors concluded the process was inadequate due to the  
19 presence of nitrogen and volatile fatty acids in the solution. Diluting this effluent with  
20 L-malic acid, which simultaneously improves hydrogen production, can partially solve  
21 this problem and a final yield of 2-10 mol H<sub>2</sub>/mol lactose has been reported. However,  
22 the energy supplementation and the need for large volume bioreactors makes the  
23 process unreliable [3].

24

1 Another interesting option for the treatment and valorisation of cheese whey effluents  
2 that has not been considered before is the use of thermochemical processes. Among  
3 these, catalytic steam reforming represents a challenging and promising alternative for  
4 the treatment of these residues. Steam reforming is one of the most widespread  
5 processes for the generation of a hydrogen-rich synthesis gas from organic compounds.  
6 This catalytic process, which is carried out at atmospheric pressure and at moderate  
7 temperatures, enables the organic matter of cheese whey to be transformed into a gas  
8 with a high hydrogen content, up to 70 vol.%, with many different posterior  
9 applications [26]. It also reduces the organic matter of the original feedstock to  
10 appropriate levels for safe discharge into the environment. A reaction pathway for  
11 lactose steam reforming is provided in section 2.4.

12

13 The catalyst plays an important role in catalytic steam reforming. Specifically, it must  
14 enhance the reaction rate of the reforming process, which includes both the reforming  
15 reaction and the subsequent water gas shift (WGS) reaction. In addition, it must have  
16 high deactivation resistance and sufficient strength if the process is to take place in a  
17 fluidised bed reactor [27, 28]. A good approach to this challenge is using Ni-based  
18 catalysts. A Ni-Co/Al-Mg catalyst, which has been proved to be suitable for the  
19 catalytic steam reforming of bio-oil aqueous fractions [29, 30], was selected for this  
20 work. This catalyst includes Ni as the active phase. Ni based catalysts meet the  
21 challenge of being active and selective towards  $H_2$ , although they are susceptible to  
22 deactivation by coking. Therefore, the catalyst was modified with Mg and Co. Mg was  
23 added as a support modifier, enhancing the water adsorption in order to gasify the coke  
24 or its precursors, as well as to provide more attrition resistance if the catalyst is to be  
25 used in a fluidised bed. Co was added as an active phase modifier to enhance the steam

1 reforming and WGS reactions and prevent catalyst deactivation by coking, as a Ni-Co  
2 interaction can be formed in the catalyst which reduces the crystallite size [30].  
3  
4 Having a theoretical hydrogen yield of 24 mol H<sub>2</sub>/mol lactose, this process could be  
5 postulated as a suitable alternative for the treatment and valorisation of cheese whey. To  
6 the best of the authors' knowledge, there are no studies in the literature concerning the  
7 catalytic steam reforming of cheese whey or lactose solutions. Furthermore, the works  
8 dealing with the catalytic steam reforming of sugars are extremely scarce. Hu and Lu  
9 [31] studied the catalytic steam reforming of glucose for H<sub>2</sub> production, analysing the  
10 effect of the reaction time (0-3 h), temperature (300-600 °C) and steam to carbon (S/C)  
11 ratio (3-9 mol H<sub>2</sub>O/mol C) on the process. Marquevich et al. [32] reported the effect of  
12 the temperature and S/C ratio on the catalytic steam reforming of xylose, glucose and  
13 sucrose. Both studies reached the same conclusions. An increase in the temperature  
14 increases gas production and the yield to H<sub>2</sub> and reduces char formation. The S/C ratio  
15 plays a very important role in the process, decreasing solid formation and enhancing gas  
16 production, therefore high S/C ratios are necessary to ensure a high carbon conversion  
17 to gas. These sugars are unstable at high temperatures and decompose before reaching  
18 the catalytic bed, which results in a serious formation of char in the upper part of the  
19 reactor, thus decreasing the efficiency of the process. Therefore, it was claimed in both  
20 works that minimising the thermal decomposition and avoiding char formation is one of  
21 the main challenges during the steam reforming of sugars.  
22  
23 Given this background, this work analyses the catalytic steam reforming of a lactose  
24 solution, both theoretically and experimentally, as a possible option for the treatment

1 and valorisation of cheese whey effluents and/or lactose solutions. The theoretical study  
2 addresses the effect of the temperature (300-600 °C), lactose concentration (1-10 wt.%),  
3 and N<sub>2</sub> (0-80 cm<sup>3</sup> STP/min) and liquid flow (0.1-0.5 mL/min) rates on the  
4 thermodynamics of the process. The experimental part includes an in depth study of the  
5 effect of the temperature (300-600 °C), lactose concentration (1-10 wt.%) and mass of  
6 catalyst/lactose mass flow ratio (4-16 g catalyst min/g lactose) in a fixed bed reactor  
7 using a Ni-based catalyst.

8

9 For cheese whey valorisation, it is not only important to produce a hydrogen rich gas  
10 from this waste, but also to come up with a carbon-free liquid stream that could be  
11 discharged to the environment. Therefore, the effect of the operating variables on gas,  
12 liquid and solid production and on the compositions of the gas and liquid phases has  
13 been exhaustively analysed. Furthermore, optimal values for the operating variables  
14 were sought and an energy balance was performed to provide a thorough technical and  
15 energetic analysis of the process. Given that the catalytic steam reforming of cheese  
16 whey or lactose solutions has never been reported before and that works dealing with  
17 the steam reforming of sugars are very scarce, this work represents a challenging and  
18 novel investigation not only for the management and valorisation of cheese whey but  
19 also for hydrogen production from sugars or sugar-based streams by catalytic steam  
20 reforming.

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## 1 **2. Experimental**

### 2 *2.1 Theoretical study*

3 Different simulations based on a 2 level 4 factor Box-Wilson Central Composite Face  
4 Centred (CCF,  $\alpha: \pm 1$ ) design were carried out to analyse the influence on the  
5 thermodynamic gas composition (vol.%) of the reforming temperature (300-600 °C),  
6 lactose concentration (1-10 wt.%), flow rate of N<sub>2</sub> (0-80 cm<sup>3</sup>STP/min) and liquid flow  
7 rate (0.1-0.5 mL/min). The gas composition (vol.%) was theoretically calculated with  
8 the aid of the software Hysys 8.4 using the Gibbs energy minimisation method. Four  
9 thermodynamic packages (PRSV, Twu-Sim-Tasonee, Lee-Kesler-Plöcker and BWRS)  
10 were used for the calculations. This Gibbs reactor utility provides the theoretical  
11 equilibrium composition minimising the Gibbs free energy of the system, which allows  
12 calculating the thermodynamic equilibrium without introducing the reaction  
13 stoichiometry, as described in the works of Chen et al. [33], Wang et al. [34] and Duo et  
14 al. [35] For this calculation, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> were considered as  
15 output products for lactose steam reforming, which is in good agreement with the output  
16 products normally selected in reforming processes [34]. The results were analysed by  
17 means of an ANOVA test with 95% confidence. Furthermore, the relative influence of  
18 the operating variables was calculated using the cause-effect Pareto principle.

19

### 20 *2.2 Experimental reforming study*

21 The experimental study addresses the influence of the reforming temperature (300-600  
22 °C), lactose concentration (1-10 wt.%) and ratio mass of the catalyst/lactose mass flow  
23 rate ( $W/m_{\text{lactose}} = 4-16$  g catalyst min/g lactose) on the catalytic steam reforming of  
24 lactose. The experiments were planned using a 2 level 3 factor Box-Wilson Central

1 Composite Face Centred (CCF,  $\alpha: \pm 1$ ) design. The results were analysed with an  
2 analysis of variance (ANOVA) with 95% confidence and the cause-effect Pareto  
3 principle was used to determine their relative influence on the process. This  
4 corresponds to a  $2^k$  factorial design, where k indicates the number of factors studied (in  
5 this case 3 operating variables) and  $2^k$  represents the number of runs (in this case 8) for  
6 the simple factorial design. 10 axial experiments were performed to study non-linear  
7 effects and interactions according to the CCF design. In addition, four replicates at the  
8 centre point (centre of the variation interval of each factor) were carried out in order to  
9 evaluate the experimental error. This experimental design is suitable not only for  
10 studying the influence of each variable (linear and quadratic effects) but also for  
11 understanding possible interactions between variables.

12  
13 The experimental rig used in the experiments was a microactivity unit designed and  
14 built by PID (Process Integral Development Eng & Tech, Spain). It consists of a small  
15 bench scale rig comprising a fixed bed reactor of 25 mm in height and 9 mm inner  
16 diameter. The lactose solutions were fed into the reactor with a HPLC pump.  $N_2$  was  
17 used as a carrier gas to facilitate the feeding of the solutions, as well as an internal  
18 standard for gas quantification. Liquid and  $N_2$  flow rates of 0.4 mL/min and 40  
19  $cm^3STP/min$  were used, respectively. Once inside the reactor, the feed down-flow  
20 passed through the catalytic bed, consisting of a mixture of catalyst and inert sand. The  
21 gaseous mixture passed to a condensation system consisting of a stainless steel vessel  
22 cooled by means of a Peltier thermoelectric cell where the condensable vapours were  
23 trapped. The permanent gases exiting the condensation system were analysed online  
24 with a micro gas chromatograph equipped with thermal conductivity detectors. More  
25 details concerning the set-up can be found in our previous communications [29, 30, 36].

1  
2 A Ni-Co/Al-Mg catalyst prepared by coprecipitation was selected. The preparation  
3 involved adding a solution of  $\text{NH}_4\text{OH}$  to a solution containing  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  
4  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  dissolved in milli-Q water until a  
5 pH of 8.2 was reached, in a similar manner as reported in the work of Wang et al. [34].  
6 The precipitation medium was maintained at 40 °C and moderately stirred. The  
7 hydrated precursor was filtered, washed at 40 °C and dried overnight at 105 °C.  
8 Afterwards it was ground and sieved to a particle size ranging from 160 to 320  $\mu\text{m}$  and  
9 calcined in an air atmosphere up to a temperature of 750 °C for 3h. Finally, it was  
10 activated in situ prior to reaction with  $\text{H}_2$  at 650 °C.

11  
12 The catalyst has a 28% (relative atomic percentage) Ni expressed as  
13  $\text{Ni}/(\text{Ni}+\text{Co}+\text{Al}+\text{Mg})$ , an atomic Mg/Al ratio of 0.26 and an atomic Co/Ni ratio of 0.10,  
14 with a BET surface area of about 132  $\text{m}^2/\text{g}$ . Crystalline phases of NiO/MgO and  
15  $\text{NiAl}_2\text{O}_4/\text{MgAl}_2\text{O}_4$  spinels were found in the X-ray diffraction (XRD) analysis of the  
16 calcined precursor. No crystalline phases of Co were detected by XRD. These  
17 crystalline phases are consistent with the TPR analyses, where two peaks were detected.  
18 A small peak was found at 300-320 °C, corresponding to the reduction of the NiO phase  
19 as well as the reduction of the  $\text{Co}_3\text{O}_4$  phase [37-39]. This may suggest a high Ni-Co  
20 interaction, which was confirmed by the positive shift of the binding energy of Ni  $2\text{p}_{3/2}$   
21 detected in the XPS analysis. A second higher intensity peak was found at 732 °C,  
22 which might correspond to the reduction of the  $\text{NiAl}_2\text{O}_4$  spinel phase. Further  
23 information about the characterisation of the catalyst can be found in our previous  
24 communication [30].

25

- 1 The lactose solutions were prepared dissolving D-lactose monohydrate ( $C_{12}H_{22}O_{11} \cdot H_2O$ )  
 2 Sigma Aldrich, CAS Number 64044-51-5, Bio-Ultra >99.5 % HPLC) in Milli-Q water.  
 3  
 4 *Table 1. Response variables. Definitions and analytical techniques used in their*  
 5 *determination.*

Product	Response variable	Analytical method
Gas	$CC \text{ gas } (\%) = \frac{C \text{ in the gas (g)}}{C \text{ fed (g)}} 100$	Micro Gas Chromatograph (Micro GC). $N_2$ as internal standard
	$\text{Composition (vol. \%)} = \frac{\text{mol of each gas}}{\text{total mol of gas}} 100$	Online analyses
Liquid	$CC \text{ liq } (\%) = \frac{C \text{ in the liquid products (g)}}{C \text{ fed (g)}} 100$	Total Organic Carbon (TOC).
	$\text{Composition (area \%)} = \frac{\text{area of each compound}}{\text{total area}} 100$	GC-MS (Gas Chromatography-Mass Spectrometry)
	$X \text{ lactose } (\%) = \frac{\text{lactose fed (g)} - \text{lactose in the liquid (g)}}{\text{lactose fed (g)}} 100$	HPLC (High Performance Liquid Chromatography) Offline analyses
Solid	$CC \text{ sol } (\%) = 100 - CC \text{ gas } (\%) - CC \text{ liq}^* (\%)$	
	$CC \text{ coke } (\%) = \frac{C \text{ on the catalyst (g)}}{C \text{ fed (g)}} 100$	Elemental Analysis Offline analysis
	$CC \text{ char } (\%) = CC \text{ sol } (\%) - CC \text{ coke } (\%)$	
	$C \text{ (mg /g cat. g org.)} = \frac{C \text{ on the catalyst (g)} * 1000}{g \text{ catalyst g lactose reacted}}$	

- 6  
 7  $CC \text{ liq}$  = Carbon conversion to liquid products (unreacted lactose free).  
 8  $CC \text{ liq}^*$  = Carbon conversion to liquids including unreacted lactose  
 9  
 10 The response variables studied were: the lactose conversion (X lactose, %), the carbon  
 11 conversion to gas, liquid and solid products (CC gas, CC liq and CC sol, %) and the  
 12 compositions of the gas (vol.%) and the liquid condensate (relative chromatographic  
 13 area free of water and unreacted lactose, %). The CC sol includes both the carbon  
 14 deposited on the catalyst (coke) and the char. The used catalyst was characterised by  
 15 elemental analysis to calculate the amount of carbon deposited on the catalyst surface.  
 16 The CC coke and the amount of C deposited with respect to the amount of catalyst and  
 17 lactose reacted (mg C/g catalyst g lactose reacted) were calculated from these analyses.

1 Table 1 summarises the response variables and the analytical methods used for their  
2 calculation.

3

### 4 *2.3 Data analysis*

5 In the simulations made for the theoretical study and in the fixed bed experiments, the  
6 lower and upper limits of all the factors (temperature, lactose concentration and liquid  
7 and N<sub>2</sub> flow rates in the theoretical study and temperature, lactose concentration and  
8 W/m<sub>lactose</sub> ratio in the experimental study) were normalised from -1 to 1 (codec factors).  
9 This codification permits all factors to vary within the same interval and helps to  
10 investigate their influence in comparable terms.

11

12 The experimental study analyses the effect of the operating conditions on the response  
13 variables as well as the evolution of the response variables with time. To analyse the  
14 evolution with time, the results are presented divided into three intervals of 60 minutes.  
15 Each interval provides the average value of the response variable obtained during 60  
16 minutes of experiment. All these values (three per experiment) have been compared  
17 using a one-way analysis of variance (one-way ANOVA) and Fisher's least significant  
18 difference (LSD) test, both with 95% confidence. The results of the ANOVA analyses  
19 are provided as p-values. P-values lower than 0.05 indicate that at least two values are  
20 significantly different. The LSD test was used to compare pairs of data, i.e. either  
21 between two intervals of the same experiment or between two intervals of two different  
22 experiments. The results of the LSD tests are presented graphically in the form of LSD  
23 bars. To ensure significant differences between any pairs of data, their LSD bars must  
24 not overlap.

1

2 The effect of the operating variables on the process has been studied considering the  
3 results corresponding to the first 60 minutes of reaction using a statistical analysis of  
4 variance (one-way ANOVA) test with 95% confidence. This avoids including the  
5 activity variation with time in the analysis. The ANOVA analysis helped to select the  
6 operating variables and interactions that significantly influence the response variables  
7 under consideration. In addition, the cause-effect Pareto principle was also used to  
8 calculate their relative importance on the process.

9

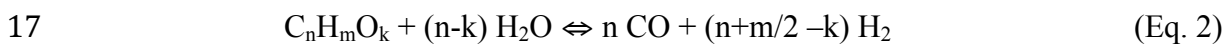
#### 10 *2.4 Possible reaction network for lactose steam reforming*

11 Lactose steam reforming includes reforming, cracking and thermal decomposition  
12 reactions due to the instability of sugars at high temperatures [31, 32].

13

##### 14 1- Reforming reactions:

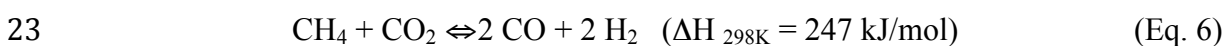
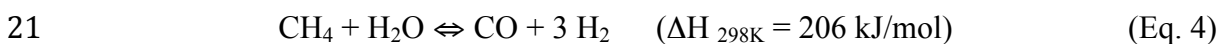
15 *Steam reforming of the oxygenated compounds: lactose and intermediate products*



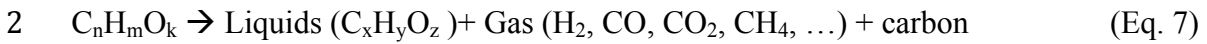
18 *Water gas shift (WGS) reaction:*



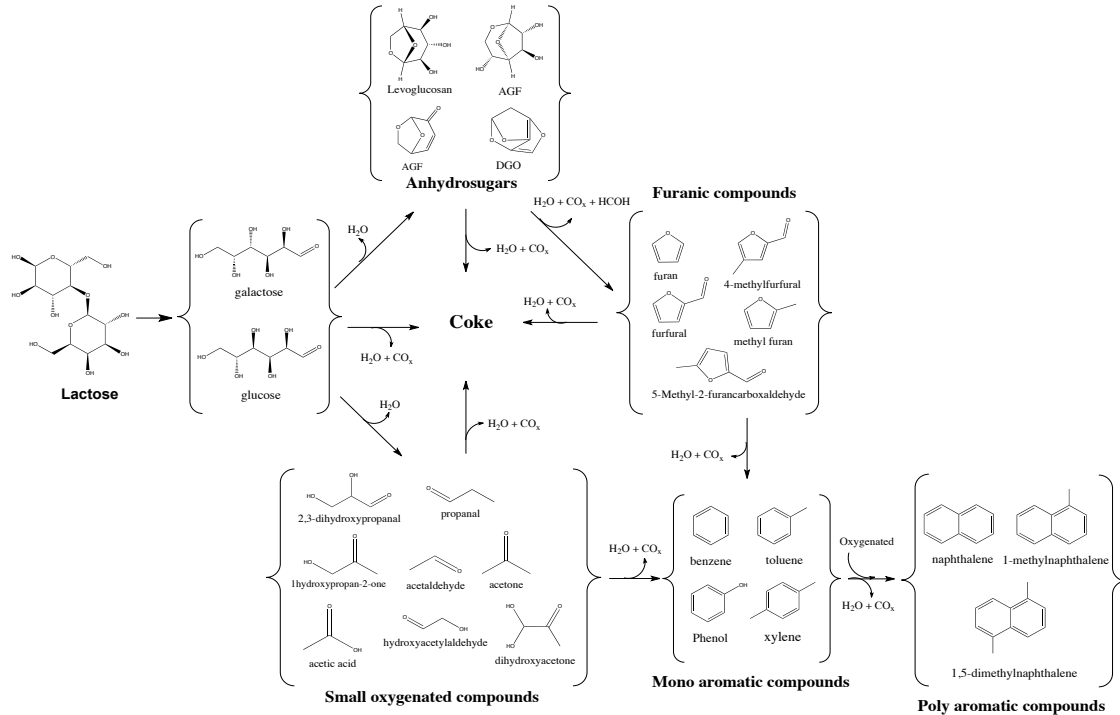
20 *Methane steam reforming and dry reforming:*



1 2- Thermal decomposition and cracking reactions



3



4

5 *Figure 1. Possible reaction pathways during the thermal decomposition of lactose.*

6

7 The thermal decomposition of lactose produces organic liquid intermediates of different  
 8 nature, gases and carbonaceous residues. Figure 1 shows a possible reaction pathway  
 9 for the formation of the most important liquid products during the thermal  
 10 decomposition of lactose, taking into account the work of Carlson et al. [40]. The  
 11 formation of these compounds starts with an initial lactose decomposition by hydrolysis  
 12 into glucose and galactose, which can be subsequently decomposed into other  
 13 intermediate liquids. At a low temperature and low pyrolysis rate, both monomers  
 14 evolve towards the formation of oxygenated compounds of low molecular mass such as  
 15 acids, aldehydes, ketones and alcohols by retro-aldol and grob fragmentation reactions.

1 At high temperatures and a fast pyrolysis rate the formation of anhydrosugars is  
2 favoured. These compounds can subsequently be dehydrated to give furanic  
3 compounds. Mono-aromatic compounds can be formed from both furans and small-  
4 oxygenates by oligomerisation, decarboxylation and decarbonylation reactions. Poly-  
5 aromatic species can be produced as a final step from mono-aromatics.

6

### 7 **3. Results and discussion**

#### 8 *3.1 Theoretical study*

9 Table 2 shows the simulations performed and the results obtained in the theoretical  
10 study. For each gas an empirical model that relates the operating variables (temperature,  
11 lactose concentration, N<sub>2</sub> and liquid flow rates) to the volumetric composition of the gas  
12 was developed according to the ANOVA analysis. The relative influence of each factor  
13 in the model was calculated making use of the cause-effect Pareto principle. The results  
14 of these analyses are summarised in Table 3.

15

16 The thermodynamic results predict a complete lactose conversion to gas for all the  
17 simulations. Lactose has a C/O ratio close to 1, which permits complete conversion to  
18 be achieved at low temperatures [31, 41]. The ANOVA analysis reveals that the  
19 temperature, lactose concentration, liquid flow rate and N<sub>2</sub> flow rate have a statistically  
20 significant influence on the equilibrium composition of the gas (p-values < 0.05),  
21 although their relative influence is different. The cause-effect Pareto analysis shows that  
22 the gas composition is strongly affected (more than 77 of relative influence) by the  
23 temperature, concentration of lactose and an interaction between these two variables.



1 The weak influence of the liquid and N<sub>2</sub> flow rates is related to the small variations in  
 2 the partial pressures inside the reactor when varying these flow rates, which have a  
 3 slight affect on the thermodynamic equilibrium [33]. As a direct consequence, the  
 4 majority of works dealing with steam reforming only consider the effects of the  
 5 concentration of the organic compounds (or steam to carbon ratio, S/C) and the  
 6 temperature in thermodynamic studies.

7  
 8 Table 2. *Thermodynamic gas composition results for the simulations. The gas*  
 9 *composition is expressed as the 95% confidence interval for the mean obtained with the*  
 10 *different thermodynamic packages.*

Sim	[Lactose] (wt.%)		Q <sub>liq</sub> (mL/min)		Q <sub>N<sub>2</sub></sub> (mL/min)		T (°C)		H <sub>2</sub> (vol.%)	CO <sub>2</sub> (vol.%)	CO (vol.%)	CH <sub>4</sub> (vol.%)
	Codec	Actual	Codec	Actual	Codec	Actual	Codec	Actual				
1	-1	1	-1	0.1	-1	0	-1	300	66.60-66.62	33.20-33.22	0.001-0.001	0.173-0.176
2	1	10	-1	0.1	-1	0	-1	300	37.21-37.27	40.55-40.57	0.039-0.039	22.14-22.18
3	-1	1	1	0.5	-1	0	-1	300	66.60-66.62	33.20-33.22	0.009-0.009	0.173-0.176
4	1	10	1	0.5	-1	0	-1	300	37.21-37.27	40.55-40.56	0.039-0.039	22.14-22.18
5	-1	1	-1	0.1	1	80	-1	300	66.76-66.76	33.17-33.17	0.009-0.009	0.065-0.066
6	1	10	-1	0.1	1	80	-1	300	42.38-42.39	39.25-39.26	0.048-0.048	18.30-18.31
7	-1	1	1	0.5	1	80	-1	300	66.66-66.66	33.20-33.20	0.009-0.009	0.137-0.138
8	1	10	1	0.5	1	80	-1	300	38.48-38.52	40.24-40.26	0.041-0.041	21.19-21.21
9	-1	1	-1	0.1	-1	0	1	600	66.77-66.78	33.07-33.07	0.154-0.155	0.00-0.00
10	1	10	-1	0.1	-1	0	1	600	66.25-66.26	32.02-32.02	1.720-1.721	0.007-0.007
11	-1	1	1	0.5	-1	0	1	600	66.77-66.78	33.07-33.07	0.154-0.155	0.00-0.00
12	1	10	1	0.5	-1	0	1	600	66.25-66.26	32.02-32.02	1.720-1.721	0.007-0.007
13	-1	1	-1	0.1	1	80	1	600	66.78-66.78	33.07-33.07	0.154-0.154	0.00-0.00
14	1	10	-1	0.1	1	80	1	600	66.26-66.26	32.02-32.02	1.720-1.721	0.003-0.003
15	-1	1	1	0.5	1	80	1	600	66.78-66.78	33.07-33.07	0.154-0.155	0.00-0.00
16	1	10	1	0.5	1	80	1	600	66.26-66.26	32.09-32.09	1.720-1.721	0.005-0.005
17	0	5.5	0	0.3	0	40	0	450	66.62-66.62	32.99-32.99	0.310-0.311	0.078-0.078
18	-1	1	0	0.3	0	40	0	450	66.82-66.82	33.13-33.13	0.053-0.053	0.00-0.00
19	1	10	0	0.3	0	40	0	450	65.54-65.54	33.05-33.05	0.585-0.585	0.819-0.819
20	0	5.5	-1	0.1	0	40	0	450	66.65-66.65	32.98-32.98	0.311-0.311	0.055-0.055
21	0	5.5	1	0.5	0	40	0	450	66.62-66.62	32.99-32.99	0.310-0.310	0.084-0.084
22	0	5.5	0	0.3	-1	0	0	450	66.61-66.61	32.98-32.98	0.309-0.309	0.095-0.095
23	0	5.5	0	0.3	1	80	0	450	66.65-66.65	32.98-32.98	0.311-0.311	0.065-0.065
24	0	5.5	0	0.3	0	40	-1	300	50.82-50.82	37.16-37.16	0.033-0.033	11.98-11.98
25	0	5.5	0	0.3	0	40	1	600	66.54-66.54	32.57-32.57	0.895-0.895	0.001-0.001

12  
 13  
 14 Taking this information into account, two different models were developed. The first  
 15 was a full model used for prediction purposes which includes all the significant effects  
 16 and interactions of the four operating variables. The second was a simplified model  
 17 which only includes the effects of the temperature, the lactose concentration and  
 18 temperature-lactose concentration interactions. This was used for studying the  
 19 thermodynamics of the process. The full model (not shown) indicates that the relative

1 amounts of H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub> in the gas vary as follows: 38.2-69.0 vol.%, 31.7-40.3  
 2 vol.%, 0.0-1.7 vol.% and 0.0-21.0 vol.%, respectively.

3

4 Table 3. *Relative influence of the studied variables and their interactions on the*  
 5 *thermodynamic composition of the gas according to the ANOVA analysis for the*  
 6 *simplified model*

7

	<b>Independent term</b>	<b>T</b>	<b>C</b>	<b>T C</b>	<b>T<sup>2</sup></b>	<b>T<sup>2</sup> C</b>	<b>Others</b>
H <sub>2</sub> (vol.%)	66.59	6.91 (26)	ns	6.82 (25)	-7.22 (10)	-7.08 (26)	(13)
CO <sub>2</sub> (vol.%)	32.99	-2.07 (30)	ns	-2 (28)	1.69 (9)	1.48 (21)	(13)
CO (vol.%)	0.31	0.46 (35)	0.27 (30)	0.38 (29)	0.17 (5)	0.13 (2)	(1)
CH <sub>4</sub> (vol.%)	0.11	-5.29 (26)	ns	-5.2 (25)	5.37 (10)	5.21 (25)	(13)

8

9 ns. Non significant with 95% confidence

10

11 Response variable = Independent term + Coefficient T·T + Coefficient C·C + Coefficient TC·TC + Coefficient T<sup>2</sup>·T<sup>2</sup> + Coefficient T<sup>2</sup>C·T<sup>2</sup>C

12

13 Table 3 shows the terms of the simplified model and the relative importance of all the  
 14 variables according to the Pareto test. The effects of the N<sub>2</sub> and liquid flow rates and  
 15 their interactions have been grouped together under the term “others”. The lack of fit for  
 16 all the simplified models is not significant in comparison with the pure error (p-value >  
 17 0.05) and their R<sup>2</sup> is higher than 0.99 in all cases. In addition, no significant differences  
 18 were observed between the values predicted with the models and the values obtained in  
 19 the simulations, with 95% confidence. This indicates that they are able to predict up to  
 20 99% of the variations observed, confirming the slight effect of the liquid and N<sub>2</sub> flow  
 21 rates on the thermodynamic results in this work and the good accuracy of the models  
 22 developed.

23

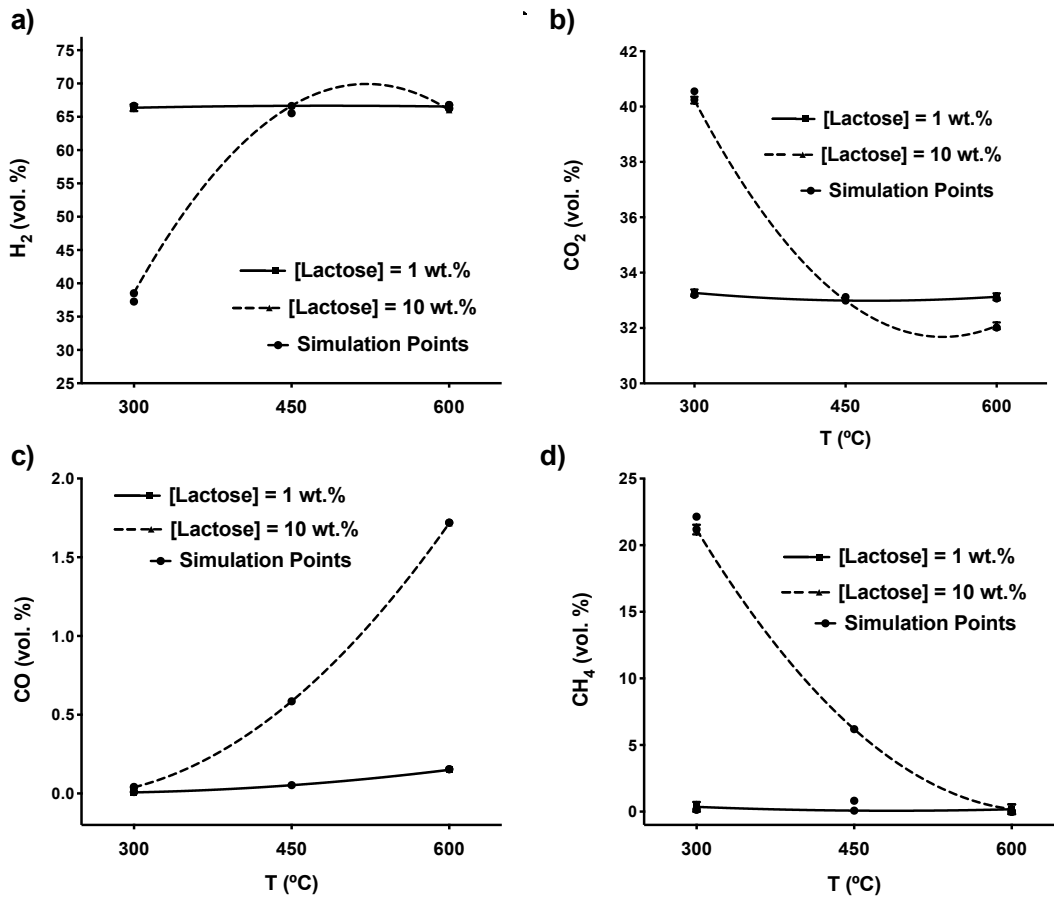
24 As regards the relative influence of the operating variables on the process, the codec  
 25 model listed in Table 3 shows that within the interval of study considered in this work,  
 26 the temperature (the linear term and its interaction with the lactose concentration) exerts

1 the highest influence on the equilibrium composition. The quadratic effect for the  
2 temperature ( $T^2$ ) is significant, which indicates the existence of maxima and minima.  
3 Conversely, quadratic terms for the lactose concentration are not significant with 95%  
4 confidence, denoting a linear evolution for this operating variable. In addition, a  
5 significant interaction between the temperature and the concentration of lactose was  
6 detected; therefore the effect of the lactose concentration depends on the temperature  
7 and vice versa. The effect of the temperature is related to the variations of the  
8 thermodynamic equilibrium constant of all the reactions involved in the process, while  
9 the effect of the concentration (1-10 wt.%) is linked to the variations in the water  
10 content of the solutions (variations in the S/C ratio from 157 to 14 mol H<sub>2</sub>O/mol C).  
11 High S/C ratios help to shift the WGS and methane reforming reactions towards the  
12 formation of H<sub>2</sub> [42].

13

14 Figure 2 shows the interaction plots between the temperature and lactose concentration  
15 obtained from the models shown in Table 3, obtained from the statistical analysis of the  
16 results obtained in the simulations listed in Table 2. Specifically, the volumetric gas  
17 composition (vol.%) is plotted as a function of the temperature for the lowest and the  
18 highest (1 and 10 wt.%) lactose concentrations employed in this work. In general, an  
19 increase in the temperature between 300 and 600 °C increases the proportions of H<sub>2</sub> and  
20 CO in the gas, reducing the relative amounts of CO<sub>2</sub> and CH<sub>4</sub>. The reforming reaction  
21 of lactose (Eq. 1) is highly endothermic and the water gas shift reaction (Eq. 3) is  
22 moderately exothermic [31], giving an overall endothermic process. Thus, an increase  
23 in temperature augments the equilibrium concentration of H<sub>2</sub> and CO in the gas. The  
24 proportions of CH<sub>4</sub> and CO<sub>2</sub> in the gas decrease due to the endothermic nature of the

1 reforming (Eqs. 4-5) and dry reforming (Eq.6) of methane as well as the exothermic  
 2 character of the WGS reaction, respectively [42].



3  
 4 *Figure 2. Evolution with temperature of the thermodynamic concentration of H<sub>2</sub> (a),*  
 5 *CO<sub>2</sub> (b), CO (c) and CH<sub>4</sub> (d) for the lowest (1 wt.%) and highest (10 wt.%) lactose*  
 6 *concentrations obtained with an ANOVA analysis of the simulations.*

7  
 8 These variations are more appreciable as the concentration of lactose in the solution  
 9 increases due to the significant interaction between the temperature and the lactose  
 10 concentration. This makes the effect of the temperature on the composition of the gas  
 11 extremely weak for very diluted lactose solutions (1 wt.%) due to the large amount of  
 12 water employed (S/C = 157 mol H<sub>2</sub>O/mol C).

1 Conversely, an increase in the lactose concentration from 1 to 10 wt.% increases the  
2 effect of the temperature. An increase in the lactose concentration has two different  
3 consequences depending on the temperature. On the one hand, between 300 and 450 °C,  
4 an increase in the amount of lactose in the solution reduces the proportion of H<sub>2</sub>,  
5 augmenting the relative amounts of CO<sub>2</sub> and CH<sub>4</sub> in the gas. Within this temperature  
6 range, an increase in the concentration of lactose diminishes the excess of water, thus  
7 decreasing the steam to carbon (S/C) ratio of the solution from 157 to 14 mol H<sub>2</sub>O/mol  
8 C. This originates a lesser shift of the WGS and methane reforming reactions towards  
9 H<sub>2</sub> production.

10

11 On the other hand, between 450 and 600 °C, the same increment in the concentration of  
12 lactose increases the proportions of H<sub>2</sub> and CO and reduces the concentration of CO<sub>2</sub> in  
13 the gas. The variation in the relative amount of H<sub>2</sub> is relatively small, since the optimum  
14 for H<sub>2</sub> production is found to be at temperatures around 500-550 °C. These variations  
15 are the consequence of the greater spread of reforming reactions at high temperature,  
16 which favours H<sub>2</sub> production.

17

## 18 *3.2 Experimental study*

### 19 *3.2.1 Global lactose conversion and carbon distribution: CC gas, CC liq and CC sol.*

20 Table 4 lists the experiments performed in the fixed bed reactor. A complete and steady  
21 global lactose conversion (X lactose) was achieved in all the experiments, indicating  
22 that all the lactose was converted into gas, liquid and solid products. The C/O ratio close  
23 to 1 of lactose allows complete conversion to be achieved even at the lowest

1 temperature used in this work [31, 41]. Complete conversions were achieved at  
 2 temperatures higher than 500 °C in the work of Hu et al. [31] during the steam  
 3 reforming of glucose. Figure 3 shows the CC gas, CC liq and CC sol obtained for the  
 4 experiments in three intervals of 60 min. The statistical analysis reveals significant  
 5 differences between the results obtained in the experiments for the CC gas, CC liq and  
 6 CC sol (p-values < 0.001), which vary as follows: 2-97%, 0-66% and 0-95%,  
 7 respectively. In addition, increases and reductions in the CC gas, CC liq and CC sol are  
 8 detected in some experiments.

9

10 *Table 4. Experimental operating conditions (actual and codec values) used in the*  
 11 *experiments.*

12

Run	Temperature (°C)		[Lactose] (wt.%)		W/m <sub>lactosa</sub> (g catalyst min/g lactose)	
	Codec	Actual	Codec	Actual	Codec	Actual
1	-1	300	-1	1	-1	4
2	1	600	-1	1	-1	4
3	-1	300	-1	1	1	16
4	1	600	-1	1	1	16
5	-1	300	1	10	1	4
6	1	600	1	10	1	4
7	-1	300	1	10	1	16
8	1	600	1	10	1	16
9* (9, 10, 11, 12)	0	450	0	5.5	0	10
13	-1	300	0	5.5	0	10
14	1	600	0	5.5	0	10
15	0	450	0	5.5	-1	4
16	0	450	0	5.5	1	16
17	0	450	-1	1	0	10
18	0	450	1	10	0	10
19	1	600	0	5.5	1	16
20	-1	300	0	5.5	1	16
21	1	600	0	5.5	-1	4
22	-1	300	0	5.5	-1	4

13

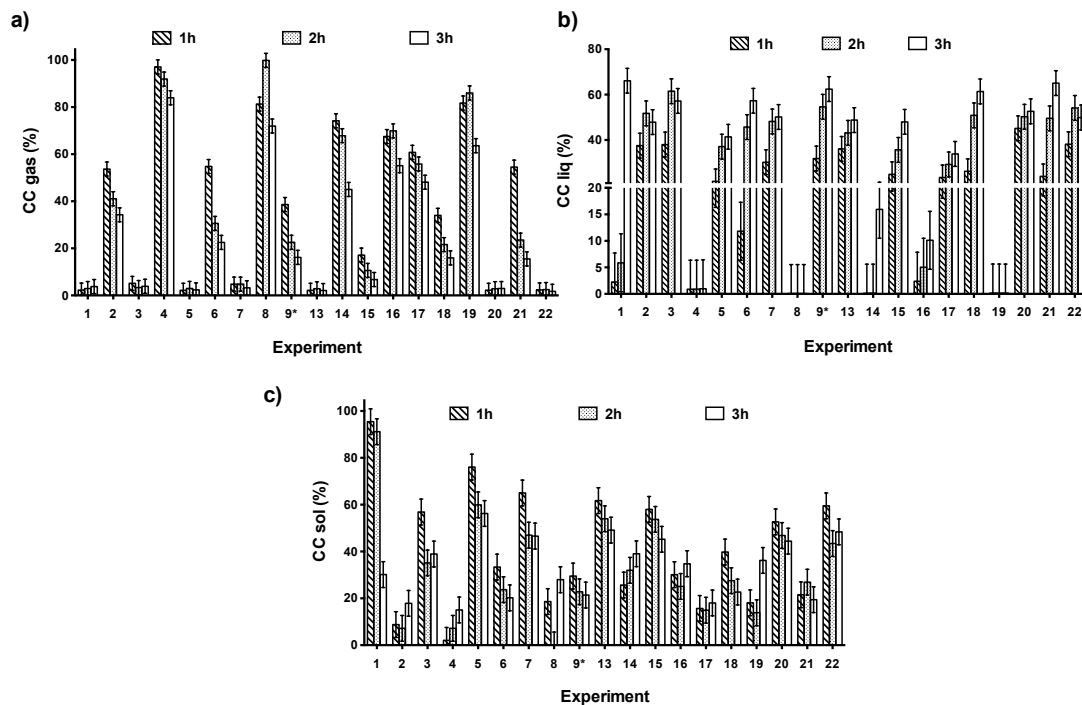
\* Four replicates at the centre point: runs 9, 10, 11 and 12

14

15 The general trend for the CC gas is a reduction with time. Reductions are clearly  
 16 observed in runs 2, 4, 6, 8, 9\*, 14-19 and 21 and might be the consequence of the  
 17 progressive deactivation of the catalyst. All these experiments were conducted at a  
 18 temperature higher than 450 °C. A decay in the CC gas with time was also reported in  
 19 the work of Hu et al. during the steam reforming of glucose [31]. A comparison  
 20 between experiments 2 and 4 shows how an increase in the W/m<sub>lactose</sub> ratio increases the

1 initial CC gas due to the positive kinetic effect that the catalyst exerts on the process.  
 2 Furthermore, a greater value of the  $W/m_{\text{lactose}}$  ratio results in a lessening of the decay of  
 3 the CC gas over time. This trend is also observed for runs 6 and 8. However, run 8  
 4 displays an initial increase in the CC gas followed by a posterior decay. This  
 5 phenomenon could account for the progressive gasification of the carbonaceous  
 6 deposits formed by an incomplete vaporisation of the feed, as has been reported in other  
 7 works dealing with the steam reforming of sugars [31, 32, 36].

8



9  
 10 *Figure 3. Conversion to gas (a), liquid (b) and solid (c) obtained during the reforming*  
 11 *experiments. Results are presented as the overall values obtained each 60 minutes and*  
 12 *expressed as mean  $\pm$  0.5 Fisher LSD intervals with 95% confidence.*

13

14 The effect of the lactose concentration is seen when comparing runs 2 with 6 and 4 with  
 15 8. An increase in the concentration of lactose decreases the excess of water, and

1 consequently the S/C ratio. This decreases the reaction rate of the gasification reactions  
2 of the carbonaceous deposits and increases the reduction over time of the CC gas.  
3 Similar trends have been reported during the steam reforming of xylose, glucose and  
4 sucrose [31, 32].

5  
6 Runs 1, 3, 5, 7, 13, 20 and 22 display a steady and low CC gas (<5%). All these  
7 experiments were conducted at 300 °C using different lactose concentrations and  
8 W/m<sub>lactose</sub> ratios. These results indicate that gas production is not favoured at low  
9 temperatures. Under these conditions, the lactose concentration and W/m<sub>lactose</sub> ratio do  
10 not exert a significant influence on the CC gas due to the endothermicity of the  
11 reforming reactions.

12  
13 The CC sol displays increases and decreases with time. On the one hand, for runs  
14 conducted at 300 °C (1, 3, 5, 7, 13, 20 and 22) the CC sol is high at the start of the  
15 experiment and progressively decreases with time. Sugar molecules are unstable at the  
16 temperatures of this process and quickly decompose through pyrolysis, leading to the  
17 formation of char particles and gases [32]. The accumulation of this char in the upper  
18 part of the reactor might have a positive catalytic effect on lactose pyrolysis and/or  
19 cracking reactions. Char obtained from the pyrolysis of different biomass materials has  
20 been reported to have catalytic activity for the reforming and cracking of different  
21 hydrocarbons [43-49], which accounts for the drops over time observed for the CC sol  
22 [31, 32] and the increases in the CC liq.

23



1 Conversely, for runs conducted at higher temperatures (450-600 °C), where the  
2 vaporisation of the solution is more favoured and carbon deposits can be removed by  
3 gasification due to the relatively high temperature and high S/C ratio of the feed, the CC  
4 sol increases or remains steady over time. The increases are the consequence of the  
5 progressive deactivation of the catalyst, which originates a decrease in the CC gas and  
6 an increase in the CC sol [31, 32]. In addition, the accumulation of char particles in the  
7 upper part of the reactor hinders the vaporisation of the feed as the atomisation system  
8 is not as effective when the liquid comes into contact with solid particles, leading to  
9 bigger droplet sizes. Consequently, the evaporation takes places at lower heating rates.  
10 This enhances the formation of more carbonaceous deposits, augmenting the formation  
11 of char over time, which increases the CC sol [50]. However these variations do not  
12 take place in runs 16, 17 and 21, where a steady CC sol is obtained. These runs were  
13 conducted using a high  $W/m_{\text{lactose}}$  ratio and a medium lactose concentration (run 16), an  
14 intermediate  $W/m_{\text{lactose}}$  ratio and a low lactose solution (run 17) and high temperature  
15 and an intermediate lactose concentration (run 21). These conditions reach a  
16 compromise between carbon deposit formation and elimination that can provide a  
17 steady evolution for the CC sol.

18

19 As regards the evolution over time for the CC liq, increases with time are observed for  
20 the vast majority of experiments. These increases have two different backgrounds. On  
21 the one hand, for the experiments with an initial high CC gas (2, 6, 9\*, 14-18), the  
22 increase in the CC liq accounts for the progressive deactivation of the catalyst, which is  
23 not able to completely transform the organic content of the feed into gas, thus increasing  
24 the proportion of intermediate liquid products originating from thermal decomposition  
25 and incomplete reforming. On the other hand, for the experiments with both an initial

1 low CC gas and a high CC sol (1, 3, 5, 7, 13, 20 and 22), the increases might be the  
2 consequence of the formation of liquid condensable products from the progressive  
3 pyrolysis of the feed and or/the carbon deposits (mainly as char), thus increasing the CC  
4 liq over time.

5

6 Interestingly, experiments 4, 8 and 19, which were conducted at a high temperature  
7 (600 °C) and high spatial time (16 g catalyst min/g lactose), display negligible CC liq  
8 and a relatively high amount of CC gas regardless of the lactose concentration. The  
9 COD values for 1, 5.5 and 10 wt.% lactose solutions are 11.5, 63.5 and 115.5 kg/m<sup>3</sup>,  
10 respectively. The liquid condensate obtained in experiments 4, 8 and 19 (1, 10 and 5.5  
11 wt.% of lactose, respectively) has COD values of 3.29, 4.60 and 1.59 kg/m<sup>3</sup>,  
12 respectively. This corresponds to a reduction in the COD of the solutions of 71, 96 and  
13 97%, respectively, with respect to the original feedstock. Therefore, high temperatures  
14 and spatial times enhance gas formation from the vaporised part of the feed, thus  
15 producing an almost carbon free liquid condensate with a considerably lower COD than  
16 that of the original feedstock.

17

18 To gain a better insight into the carbon deposition, the carbon deposited on the used  
19 catalysts was examined and the solid carbon distribution between char and coke was  
20 calculated. Table 5 lists the CC coke, CC char and the amount of C deposited on the  
21 catalysts during the reforming experiments. The results indicate that the vast majority of  
22 the CC sol is due to the formation of char. In general more than 80% of the total solid C  
23 is due to char formation. This proportion increases up to 90% for the experiments  
24 conducted at 300 °C, confirming the significant formation of carbonaceous solid at low

1 temperatures. Char production is highly likely to occur during the thermal  
 2 decomposition of lactose. Lactose is unstable when heated at the temperatures  
 3 employed in this work and it decomposes before reaching the catalytic bed, resulting in  
 4 severe char formation in the upper part of the reactor. This tendency of sugars to  
 5 decompose giving char has also been reported for xylose, glucose and sucrose [31, 32].  
 6 The statistical analysis of the amount of carbon (expressed as mg C/g catalyst g lactose  
 7 reacted to produce gases) reveals that the highest deposition takes place at 300 °C  
 8 (groups A to G). Furthermore, a relatively high amount of this carbon is deposited on  
 9 the catalyst surface, proving evidence for the experimentally observed catalyst  
 10 deactivation. This catalyst deactivation by coking has been reported in other works  
 11 dealing with the steam reforming of other oxygenated compounds. A very detailed  
 12 mechanism for coke deposition, explaining the deactivation of Ni-based catalysts by  
 13 coking, is provided in the work of Wang et al. [51].

14

15 *Table 5. Solid carbon distribution. Overall 3 hours carbon conversion to solid, char*  
 16 *and coke and C deposited on the catalyst.*

17

Run	CC solid (%)	CC char (%)	CC coke (%)	C (mg C/g cat. g org.)
1	72.27 <sup>A</sup>	70.83 <sup>A</sup>	1.44 <sup>H</sup>	39.84 <sup>A</sup>
2	11.28 <sup>K,L</sup>	10.67 <sup>L</sup>	0.61 <sup>I</sup>	1.21 <sup>I</sup>
3	43.64 <sup>F</sup>	39.54 <sup>F</sup>	4.10 <sup>C</sup>	21.50 <sup>D</sup>
4	8.10 <sup>L</sup>	6.01 <sup>M</sup>	2.09 <sup>F,G</sup>	0.51 <sup>L,M,N</sup>
5	64.08 <sup>B</sup>	62.20 <sup>B</sup>	1.88 <sup>F,G,H</sup>	25.09 <sup>C</sup>
6	25.76 <sup>H,I</sup>	22.84 <sup>H,I</sup>	2.93 <sup>E</sup>	0.68 <sup>J,K,L</sup>
7	52.86 <sup>C,D</sup>	47.17 <sup>E</sup>	5.69 <sup>B</sup>	11.03 <sup>G</sup>
8	15.55 <sup>J,K</sup>	9.03 <sup>L,M</sup>	6.52 <sup>A</sup>	0.16 <sup>N</sup>
9*	25.06 ± 0.98 <sup>I</sup>	24.55 ± 0.72 <sup>J</sup>	0.51 ± 0.12 <sup>D</sup>	0.84 ± 0.08 <sup>J,K</sup>
13	54.96 <sup>C</sup>	51.58 <sup>C</sup>	3.37 <sup>D,E</sup>	18.17 <sup>F</sup>
14	30.00 <sup>GH</sup>	25.87 <sup>G,H</sup>	4.13 <sup>C</sup>	0.58 <sup>K,L,M</sup>
15	52.32 <sup>C,D,E</sup>	50.79 <sup>C,D</sup>	1.53 <sup>H</sup>	4.15 <sup>H</sup>
16	29.99 <sup>G,H</sup>	26.10 <sup>G</sup>	3.89 <sup>C,D</sup>	0.23 <sup>M,N</sup>
17	16.21 <sup>J</sup>	14.53 <sup>K</sup>	1.68 <sup>G,H</sup>	1.01 <sup>I,J</sup>
18	32.24 <sup>G</sup>	26.17 <sup>G</sup>	6.07 <sup>A,B</sup>	0.59 <sup>K,L,M</sup>
19	22.72 <sup>I</sup>	16.32 <sup>K</sup>	6.40 <sup>A</sup>	0.32 <sup>L,M,N</sup>
20	47.98 <sup>E,F</sup>	41.49 <sup>F</sup>	6.49 <sup>A</sup>	19.65 <sup>E</sup>
21	22.62 <sup>I</sup>	20.22 <sup>I,J</sup>	2.40 <sup>F</sup>	1.20 <sup>I</sup>
22	50.43 <sup>D,E</sup>	48.21 <sup>D,E</sup>	2.21 <sup>F</sup>	32.91 <sup>B</sup>

18

19

Letters in each column represent LSD statistically significant groups with 95% confidence according to the ANOVA analysis.

1  
2 The specific effect of the operating conditions as well as their possible interactions on  
3 the process has been studied using the results obtained during the first 60 minutes of  
4 reaction. The models created in terms of codec factors considering the ANOVA analysis  
5 of the experiments performed (Table 4) are presented in Table 6. The reaction  
6 temperature is the operating variable with the highest influence on the CC gas and CC  
7 sol. An increase in the temperature increases and decreases the CC gas (positive term in  
8 the model) and CC sol (negative term in the model), respectively. An increase in the  
9 temperature not only facilitates the vaporisation of the feed, decreasing the formation of  
10 solid carbon, but also favours the reforming process due to its endothermic nature [31,  
11 32]. Furthermore, the effect of the temperature depends on the  $W/m_{\text{lactose}}$  ratio due to the  
12 significant interaction between these two variables. The CC liq is significantly  
13 influenced by the temperature and  $W/m_{\text{lactose}}$  ratio. An increase in the temperature  
14 decreases the CC liq (negative term in the model) due to the positive effect that the  
15 temperature exerts on the gas production from the intermediate liquid compounds  
16 resulting from the thermal decomposition of lactose.

17

18 *Table 6. Relative influence of the operating conditions on the CC gas, CC liq and CC*  
19 *sol according to the ANOVA analysis for the first hour of reaction.*

20

Variable	R <sup>2</sup>	I. Term	T	W	C	TW	TC	WC	TWC	T <sup>2</sup>	W <sup>2</sup>	C <sup>2</sup>	T <sup>2</sup> W	T <sup>2</sup> C	TW <sup>2</sup>	TC <sup>2</sup>	WC <sup>2</sup>	TWC <sup>2</sup>
CC gas (%)	0.98	38.6	34.01 (52)	25.18 (17)	-13.39 (5)	7.64 (11)	ns	ns	ns	ns	ns	ns	-16.64 (9)	11.5 (6)	ns	ns	Ns	ns
CC liq (%)	0.95	30.72	-15.85 (22)	-11.24 (7)	ns	-10.28 (22)	-4.78 (8)	ns	6.53 (11)	ns	-11.97 (9)	ns	9.49 (8)	ns	ns	10.61 (12)	Ns	ns
CC sol (%)	0.99	26.74	-18.1 (35)	-13.94 (11)	12.04 (7)	ns	6.56 (7)	ns	-4.45 (5)	10.21 (8)	10.55 (4)	-5.77 (0.1)	11.37 (4)	-8.3 (4)	ns	-10.71 (8)	-6.32 (4)	3.53 (4)

21

22

ns. Non significant with 95% confidence

23

24

Response variable = Independent term + Coefficient T·T + Coefficient W·W + Coefficient C·C + Coefficient TW·TW + Coefficient TC·TC + Coefficient WC·WC + Coefficient TWC·TWC + Coefficient T<sup>2</sup>·T<sup>2</sup> + Coefficient W<sup>2</sup>·W<sup>2</sup> + Coefficient C<sup>2</sup>·C<sup>2</sup> + Coefficient T<sup>2</sup>W·T<sup>2</sup>W + Coefficient T<sup>2</sup>C·T<sup>2</sup>C + Coefficient TW<sup>2</sup>·TW<sup>2</sup> + Coefficient TC<sup>2</sup>·TC<sup>2</sup> + Coefficient WC<sup>2</sup>·WC<sup>2</sup> + Coefficient TWC<sup>2</sup>·TWC<sup>2</sup>

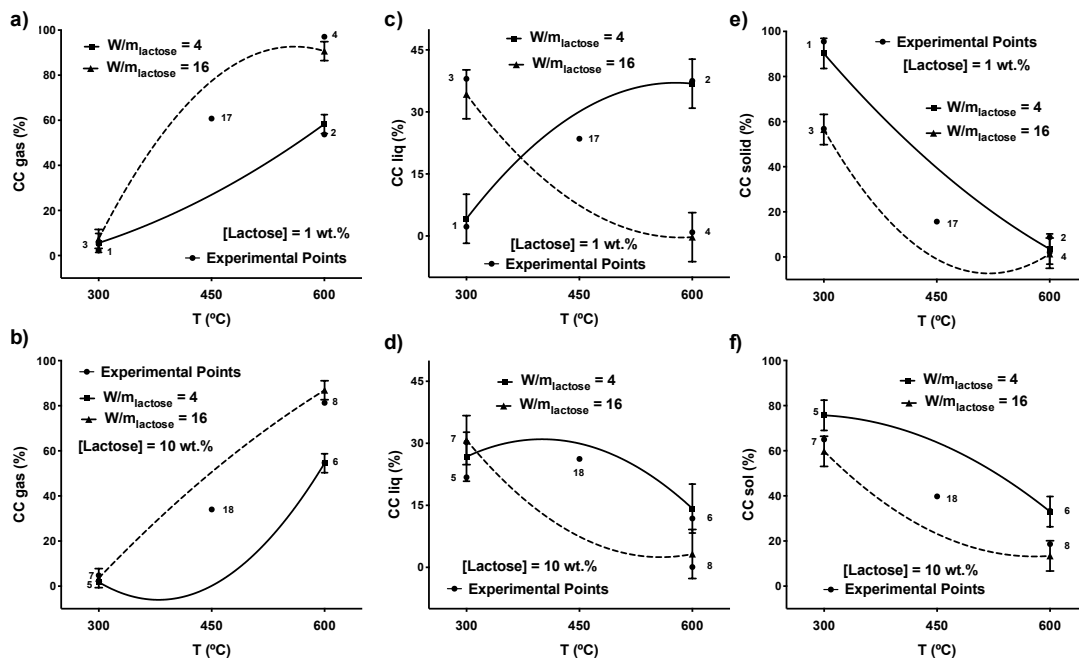
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26

27

28

1 The effects of the operating variables on the CC gas, CC liq and CC sol are shown in  
 2 Figure 4. The evolution of these variables was obtained from the ANOVA analysis  
 3 (Table 6) of all the experiments performed (Table 4). In addition, when possible, some  
 4 experimental points were added. Specifically, Figures 4 a and b show the effect on the  
 5 CC gas of the temperature for  $W/m_{\text{lactose}}$  ratios of 4 and 16 g catalyst min/g lactose when  
 6 1 and 10 wt.% lactose solutions were used, respectively. Figures 4 c and d and e and f  
 7 illustrate these effects for the CC liq and CC sol, respectively. In general, the CC gas  
 8 and CC sol show opposite trends. An increase in the temperature augments the CC gas  
 9 and reduces the CC sol, as discussed above.



10

11 *Figure 4. Interaction plots for the initial CC gas (a and b) and CC liq (c and d) and CC*  
 12 *sol (e and f). Bars are LSD intervals with 95% confidence.*

13

14 With respect to the effect of the  $W/m_{\text{lactose}}$  ratio, an increase from 4 to 16 g catalyst  
 15 min/g lactose increases the CC gas and decreases the CC sol due to the positive catalytic

1 effect the catalyst has on the reforming reaction and the pyrolysis and gasification of  
2 solid deposits [31, 32]. However, this increment depends on the temperature and lactose  
3 concentration. At temperatures between 300 and 350 °C, an increase in the  $W/m_{\text{lactose}}$   
4 ratio from 4 to 16 g catalyst min/g lactose does not have a statistically significant  
5 influence on the CC gas. Within this temperature range, the vaporisation of the feed is  
6 not favoured and the vast majority of the organics are converted into carbonaceous  
7 deposits or liquid intermediates. Therefore an increment in the amount of catalyst  
8 ( $W/m_{\text{lactose}}$  ratio) does not have a significant influence on the CC gas.

9

10 Conversely, as the temperature increases and the formation of gas is most favoured, an  
11 increase in the  $W/m_{\text{lactose}}$  ratio significantly augments the CC gas. An almost complete  
12 CC gas can be achieved at temperatures higher than 500 °C when a 1 wt.% lactose  
13 solution is fed. This increment in the  $W/m_{\text{lactose}}$  ratio diminishes the CC solid regardless  
14 of the temperature. However, this drop depends on the concentration of lactose and the  
15  $W/m_{\text{lactose}}$  ratio.

16

17 The effect of the concentration of lactose can be gathered comparing Figures 4 a with b  
18 and e with f. An increase in the concentration of lactose in the solution from 1 to 10  
19 wt.% reduces the CC gas between 350 and 550 °C, as explained above. As the lactose  
20 concentration increases, the formation of carbonaceous deposits obtained from an  
21 incomplete vaporisation of the feed is most favoured due to the reduction of the S/C  
22 ratio (157 and 14 mol  $\text{H}_2\text{O}$ /mol C for 1 and 10 wt.% lactose solutions, respectively) that  
23 lowers the excess of water. The excess of water in the feed not only helps the  
24 vaporisation of lactose but also helps the conversion of the carbonaceous deposits to

1 take place. Hu et al. [31] reported these trends when increasing the S/C ratio from 3 to 9  
2 mol H<sub>2</sub>O/mol C during the steam reforming of glucose and concluded that at high S/C  
3 ratios the high partial pressure of steam in the reactor favours char removal by  
4 gasification and promotes the adsorption of steam on the active sites of the catalyst,  
5 helping to reduce coke formation. Markevich et al. [32] found an increase in gas  
6 production together with a decrease in solid formation during the steam reforming of  
7 glucose and xylose when increasing the S/C ratio from 7 to 47 and 14 to 37 mol  
8 H<sub>2</sub>O/mol C, respectively.

9

10 Employing a W/m<sub>lactose</sub> ratio of 16 g catalyst min/g lactose, a complete CC gas can be  
11 obtained at temperatures higher than 500 and 600 °C when lactose solutions of 1 and 10  
12 wt.% are fed, respectively. This increase in the concentration of lactose increases the  
13 CC sol for the whole range of temperatures studied in this work except for temperatures  
14 lower than 350 °C, where the formation of carbonaceous deposits is similar.

15

16 The effect of the temperature on the CC liq depends on the lactose concentration and  
17 W/m<sub>lactose</sub> ratio, since a significant interaction between these variables was detected. For  
18 a 1 wt.% lactose solution, an increase in the temperature between 300 and 600 °C has  
19 two different effects depending on the W/m<sub>lactose</sub> ratio. On the one hand, when a  
20 W/m<sub>lactose</sub> ratio of 4 g catalyst min/ g lactose is used, the CC liq increases as the  
21 temperature increases. However, the opposite trend is found when a W/m<sub>lactose</sub> ratio of  
22 16 g catalyst is used. This increase in temperature favours the reforming process,  
23 decreasing the CC sol. However, when a low amount of catalyst is used the CC liq  
24 increases, since this amount of catalyst in the bed may be insufficient for a complete

1 conversion of the organics of the feed (lactose and its decomposition products) into  
2 gases, thus increasing the production of intermediate liquids. However, when a higher  
3 amount of catalyst is used, the reaction rate of the reforming reactions towards gas  
4 production increases and therefore both the CC sol and CC liq decrease.

5

6 The effect of the concentration of lactose on the CC liq can be seen when comparing  
7 Figure 4 c with 3d. This effect depends on the  $W/m_{\text{lactose}}$  ratio. When a  $W/m_{\text{lactose}}$  ratio  
8 of 4 g catalyst min/g lactose is used, two different tendencies are found for the CC liq,  
9 depending on the temperature. For temperatures lower than 450 °C, an increase in the  
10 lactose concentration augments the CC liq. At this temperature range, the reforming  
11 process is not favoured. In addition, this increase in the lactose concentration reduces  
12 the excess of water of the feed, leading to a lower extension of the reforming reactions  
13 and thus increasing the CC liq. In contrast, at temperatures higher than 450 °C the same  
14 increment in the concentration of lactose reduces the CC liq. At these temperatures, the  
15 CC sol is lower for a 1 wt.% than for a 10 wt.% solution. This drop in the CC sol  
16 enhances the formation of intermediate liquid products, increasing the CC liq.

17

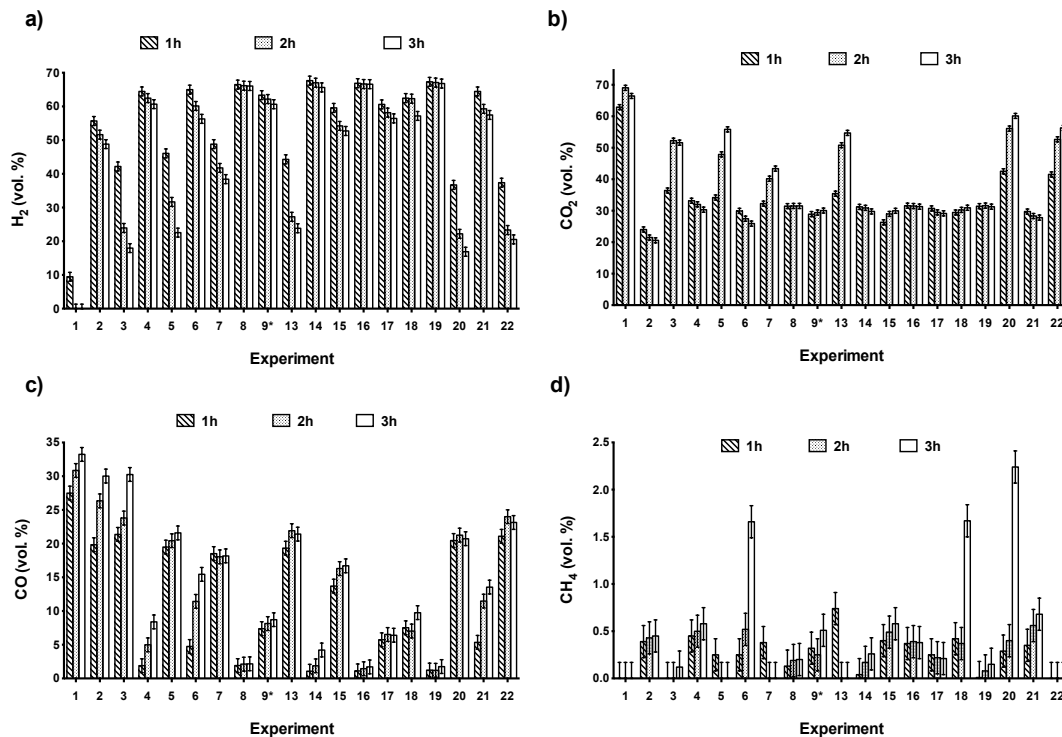
### 18 *3.2.2 Gas composition*

19 Figure 5 shows the gas composition obtained for the different experiments. The gas  
20 phase consists of a mixture of H<sub>2</sub> (0-70 vol.%), CO<sub>2</sub> (20-70 vol.), CO (2-34 vol.%) and  
21 CH<sub>4</sub> (0-2.4 vol.%). Statistically significant (p-values<0.05) variations are observed for  
22 the gas composition between experiments and intervals of the same experiment.

23



1 The highest variations with time for the relative amounts of H<sub>2</sub> and CO<sub>2</sub> in the gas are  
 2 observed for runs conducted at 300 °C (3, 5, 7, 13, 20 and 22), where the proportions of  
 3 H<sub>2</sub> and CO<sub>2</sub> in the gas decrease and increase, respectively. These experiments were  
 4 conducted at the lowest temperature employed in this work (300 °C), and where the  
 5 greatest amount of coke was deposited on the used catalysts (more than 11 mg C/g  
 6 catalyst g organic reacted). This accounts for the catalyst deactivation by coking and  
 7 indicates that the temperature exerts a significant influence on catalyst deactivation. The  
 8 temperature significantly influences the reforming process, increasing the reaction rate  
 9 of the reforming reactions, thus partially compensating for the catalyst deactivation.



10

11 *Figure 5. Concentration (vol.%) of H<sub>2</sub> (a), CO<sub>2</sub> (b) CO (c) and CH<sub>4</sub> (d) in the gas.*

12 *Results are presented as the overall values obtained each 60 minutes and expressed as*

13 *mean ± 0.5 Fisher LSD intervals with 95% confidence.*

14

1 In addition, during the reforming process an initial thermal decomposition of the  
2 organic compounds might occur before reaching the catalytic bed. This produces gases  
3 (mainly H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>), other intermediate or decomposition products and char  
4 [32]. The gases and the intermediate products evolve towards achieving the  
5 thermodynamic composition for the gas when passing through the catalytic bed, which  
6 results in an increase and a decrease in the proportions of H<sub>2</sub> and CO<sub>2</sub>, respectively.

7

8 Comparing the experiments conducted at the same temperature, the lower the  $W/m_{\text{lactose}}$   
9 ratio, the higher are the reductions with time in the proportion of H<sub>2</sub>. High  $W/m_{\text{lactose}}$   
10 ratios allow having a greater amount of active catalyst in the bed, thus minimising the  
11 decay observed for the proportion of H<sub>2</sub> in the gas. This finding can be appreciated by  
12 comparing the following experiments: 2 and 4; 6 and 8; and 9, 15 and 16.

13

14 Some variations with time are observed for the proportions of CO and CH<sub>4</sub> in the gas.  
15 The proportion of CO increases with time due to the progressive deactivation of the  
16 catalyst and the lesser shift of the WGS reaction towards H<sub>2</sub> and CO<sub>2</sub>. The greatest  
17 increases in the proportion of CO occur at low temperatures, where the highest  
18 deactivation of the catalyst is observed. An exception to this occurs in experiment 3,  
19 where the decrease in the proportion of H<sub>2</sub> is accompanied by an increase in both the  
20 proportions of CO and CO<sub>2</sub>, probably due to the decrease over time observed in the  
21 evolution of the CC sol, which slightly increases the amount of C in the gas. The  
22 proportion of CH<sub>4</sub> in the gas remains steady with time for the vast majority of the  
23 experiments.

24

1 The specific effects of the operating conditions as well as their possible interactions on  
2 the volumetric composition of the gas were studied considering the results obtained  
3 during the first 60 minutes of reaction. Table 7 lists the results of the statistical analyses.  
4 The temperature (linear and quadratic terms) is the operating variable exerting the  
5 highest influence on the proportions of H<sub>2</sub>, CO<sub>2</sub> and CO in the gas (relative importance  
6 of 31%, 19% and 31%, respectively). The interaction between the temperature and the  
7 quadratic term for the W/m<sub>lactose</sub> ratio has the highest influence (21%) on the  
8 concentration of CH<sub>4</sub> in the gas. The coefficients of the codec models show how an  
9 increase in the temperature increases the concentration of H<sub>2</sub> in the gas (positive term)  
10 while reducing the proportion of the other gases (negative term). The concentration of  
11 lactose individually does not influence the gas composition. However, significant  
12 interactions with the temperature and the W/m<sub>lactose</sub> ratio are detected.

13

14 *Table 7. Relative influence of the operating conditions on the gas composition*  
15 *according to the ANOVA analysis for the first hour of reaction*

16

Variable	R <sup>2</sup>	I. Term	T	W	C	TW	TC	WC	TWC	T <sup>2</sup>	W <sup>2</sup>	C <sup>2</sup>	T <sup>2</sup> W	T <sup>2</sup> C	TW <sup>2</sup>	TC <sup>2</sup>	WC <sup>2</sup>	TWC <sup>2</sup>
H <sub>2</sub> (vol.%)	0.99	62.8	13.29 (31)	ns	ns	ns	-3.99 (7)	-4.66 (8)	2.84 (5)	-9.32 (17)	ns	-3.75 (4)	ns	6.83 (12)	ns	ns	5.73 (10)	-3.15 (6)
CO <sub>2</sub> (vol.%)	0.99	29.69	-2.1 (19)	2.65 (2)	ns	ns	4.63 (12)	2.11 (6)	-4.02 (11)	4.87 (13)	ns	1.64 (1)	-1.97 (5)	-3.58 (9)	-3.74 (5)	ns	-2.89 (4)	4.88 (13)
CO (vol.%)	0.99	6.25	-8.87 (31)	-6.29 (13)	ns	-1.43 (5)	ns	2.53 (8)	1.25 (4)	4.75 (14)	1.96 (4)	ns	5.1 (5)	-3.24 (10)	ns	1.56 (3)	-2.3 (4)	Ns
CH <sub>4</sub> (vol.%)	0.99	0.29	-0.35 (1)	ns	0.09 (5)	-0.16 (12)	-0.14 (19)	ns	-0.04 (6)	Ns	ns	-0.08 (4)	ns	-0.06 (4)	0.37 (21)	0.06 (17)	ns	0.13 (11)

17

18

ns. Non significant with 95% confidence

19

20

Response variable = Independent term + Coefficient T·T + Coefficient W·W + Coefficient C·C + Coefficient TW·TW + Coefficient  
21 TC·TC + Coefficient WC·WC + Coefficient TWC·TWC + Coefficient T<sup>2</sup>·T<sup>2</sup> + Coefficient W<sup>2</sup>·W<sup>2</sup> + Coefficient C<sup>2</sup>·C<sup>2</sup> + Coefficient  
22 T<sup>2</sup>W·T<sup>2</sup>W + Coefficient T<sup>2</sup>C·T<sup>2</sup>C + Coefficient TW<sup>2</sup>·TW<sup>2</sup> + Coefficient TC<sup>2</sup>·TC<sup>2</sup> + Coefficient WC<sup>2</sup>·WC<sup>2</sup> + Coefficient TWC<sup>2</sup>·TWC<sup>2</sup>

23

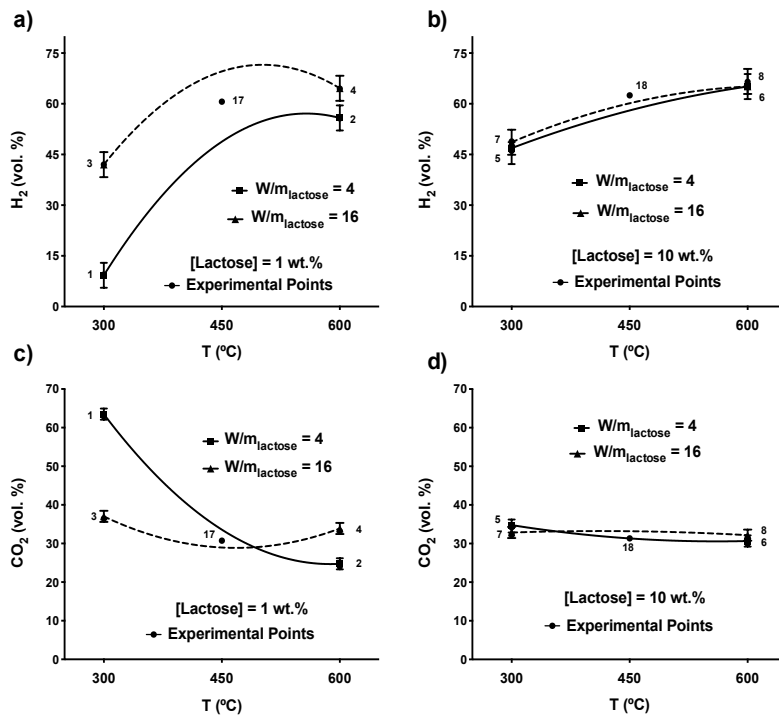
24

25 The effects of the operating conditions on the composition of the gas obtained with the  
26 ANOVA analysis are plotted in Figures 6 and 7. Specifically, Figures 6 a and c show  
27 the effect of the temperature using a 1 wt.% lactose solution and W/m<sub>glycerol</sub> ratios of 4  
28 and 16 g catalyst min / g lactose on the concentrations of H<sub>2</sub> and CO<sub>2</sub>. The influence of

1 the temperature and the  $W/m_{\text{glycerol}}$  for a 10 wt.% lactose solution is shown in Figures 6  
 2 b and d. Figure 7 plots these effects for the concentrations of  $\text{CO}$  and  $\text{CH}_4$  in the gas.  
 3 The evolution of these variables was obtained from the ANOVA analysis (Table 7) of  
 4 all the experiments performed (Table 4). In addition, when possible, some experimental  
 5 points were added.

6

7 **3.2.2.1  $\text{H}_2$  and  $\text{CO}_2$**



8

9 *Figure 6. Interaction plots for initial relative amounts (vol.%) of  $\text{H}_2$  (a and b) and  $\text{CO}_2$*   
 10 *(c and d) in the gas. Bars are LSD intervals with 95% confidence.*

11

12 Figure 6 shows how an increase in the temperature from 300 to 600 °C increases the  
 13 concentration of  $\text{H}_2$  in the gas regardless of the other operating variables and decreases  
 14 the proportion of  $\text{CO}_2$  in some cases. This development in the proportion of  $\text{H}_2$ , where  
 15 an optimum takes place at 450-500 °C, has also been reported in other works dealing

1 with steam reforming of other saccharides [31, 32] and is the consequence of the  
2 endothermic character of lactose steam reforming. The temperature exerts the greatest  
3 effect on the proportion of these two gases for a 1 wt.% lactose solution, while its effect  
4 is relatively weak as the concentration of lactose increases up to 10 wt.%. As an  
5 exception, the temperature does not exert a significant effect on the proportion of CO<sub>2</sub>  
6 for a 1 wt.% lactose solution using a W/m<sub>lactose</sub> ratio of 16 g catalyst min/ g lactose. This  
7 high W/m<sub>lactose</sub> ratio produces a concentration of CO<sub>2</sub> close to that predicted  
8 thermodynamically over the whole temperature range.

9

10 A comparison between Figures 6 a with b and c with d reveals that the proportion of H<sub>2</sub>  
11 in the gas increases between 300 and 450 °C when increasing the lactose concentration  
12 from 1 to 10 wt.% and reduces the relative amount of CO<sub>2</sub> in the gas for a W/m<sub>lactose</sub>  
13 ratio of 4 g catalyst min/g lactose. These developments account for the formation of C  
14 deposits that lower the amount of C in the gas as the concentration of lactose increases,  
15 thus increasing and decreasing the proportions of H<sub>2</sub> and CO<sub>2</sub>, respectively, especially  
16 at low temperatures. An increase in temperature decreases the solid carbon formation  
17 allowing thermodynamic composition to be reached for the proportions of H<sub>2</sub> and CO<sub>2</sub>.

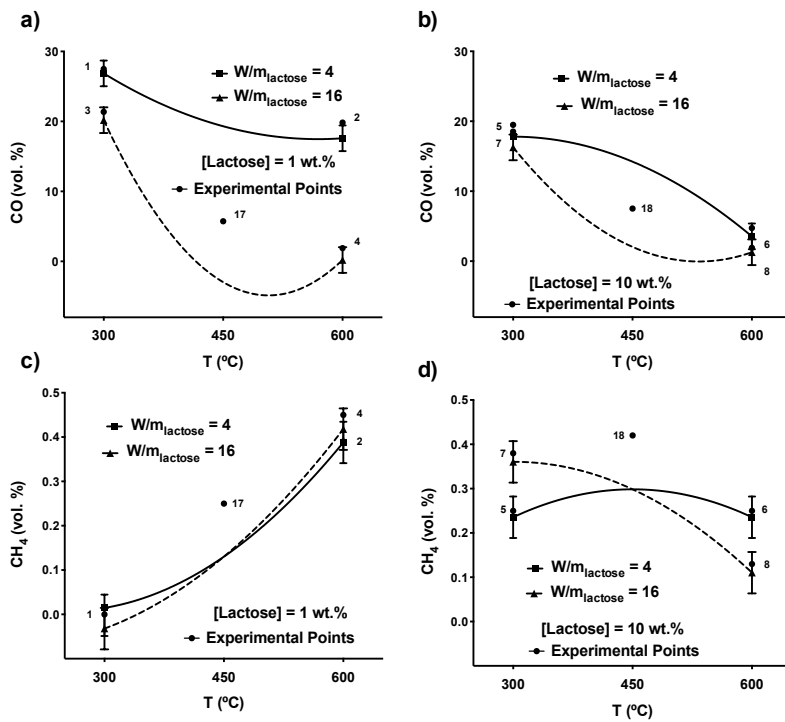
18

19 An increase in the W/m<sub>lactose</sub> ratio increases the proportion of H<sub>2</sub> in the gas and reduces  
20 the concentration of CO<sub>2</sub> between 300 and 500 °C for a 1 wt.% lactose solution. Lactose  
21 steam reforming involves an initial thermal decomposition forming CO<sub>2</sub>, CO and other  
22 intermediate products that subsequently evolve towards the thermodynamic  
23 composition of the gas [32]. At low temperatures, decomposition reactions might  
24 prevail over reforming reactions, which results in a gas with a higher and lower

1 proportion of H<sub>2</sub> and CO<sub>2</sub>, respectively, than those thermodynamically predicted. An  
 2 increase in the temperature or in the W/m<sub>lactose</sub> ratio increases the reaction rates of the  
 3 reforming reactions shifting the proportions of H<sub>2</sub> and CO<sub>2</sub> towards their  
 4 thermodynamic value. For a 10 wt.% lactose solution the W/m<sub>lactose</sub> ratio exerts a  
 5 negligible effect on the proportions of H<sub>2</sub> and CO<sub>2</sub>. This is the consequence of the trade-  
 6 off between the gasification of the carbon deposits (which decreases and increases the  
 7 proportions of H<sub>2</sub> and CO<sub>2</sub>, respectively) and reforming reactions (which shift the  
 8 proportion of H<sub>2</sub> and CO<sub>2</sub> towards their thermodynamic value).

9

10 3.2.2.2 CO and CH<sub>4</sub>



11

12 Figure 7. Interaction plots for initial relative amounts (vol.%) of CO (a and b) and CH<sub>4</sub>  
 13 (c and d) in the gas. Bars are LSD intervals with 95% confidence.

1 Figure 7 shows how an increase in the temperature decreases the relative amount of CO  
2 in the gas. At low temperatures (300-450 °C), lactose is thermally decomposed into a  
3 gas with a high proportion of CO and CO<sub>2</sub> [31]. This high proportion of CO in the gas  
4 decreases towards its thermodynamic value when increasing the temperature. In  
5 general, an increase in the  $W/m_{\text{lactose}}$  ratio from 4 to 16 g catalyst min/g lactose  
6 decreases the relative amount of CO in the gas due the greater spread of the water gas  
7 shift reaction.

8

9 The effect of the lactose concentration on the relative amount of CO in the gas can be  
10 observed comparing Figure 7 a with b. An increase in the lactose concentration for a  
11  $W/m_{\text{lactose}}$  ratio of 4 g catalyst min/ g lactose decreases the proportion of CO in the gas,  
12 especially at temperatures higher than 450 °C due to the low amount of C of the gas  
13 phase. Conversely, for a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g lactose the effect of the  
14 concentration of lactose is not significant. At temperatures higher than 450 °C, the  
15 reforming process is favoured and a thermodynamic concentration for the CO is  
16 obtained. At temperatures lower than 450 °C there is a trade-off between the  
17 gasification of carbon deposits and the higher extension of the WGS reaction.

18

19 The proportion of CH<sub>4</sub> in the gas is lower than 0.5 vol.% in all cases. For a 1 wt.%  
20 lactose solution the concentration of CH<sub>4</sub> increases with temperature regardless of the  
21  $W/m_{\text{lactose}}$  ratio. The proportion of C in the gas increases with temperature, which can  
22 increase the concentration of CH<sub>4</sub>. For a 10 wt.% lactose solution and employing 4 g  
23 catalyst min/g lactose, the temperature does not have a significant influence, while for a  
24 16 g catalyst min/g lactose the relative amount of CH<sub>4</sub> drops as the temperature

1 increases. At temperatures higher than 450 °C the evaporation of the feed and the  
2 reforming process are favoured but the thermodynamic proportion of CH<sub>4</sub> decreases. A  
3 comparison between Figure 7 c and d shows how an increase in the concentration of  
4 lactose increases the proportion of CH<sub>4</sub> in the gas between 300 and 500 °C due to the  
5 thermodynamics. Between 450 and 600 °C the same increase in the concentration of  
6 lactose causes a decrease in the concentration of CH<sub>4</sub> in the gas.

7

### 8 3.2.3 *Liquid composition*

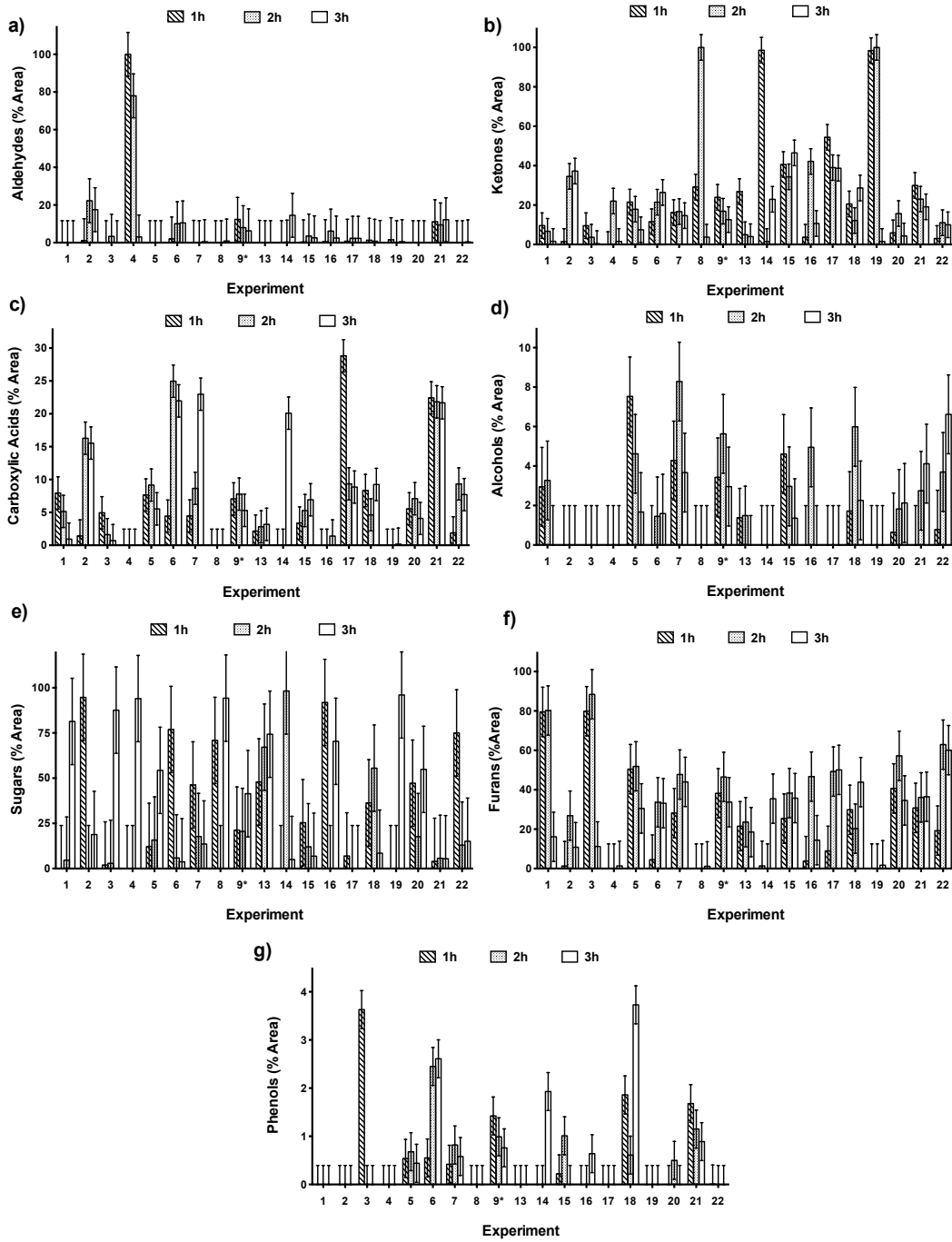
9 The liquid phase is made up of a mixture of aldehydes (acetaldehyde and propanal),  
10 ketones (2-propanone), carboxylic acids (acetic and propionic acids), sugars  
11 (levoglucosan and D-lose), furans (furfural, 2-furancarboxaldehyde and 2,5-  
12 furandicarboxaldehyde), alcohols (ethanol, propanol and cyclic alcohols) and phenolic  
13 compounds (phenol and methyl-phenols). The presence of these compounds in the  
14 liquid phase, which is consistent with the reaction pathway proposed in Figure 1, is the  
15 result of the thermal decomposition of lactose and the incomplete reforming of lactose  
16 and its liquid intermediates. All these reaction intermediates have a high tendency to  
17 form coke (especially sugars, furans and aromatic species) [36, 52-55] which explains  
18 the formation of coke observed experimentally and the high proportion of CO and CO<sub>2</sub>  
19 in the gas under some experimental conditions.

20

21 Figure 8 plots the relative amounts of each of the different families of liquid compounds  
22 for the different experiments represented in 3 intervals of 60 minutes, together with the  
23 results of the Fischer's LSD test. The results from the statistical analysis (ANOVA)  
24 revealed significant differences in the concentrations of aldehydes, ketones, carboxylic



1 acids, sugars, furans, alcohols and phenols ( $p$ -values  $< 0.05$ ). The proportion of these  
2 compounds in the liquid, expressed as relative chromatographic area, is as follows.  
3 Aldehydes: 0-100 %, ketones: 0-99%, carboxylic acids: 0-29%, furans: 0-99%, sugars:  
4 0-89%, alcohols: 0-9% and phenols: 0-4%. For the operating conditions where a  
5 negligible formation of liquid is achieved (high temperature and  $W/m_{\text{lactose}}$  ratio), the  
6 liquid phase is made up of aldehydes and of a mixture of ketones and sugars when  
7 feeding a 1 and a 10 wt.% lactose solution, respectively.  
8



1

2 *Figure 8. Liquid composition results are presented as the relative chromatographic*  
 3 *area divided into three intervals of 1 h for the different families of compounds and*  
 4 *expressed as mean  $\pm$  0.5 Fisher LSD intervals with 95% confidence.*

5

6

1 Studying the evolution over time for these compounds, two tendencies are found.  
2 Aldehydes, alcohols and phenols remain relatively steady, while high variations over  
3 time can be seen for ketones, carboxylic acids, sugars and furans. Aldehydes display a  
4 decrease in their relative area in run 4. The relative amount of phenols decreases for run  
5 3 and increases for runs 6, 14 and 18. Increases in the proportion of ketones are found  
6 for runs 2 and 6 while decreases take place for runs 5, 8, 13, 14, 17 and 19. Carboxylic  
7 acids display increases for runs 2, 6, 7, 14 and 22 and decreases for runs 1 and 17. The  
8 proportion of sugars increases for runs 1, 3, 4 and 19 and decreases for runs 2, 6 and 22.  
9 The relative amount of furans in the liquid increases for runs 6, 14, 17 and 22 and  
10 decreases for runs 1 and 3.

11

12 To gain a better insight into the variations over time of these compounds, a multivariate  
13 analysis by means of Spearman's test was conducted to find significant relationships  
14 between the proportions of these compounds in the liquid phase. This test reveals  
15 significant relationships with 95% confidence between the proportions of furans and  
16 carboxylic acids (p-value = 0.0001;  $R^2 = 0.65$ ); carboxylic acids and ketones (p-value =  
17 0.0001;  $R^2 = 0.35$ ); carboxylic acids and sugars (p-value = 0.0001;  $R^2 = 0.65$ ); furans  
18 and alcohols (p-value = 0.0001;  $R^2 = 0.63$ ); furans and sugars (p-value = 0.0001;  $R^2 =$   
19 0.36); alcohols and phenols (p-value = 0.0001;  $R^2 = 0.46$ ) and phenols and carboxylic  
20 acids (p-value = 0.0001;  $R^2 = 0.56$ ). These relationships account for the experimental  
21 observations and the reaction pathway shown in Figure 1. The test reveals that the  
22 increase in the proportion of sugars takes place together with decreases in the  
23 proportions of furans and ketones.

24

1 The specific effects of the operating conditions as well as their possible interactions on  
 2 the liquid composition were studied considering the results obtained during the first 60  
 3 minutes of reaction. Table 8 shows the significant terms in the codec model and their  
 4 relative influence in the process according to the cause-effect Pareto test and the  
 5 ANOVA analysis for the different families of compounds. Sugars, furans, aldehydes,  
 6 ketones and carboxylic acids are the compounds displaying the highest variations in  
 7 their proportions during the first hour of experiment, and consequently they are the most  
 8 influenced by the operating conditions. Thus, only the influence of the operating  
 9 conditions on the proportion of these families has been discussed in depth.

10

11 *Table 8. Relative influence of the operating conditions on the liquid composition*  
 12 *according to the ANOVA analysis for the first hour of reaction.*

13

Variable	R <sup>2</sup>	I. Term	T	W	C	TW	TC	WC	TWC	T <sup>2</sup>	W <sup>2</sup>	C <sup>2</sup>	T <sup>2</sup> W	T <sup>2</sup> C	TW <sup>2</sup>	TC <sup>2</sup>	WC <sup>2</sup>	TWC <sup>2</sup>
<b>Ketones (%)</b>	0.98	39.11	31.87 (13)	-18.45 (3)	-16.92 (2)	16.4 (7)	ns	ns	ns	16.42 (1)	-24.13 (13)	-8.82 (9)	36.27 (9)	24.14 (9)	ns	-33.7 (18)	-16.48 (8)	-13.72 (6)
<b>C. Acids (%)</b>	0.99	13.26	ns	-1.69 (10)	-10.25 (7)	-6.52 (9)	ns	ns	ns	-7.68 (7)	-7.07 (10)	9.81 (7)	-3 (4)	10.52 (15)	3.75 (1)	-6.14 (11)	3.18 (5)	6.56 (12)
<b>Furans (%)</b>	0.99	24.44	-8.22 (28)	-10.78 (6)	10.43 (7)	-13.1 (4)	10.5 (11)	-3.24 (3)	ns	-9.06 (2)	-5.91 (0.5)	ns	7.69 (4)	-20.12 (9)	ns	-20.81 (14)	ns	15.07 (9)
<b>Sugars (%)</b>	0.99	7.81	-23.94 (1)	33.26 (2)	13.9 (11)	5.94 (8)	ns	15.07 (11)	7.07 (5)	Ns	35.45 (10)	-1.53 (2)	41.31 (14)	ns	-5.61 (2)	52.29 (24)	ns	-23.03 (10)
<b>Aldehydes (%)</b>	0.99	-0.64	ns	ns	ns	-2.39 (9)	-12.4 (11)	-12.6 (11)	-12.64 (11)	2.74 (4)	3.11 (2)	3.69 (7)	-2.38 (2)	-12.36 (11)	3.18 (2)	9.68 (12)	14.52 (11)	14.48 (8)
<b>Alcohols (%)</b>	0.90	2.66	ns	-2.3 (13)	1.06 (15)	ns	-1.11 (14)	ns	ns	-1.29 (12)	ns	-1.12 (3)	1.78 (10)	ns	ns	-1.84 (23)	ns	0.77 (10)
<b>Phenols (%)</b>	0.98	1.32	ns	ns	0.93 (1)	-0.48 (13)	0.4 (9)	-0.54 (12)	0.4 (9)	-0.61 (9)	-0.5 (3)	ns	-0.42 (3)	-1.19 (12)	0.42 (6)	-0.92 (12)	0.79 (10)	ns

14

ns. Non significant with 95% confidence

15

16

Response variable = Independent term + Coefficient T·T + Coefficient W·W + Coefficient C·C + Coefficient TW·TW + Coefficient TC·TC + Coefficient WC·WC + Coefficient TWC·TWC + Coefficient T<sup>2</sup>·T<sup>2</sup> + Coefficient W<sup>2</sup>·W<sup>2</sup> + Coefficient C<sup>2</sup>·C<sup>2</sup> + Coefficient T<sup>2</sup>W·T<sup>2</sup>W + Coefficient T<sup>2</sup>C·T<sup>2</sup>C + Coefficient TW<sup>2</sup>·TW<sup>2</sup> + Coefficient TC<sup>2</sup>·TC<sup>2</sup> + Coefficient WC<sup>2</sup>·WC<sup>2</sup> + Coefficient TWC<sup>2</sup>·TWC<sup>2</sup>

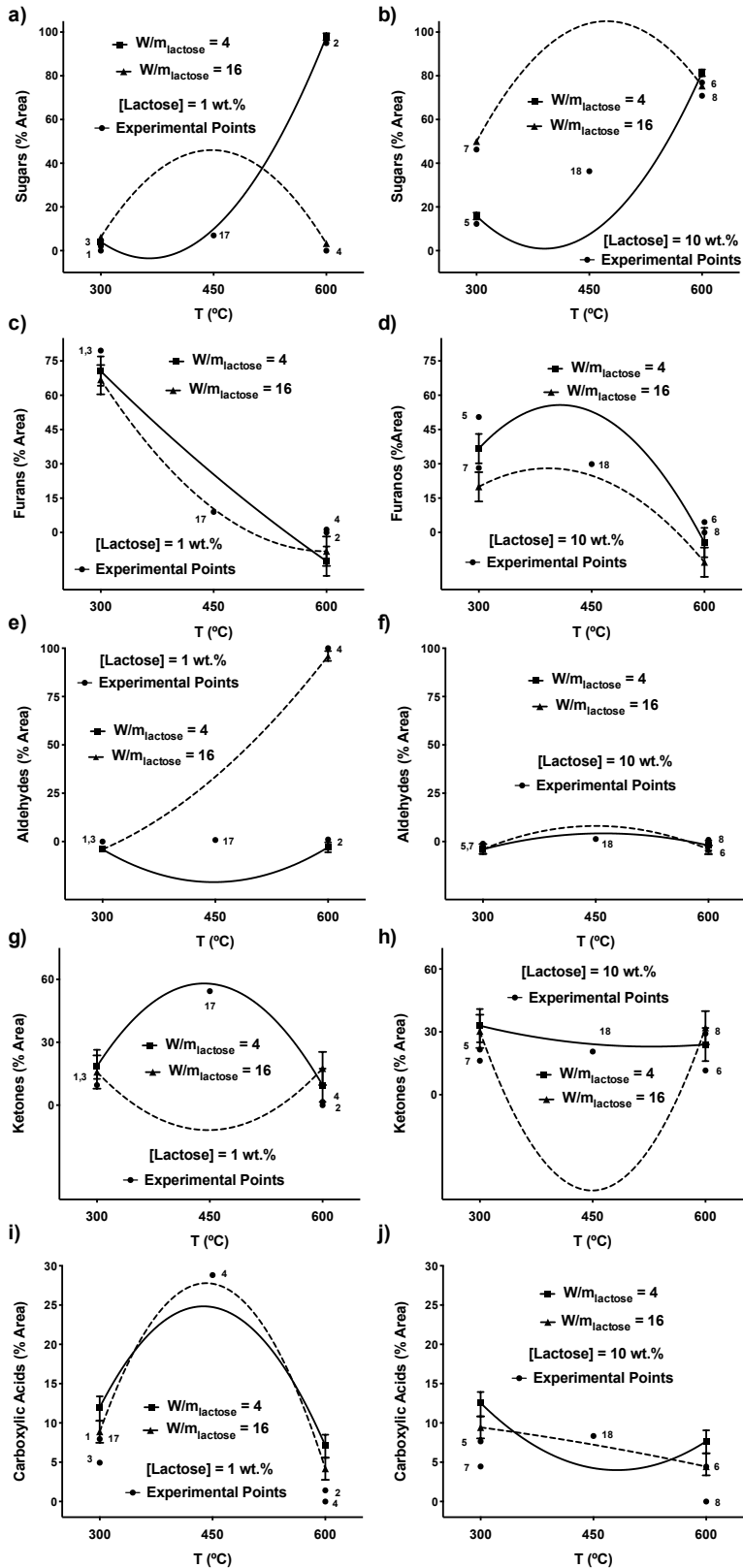
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18

19

20

21 The relative influence of the operating conditions on the liquid composition summarised  
 22 in Table 8 indicates that the temperature and the  $W/m_{\text{lactose}}$  exert the greatest influence  
 23 on the proportion of these liquids. Lactose decomposition is a competitive process  
 24 involving competition between fragmentation and polymeric reactions. Therefore the  
 25 operating conditions significantly influence the composition of the liquid phase [56].



1  
 2 Figure 9. Interaction plots for initial relative amounts (vol.%) of sugars (a and b),  
 3 furans (c and d), aldehydes (e and f), ketones (g and h) and carboxylic acids (i and j).  
 4 Bars are LSD intervals with 95% confidence.

1  
2 The temperature, residence time and pH are the most influential parameters affecting  
3 product distribution during the thermal decomposition of carbohydrates [57]. Figure 9  
4 summarises the effect of the operating variables and the most important interactions on  
5 the liquid product distribution according to the ANOVA analysis. The evolution of  
6 these variables was obtained from the ANOVA analysis (Table 8) of all the experiments  
7 performed (Table 4). In addition, when possible, some experimental points were added.  
8 Some plots predict slightly negative relative areas due to the experimental character of  
9 the models. Specifically, Figures 9 a, c, e, g and i show the effect of the temperature on  
10 the proportion of sugars, furans, aldehydes, ketones and carboxylic acids in the liquids  
11 for  $W/m_{\text{lactose}}$  ratios of 4 and 16 g catalyst min/g lactose when a 1 wt.% lactose solution  
12 was used. These effects are plotted for a 10 wt.% lactose solution in Figures 9 b, d, f, h  
13 and j.

14

### 15 3.2.3.1 Sugars

16 The influence of the temperature on the proportion of sugars in the liquid depends on  
17 the  $W/m_{\text{lactose}}$  ratio. For 4 g catalyst min/g lactose the temperature does not exert a  
18 significant effect between 300 and 400 °C, where a liquid free of sugars is obtained. An  
19 increase in the temperature between 400 and 600 °C dramatically increases the  
20 proportion of sugars as their formation is favoured at high temperatures [40].  
21 Conversely, for a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g lactose, a rise in the proportion  
22 of sugars takes place as the temperature increases from 300 to 450 °C. A posterior drop  
23 follows this increase when the temperature is further increased up to 600 °C. The  
24 increase in the  $W/m_{\text{lactose}}$  ratio promotes the transformation of sugars into gases, thus  
25 reducing their proportion in the liquid phase.

1

2 The  $W/m_{\text{lactose}}$  ratio exerts a significant influence on the proportion of sugars. Between  
3 300 and 450 °C an increase in this ratio leads to an increase in the proportion of sugars  
4 in the liquid. Within this temperature range, an increment in the amount of catalyst  
5 helps to decrease the formation of carbon deposits, which increases the formation of  
6 liquid products. However, at temperatures of 450 °C and beyond, where the reforming  
7 process is more favoured, this same increase leads to a decrease in the proportion of  
8 sugars for a 1 wt.% solution, probably due to their steam reforming to produce gases.  
9 This effect is not observed for a 10 wt.% solution, since the formation of sugars is more  
10 favoured when increasing the concentration of lactose in the feed.

11

12 The effect of the lactose concentration on the proportion of sugars in the liquid depends  
13 on the  $W/m_{\text{lactose}}$  ratio. For 4 g catalyst min/g lactose, the effect of the concentration is  
14 relatively small, while for 16 g catalyst min/g lactose an increase in the concentration of  
15 lactose in the feed greatly increases the relative amount of sugars in the liquid. A lower  
16 amount of water can help to shift the dehydration reactions of glucose and galactose  
17 towards the production sugars.

18

### 19 3.2.3.2 *Furans*

20 The highest proportion of furans in the liquid occurs at low temperatures, where their  
21 formation might be favoured. An increase in the temperature decreases their proportion  
22 in the liquid due to the greater extension of reforming reactions to produce gases. The  
23 effect of the  $W/m_{\text{lactose}}$  ratio is only significant for a concentrated lactose solution (10  
24 wt.%). Under these conditions, an increase in the amount of catalyst reduces the relative

1 amount of furans in the liquid between 300 and 450 °C. Within this temperature range,  
2 an increase in the  $W/m_{\text{lactose}}$  ratio increases the CC gas, which increases the proportion  
3 of sugars, thus reducing the relative amount of furans in the liquid. Moreover, an  
4 increase in the  $W/m_{\text{lactose}}$  ratio also aids the transformation of furans into phenolic  
5 compounds and gases, which accounts for the drop observed for this family and is in  
6 agreement with the reaction pathway proposed in Figure 1. The lactose concentration is  
7 only significant at temperatures between 300 and 400 °C, where an increase from 1 to  
8 10 wt.% reduces the proportion of furans in the liquid. The increase observed in the  
9 proportion of sugars due to the lower excess of water accounts for this variation.

10

### 11 3.2.3.3 Aldehydes

12 The influence of the temperature on the proportion of aldehydes in the liquid depends  
13 on the concentration of lactose and the  $W/m_{\text{lactose}}$  ratio. For a 1 wt.% lactose solution  
14 employing a  $W/m_{\text{lactose}}$  ratio of 4 g catalyst min/g lactose, the temperature does not exert  
15 a significant effect on the proportion of aldehydes in the liquid. For a ratio of 16 g  
16 catalyst min/g lactose, an increase in temperature increases the proportion of aldehydes.  
17 Acetaldehyde, obtained from the fragmentation of glucose and galactose, is the major  
18 constituent of this family. High temperatures favours linear aldehyde production [56],  
19 which is in agreement with the experimental results of this work. For a 10 wt.% solution  
20 the effect of the temperature and  $W/m_{\text{lactose}}$  on the proportion of aldehydes is weak, and  
21 a proportion of aldehydes lower than 5% is obtained within the whole temperature range  
22 considered in this work.

23

24



### 1 3.2.3.4 Ketones

2 The effect of the temperature on this family depends on the other two operating  
3 variables. When a 1 wt.% lactose solution and a  $W/m_{\text{lactose}}$  ratio of 4 g catalyst min/g  
4 lactose are used, an increase in the temperature initially increases the proportion of  
5 ketones from 300 to 450 °C, while a further increase up to 600 °C reduces their relative  
6 amount. For a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g lactose, the opposite trend with the  
7 temperature is observed. Low temperatures can favour the extension of retroaldolic  
8 reactions, increasing the proportion of ketones in the liquid. An increase in temperature  
9 might favour their transformation into other liquid intermediates and/or gases. For 16 g  
10 catalyst min/g lactose, the initial decrease in the proportion of ketones takes place  
11 together with an increase in the relative amounts of aldehydes and sugars, which might  
12 indicate a lower reactivity of ketones in steam reforming [36, 58, 59].

13

14 For a 10 wt.% lactose solution the temperature does not exert a significant influence for  
15 a  $W/m_{\text{lactose}}$  ratio of 4 g catalyst min/g lactose. However, an initial decrease in the  
16 proportion of ketones takes place for temperatures from 300 to 450 °C followed by a  
17 posterior increase from 450 to 600 °C when a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g  
18 lactose is used. The higher formation of carbon deposits when feeding a concentrated  
19 lactose solution, which decreases the fraction of vaporised organic compounds, might  
20 hinder any increase in ketones with the temperature; thus the ketones follow the same  
21 trend as found for a 1 wt.% lactose solution. As the temperature increases and the CC  
22 sol decreases, the proportion of ketones reaches the same value as that for a 1 wt.%  
23 solution.

24

1 The effect of the concentration of lactose is found to be significant only between 400  
2 and 500 °C for a  $W/m_{\text{lactose}}$  ratio of 4 g catalyst min/g lactose. Under these conditions an  
3 increase in the concentration of lactose decreases the relative amount of ketones in the  
4 liquid. Retroaldolic reactions might be favoured when high S/C and low  $W/m_{\text{lactose}}$  ratios  
5 are used. A greater amount of catalyst might increase the reaction rates of the reforming  
6 reactions, thus increasing gas production.

7

### 8 *3.2.3.5 Carboxylic acids*

9 Carboxylic acids are intermediate products in lactose steam reforming. They are  
10 obtained at low temperatures from the decomposition of glucose and galactose by  
11 fragmentation and retroaldol reactions [40]. They can be obtained from alcohol  
12 dehydration and aldehyde oxidation. The effect of the temperature depends on the  
13 concentration of lactose. For a 1 wt.% solution, an increase in their relative amount  
14 takes place between 300 and 450 °C regardless of the  $W/m_{\text{lactose}}$  ratio, reaching a  
15 maximum in the proportion of carboxylic acids at 450 °C. Lactose decomposition  
16 through retroaldol and fragmentation reactions might be favoured at this temperature  
17 range. A further increase in the temperature up to 600 °C reduces the proportion of  
18 carboxylic acids, probably due to their transformation into other liquid products and/or  
19 gases. For a 10 wt.% lactose solution a mild decrease with temperature takes places.  
20 The  $W/m_{\text{lactose}}$  ratio does not significantly influence the proportion of carboxylic acids,  
21 while the concentration of lactose exerts a significant influence decreasing the  
22 proportion of acids in the condensate as the lactose concentration increases from 1 to 10  
23 wt.%.

24

1 3.3 Theoretical prediction of optimal operating conditions and energetic assessment

2 Optimal conditions for hydrogen production were sought making use of the  
 3 experimental models developed for the optimisation and scaling-up of this valorisation  
 4 process. The predicted  $R^2$  of all the models is higher than 0.90, allowing their use for  
 5 prediction purposes. Three different optimisations were carried out. The first was the  
 6 optimisation of the temperature for processing the highest amount of lactose, i.e.  
 7 maximising the concentration of lactose in the feed. The second and the third aimed at  
 8 optimising the process for the treatment of real cheese whey, fixing the concentration of  
 9 lactose at 5.5 wt.% (the usual concentration of lactose in cheese whey) and maximising  
 10 the CC gas and the proportion of  $H_2$  in the gas. In the second optimisation the  
 11 temperature and the  $W/m_{\text{lactose}}$  ratio were minimised, while no restrictions for these two  
 12 variables were considered in the third optimisation. Additionally, the evolution over  
 13 time of the CC gas and the proportion of  $H_2$  in the gas were minimised in all the  
 14 optimisations.

16 Table 9. Theoretical optimisation: Objectives, optimum values for the operating  
 17 variables and optimised values for some responses

Variable	Optimisation 1			Optimisation 2			Optimisation 3		
	Objective	Importance	Optimum	Objective	Importance	Optimum	Objective	Importance	Optimum
T (°C)	Minimum	1	559	Minimum	2	506	None	2	586
[Lactose] (wt.%)	Maximum	2	10	Fixed	2	5.5	Fixed	2	5.5
$W/m_{\text{lactose}}$ (g cat min/g lactose)	None	2	16	Minimum	1	15	None	1	16
CC gas (%)	Maximum	5	78	Maximum	5	72	Maximum	5	88
CC liq (%)	Minimum	3	2.5	Minimum	3	6	Minimum	3	0
CC sol (%)	Minimum	5	14	Minimum	5	18	Minimum	5	12
$H_2$ (vol.%)	Maximum	4	65	Maximum	4	66	Maximum	4	67
$CO_2$ (vol.%)	None	3	33	None	3	31	None	3	29
CO (vol.%)	None	3	0.2	None	3	0	None	3	0.7
$CH_4$ (vol.%)	None	3	0.2	None	3	0.2	None	3	0.2
Var CC gas (%)	Minimum	2	13	Minimum	2	26	Minimum	2	8
Var vol. $H_2$ (%)	Minimum	2	-5	Minimum	2	-6	Minimum	2	-2

19  
 20 Var CC gas (%), Var vol.  $H_2$  (%): time variation percentage for the CC gas and relative amount of  $H_2$  in the gas (%), respectively.  
 21 Positive and negative values indicate decreases and increases over time, respectively.  
 22 Var CC gas (%) =  $43.3+14.43\cdot T-9.71\cdot W-9.58\cdot T\cdot W-18.56\cdot T^2-14.56\cdot W^2$  ( $R^2 = 0.85$ )  
 23 Var vol.  $H_2$  (%) =  $0.63-20.33\cdot T-3.55\cdot W-4.25\cdot T\cdot W+9.13\cdot T\cdot C+20.13\cdot T^2+3.12\cdot W^2+3.13\cdot C^2+4.25\cdot T^3\cdot W-9.38\cdot T^2\cdot C-2.29\cdot T\cdot C^2-$   
 24  $10.38\cdot W\cdot C^2+10.13\cdot T\cdot W\cdot C^2$  ( $R^2 = 1$ )  
 25  
 26

1 To meet these objectives, a solution that strikes a compromise between the optimum  
2 values for all the response variables was sought. To do so, a relative importance (from 1  
3 to 5) was given to each of the objectives in order to come up with the solution that  
4 satisfies all the criteria. Table 9 lists the relative importance assigned to each variable,  
5 the criteria used in the optimisations and the optimisation results.

6

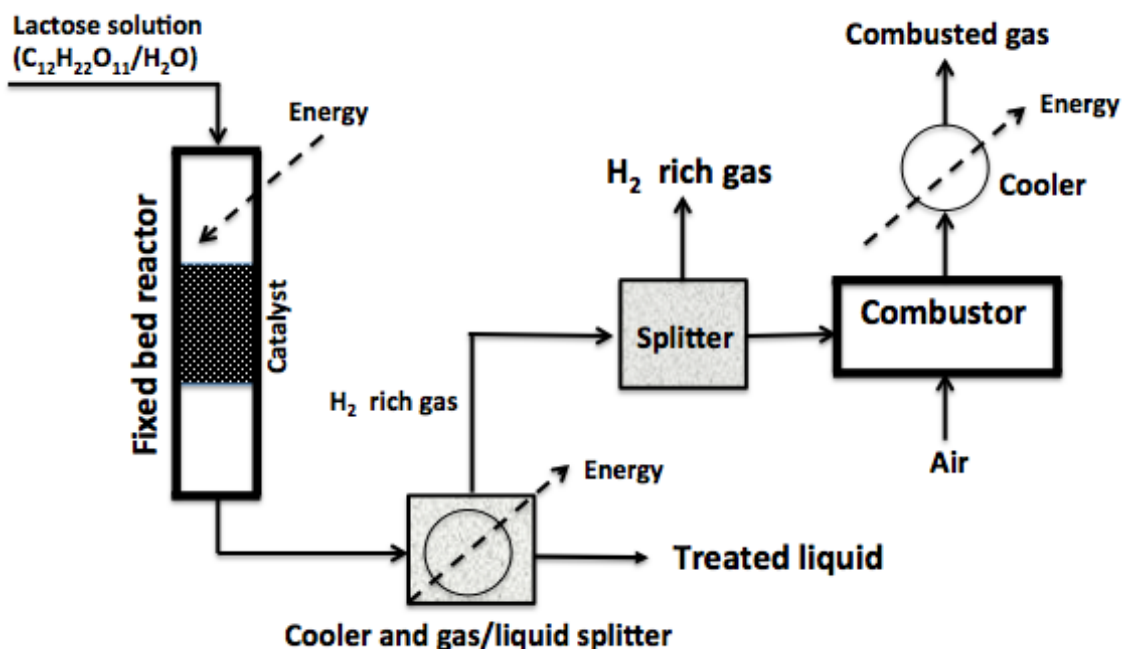
7 A possible optimum for maximising the concentration of lactose in the feed was found  
8 at 559 °C employing a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g lactose (Opt. 1). These  
9 conditions provide a CC gas of 78% with a proportion of H<sub>2</sub> in the gas of 65 vol.%.  
10 When feeding a lactose concentration of 5.5%, an optimum for H<sub>2</sub> production takes  
11 place at 506 °C using a  $W/m_{\text{lactose}}$  ratio of 15 g catalyst min/g lactose (Opt. 2). These  
12 conditions provide a CC gas of 72% with a relative amount of H<sub>2</sub> in the gas of 66 vol.%.  
13 The second optimisation predicts a lower temperature than that of the first due to the  
14 lower concentration of lactose. For maximising the CC gas and the relative amount of  
15 H<sub>2</sub> in the gas (Opt. 3), the temperature must be increased up to 586 °C. As a result a CC  
16 gas of 88% and a proportion of H<sub>2</sub> in the gas of 67 vol.% can be obtained. This increase  
17 of 80 °C reduces the CC liq from 6 to 0% and the CC sol from 18 to 12%. These  
18 conditions not only produce a H<sub>2</sub> rich gas from cheese whey, but also provide a carbon-  
19 free liquid product that can be discharged to the environment without any further  
20 treatment, thus helping to improve the economy and sustainability of the cheese  
21 manufacturing companies.

22

23 An energy balance for the process was conducted for the third optimisation using Hysys  
24 8.4 simulation software with a PRSV thermodynamic package. The input energy,  
25 calculated as the sum of energy needed to heat the feed up to the reforming temperature

1 and the energy needed for the steam reforming reaction, is 3555 kJ/kg of solution. The  
 2 theoretical output energy, calculated as the energy recovered from the gas as it is cooled  
 3 from the reforming temperature to 25 °C (assuming water in liquid state), is 3338 kJ/kg  
 4 of solution. As a result, it is necessary to provide 217 kJ/kg of solution for the process.  
 5 This energy can be theoretically generated by the combustion of 20% of the reforming  
 6 gas with the stoichiometric amount of air (0.07 kg air/kg solution) and with the energy  
 7 recovered from the gas as it is cooled from the adiabatic combustion temperature (1632  
 8 °C) to 25 °C (assuming water in liquid state). Figure 10 shows a schematic diagram of  
 9 this reforming-combustion process. Overall, with the combustion of 20% of the gas  
 10 produced in the process, 68 % of the carbon present in the original feed can be  
 11 transformed into a rich hydrogen gas (67 vol.%), with a global H<sub>2</sub> yield of 16 mol  
 12 H<sub>2</sub>/mol lactose in a neutral energy process.

13



14

15 Figure 10. Schematic diagram of the reforming-combustion process

16

1 To study a more realistic case, it has been considered that 5% of the energy recovered in  
2 the coolers and produced by combustion is lost. In this case, considering an energy loss  
3 of 5% in the burner and the subsequent cooler, the combustion of 41% of the reforming  
4 gas would be required to provide the energy necessary for the process. The  
5 stoichiometric amount of air and the adiabatic combustion temperature are 0.13 kg  
6 air/kg solution and 1606 °C, respectively. Taking these heat losses into account, an  
7 overall carbon conversion to gas of 52 % and a global H<sub>2</sub> yield of 12.5 mol H<sub>2</sub>/mol  
8 lactose could be obtained from this valorisation-combustion process.

9  
10 This H<sub>2</sub> yield is close to the theoretical maximum of the process (24 mol H<sub>2</sub>/mol  
11 lactose) and is higher than those obtained in anaerobic fermentation (4 mol H<sub>2</sub>/mol  
12 lactose) or anaerobic fermentation plus photo-fermentation with L-malic acid (2-10 mol  
13 H<sub>2</sub>/mol lactose). In addition, the energy calculations indicate that catalytic steam  
14 reforming is energetically feasible for energy and H<sub>2</sub> production.

15

#### 16 **4. Conclusions**

17 The catalytic steam reforming of lactose, the major organic constituent of cheese whey,  
18 has been evaluated both theoretically and experimentally in a fixed bed reactor using a  
19 Ni-based catalyst. The most important conclusions obtained from this preliminary study  
20 for the valorisation of this waste stream obtained during the cheese making process are  
21 summarised as follows.

22 1. This process enables the lactose present in cheese whey effluents to be transformed  
23 into a rich H<sub>2</sub> gas, reducing the amount of carbon present in the liquid effluent and  
24 resulting in an almost carbon-free liquid stream under certain operating conditions.

1 2. The temperature and the concentration of lactose are the factors with the highest  
2 influence on the thermodynamics of lactose steam reforming. A thermodynamic  
3 optimum for H<sub>2</sub> production is found to be at a temperature between 430 and 570 °C for  
4 the whole range of lactose concentrations considered in this work (1-10 wt.%).

5 3. The temperature, lactose concentration and W/m<sub>lactose</sub> ratio have a statistically  
6 significant influence on the carbon conversions to gas, solid and liquid products as well  
7 as on the composition of the gas and liquid phases. An increase in the temperature  
8 augments the CC gas, due to the endothermic nature of the reforming process. In  
9 addition, the temperature enhances the vaporisation of the feed and promotes the  
10 gasification of the carbonaceous deposits derived from an incomplete vaporisation.

11 4. The gas phase was made up of a mixture of H<sub>2</sub> (10-68 vol.%), CO<sub>2</sub> (24-63 vol.%),  
12 CO (1-28 vol.%) and CH<sub>4</sub> (0-1 vol.%). The temperature is the operating variable with  
13 the greatest influence on the composition of the gas. An increase in the reforming  
14 temperature increases the proportion of H<sub>2</sub> and reduces the concentration of CO in the  
15 gas. An increase in the W/m<sub>lactose</sub> ratio favours the reforming and the water gas shift  
16 reactions. The effect of the concentration of lactose on the composition of the gas phase  
17 depends on the temperature and W/m<sub>lactose</sub> ratio due to the coexistence and competition  
18 of kinetic (vaporisation and reforming reaction rates) and thermodynamic effects.

19 5. The liquid phase is made up of a mixture of aldehydes, ketones, carboxylic acids,  
20 sugars, furans, alcohols and phenols derived from the thermal decomposition of lactose.  
21 This thermal decomposition involves competition between fragmentation and  
22 condensation reactions.

23 6. The maximum CC gas (88%) together with the highest proportion of H<sub>2</sub> (67 vol.%) in  
24 the gas, along with a carbon-free liquid stream when feeding a 5.5 wt.% lactose solution  
25 (typical of cheese whey), are achieved using a reforming temperature of 586 °C and

1 employing a  $W/m_{\text{lactose}}$  ratio of 16 g catalyst min/g lactose. The combustion of 20% of  
2 this reforming gas provides the energy necessary for the process. Considering the global  
3 process (reforming and combustion) a rich hydrogen gas with a global  $H_2$  yield of 16  
4 mol  $H_2$ /mol lactose can be obtained. If heat losses are considered, the proportion of the  
5 reforming gas needed for combustion increases up to 40%, and the global  $H_2$  yield  
6 decreases up to a value of 12.5 mol  $H_2$ /mol lactose.

7

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14

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