Cheese whey management by catalytic steam reforming and aqueous phase reforming

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ABSTRACT

Cheese whey is a yellowish liquid by-product of the cheese making process. Owing to its high BOD and COD values, this feedstock should not be directly discharged into the environment without appropriate treatment. The management of this wastewater has become an important issue, and new treatments must be sought. This work addresses the valorisation of cheese whey by steam reforming and aqueous phase reforming. The catalytic steam reforming of cheese whey turned out to be a promising valorisation route for H_2 production from this effluent. This process enabled the organic compounds present in the cheese whey to be transformed into a rich H_2 gas (35% of the C of the feed was transformed into a gas with 70 vol.% of H_2). This significantly reduced the amount of carbon present in the original feedstock, producing an almost carbon-free liquid stream. The aqueous phase reforming of cheese whey allowed 35% of the carbon present in the whey to be transformed into gases and 45% into valuable liquids. The gas was principally made up of H_2 and CO_2, while a mixture of added-value liquids such as aldehydes, carboxylic acids, alcohols and ketones constituted the liquid phase. However, both valorisation routes produced a substantial amount of solid. The formation of this solid was promoted by the presence of salts in the original feedstock and caused operational problems for both valorisation processes. In addition, it hampered gas production in the case of steam reforming and reduced gas and liquid formation when using aqueous phase reforming as the valorisation route. The filtration

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of cheese whey slightly decreased the solid formation in both processes due to the reduction of proteins and fats, both of which partly contribute to such formation. Less solid was formed in the experiments conducted with lactose than in those conducted with whole and with filtered cheese whey.

1. Introduction

Cheese whey is a yellowish liquid resulting from the coprecipitation and removal of milk casein in cheese-making processes. On average, 9 kg of cheese whey is produced during the production of 1 kg of cheese, which corresponds to a worldwide production of 5 million tons a year. The typical composition of this effluent is 4.5-6 wt.% lactose, 0.6-1.1 wt.% proteins, 0.8-1 wt.% minerals, 0.05-0.9 wt.% lactic acid, 0.06-0.5 wt.% fats and 93-94 wt.% water [1-4]. It has BOD and COD values ranging from 27-60 kg/m^3 and 50-102 kg/m^3, respectively; therefore, it should not be directly discharged into the environment without appropriate treatment and/or valorisation [3]. As a result of stricter regulations for waste disposal and environmental concerns, cheese effluent management has become an important issue [1-4].

Two options for cheese whey management have normally been considered [3]. The first is the application of physicochemical treatments and filtration technologies to recover the most valuable compounds from cheese whey, i.e. proteins and lactose. Physicochemical treatments include thermal and isoelectric precipitation [5, 6] and protein precipitation [7], while filtration technologies involve the use of ultrafiltration membranes and reverse osmosis [2]. The second option relies on the application of biological treatments without valorisation, such as aerobic digestion, and with valorisation such as anaerobic digestion, lactose hydrolysis and fermentation [3]. Aerobic digestion consists of the degradation of the organic matter of whey at room temperature using short hydraulic retention times [8]. Anaerobic digestion is conducted to convert lactose into propionic acid, ethanol and lactose acetates [9]. Lactose hydrolysis is a preliminary step for other processes, as the number of microorganisms

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able to metabolise glucose and galactose are significantly higher than those that directly metabolise lactose. [4]. Cheese whey fermentation aims at the production of ethanol, lactic acid, and hydrogen [10, 11]. The production of lactic acid has usually been carried out using the concentrated cheese whey coming from ultrafiltration [12-16]. The anaerobic fermentation produces a gas made up of a mixture of H_2, CO_2 and CH_4 with a theoretical yield of 4 mol H_2/mol lactose. Different clostridium species [17] and facultative anaerobic species [18] have been used employing CSTR, batch, and UASB reactors [3]. COD reductions of around 80-90 % and lactose consumption between 87 and 97% have been reported [17-22]. Shukla et al. [23] produced a probiotic beverage from whey blended with pineapple juice. The whey and pineapple juice were blended in four different proportions i.e. 80:20, 75:25, 70:30 and 65:35. The highest score for flavour, consistency, colour and appearance was given to the beverage containing whey and pineapple juice in the ratio of 65:35. The characteristics of whey-based fruit drinks, which make them widely acceptable to consumers in Europe, are described in the work of Prendergast [24]. In addition, methods of production, based on fermentation and on direct acidification, are also described.

When seeking different options for the management and valorisation of cheese whey, the use of thermochemical processes emerges as a novel route for the valorisation of this effluent. Among these, catalytic steam reforming and aqueous phase reforming are two challenging and very promising alternatives for the treatment of this wastewater. Steam reforming is one of the most widespread processes for the generation of a hydrogen-rich synthesis gas from organic compounds. This catalytic process, which is carried out at atmospheric pressure and at moderate temperatures (400-700 ºC), enables the organic matter of cheese whey to be transformed into a gas with a high hydrogen

content, up to 70 vol.%, with many different posterior applications [25]. In addition, it can decrease the carbon content of the original feedstock to appropriate levels for safe discharge into the environment. Aqueous phase reforming (APR) is a relatively new catalytic process carried out at quite low temperatures (200-240 ºC) and moderate pressures (30-50 bar), during which various liquid-gas-solid chemical reactions take place. The process allows the simultaneous production of different chemicals (gases and liquids) from an organic feedstock. The gas phase consists of a gas with a high H_2 content. The liquid phase is a complex mixture of different organic compounds in water such as alcohols, ketones, acids, esters, aldehydes, furans, phenols, anhydro-sugars and other oxygenated compounds with different compositions depending on the operating conditions of the process and the nature of the feed [26-29]. Therefore, APR can be customised either for the production of gases, helping to reduce the BOD and COD values of the feed, or for the production of valuable liquids that can be used as starting platform molecules for other processes. In addition, the APR process dispenses with the need to vaporise the water and the organic compounds of the feedstock, thus reducing the energy requirements [30]. This versatility converts the process into a very promising tailor-made route for the treatment and valorisation of cheese whey effluents.

To the best of the authors' knowledge, there are no studies in the literature concerning the use of these two thermochemical processes for the valorisation of cheese whey. Furthermore, works dealing with the catalytic steam reforming or the aqueous phase reforming of sugars are extremely scarce. In a previous work Remón et al. [31] analysed the catalytic steam reforming of lactose, the major organic compound of cheese whey. Using a lactose concentration similar to that of cheese whey (5.5 wt.%), maxima for the CC gas (88%) and the proportion of H_2 (67 vol.%) in the gas together with a carbon-free

liquid stream were achieved at 586 ºC using a spatial time of 16 g catalyst min/g lactose. In addition, the process was energetically optimised, and it was found that the combustion of 20% of this gas could provide the energy necessary for the process.

As regards steam reforming of other oxygenated compounds, Hu and Lu [32] studied the catalytic steam reforming of glucose for H_2 production, analysing the effect of the reaction time (0-3 h), temperature (300-600 ºC) and steam to carbon (S/C) ratio (3-9 mol H_2O/mol C) on the process. Marquevich et al. [33] reported the effect of the temperature and S/C ratio on the catalytic steam reforming of xylose, glucose and sucrose. Both studies reached the same conclusions. An increase in the temperature increases gas production and the yield to H_2 and reduces char formation. The S/C ratio plays a very important role in the process, decreasing solid formation and enhancing gas production, and therefore high S/C ratios are necessary to ensure a high carbon conversion to gas. However, these sugars are unstable at high temperatures and decompose before reaching the catalytic bed. This leads to substantial char formation in the upper part of the reactor, thus decreasing the efficiency of the process. Tosti et al. [34] used a membrane reactor consisting of a dense self-supported Pd-Ag tube for the oxidative reforming of a mixture of ethanol in water containing traces of glycerol and acetic acid, which simulated a residue produced in the dairy industry. An optimum for H_2 production was found at 400 ºC and 200 kPa.

The aqueous phase reforming of sugars has been considered for xylitol, sorbitol and galactitol. Jiang et al. [35] studied the APR of xylitol for pentane production over Pt/HZSM-5 and Ni/HZSM-5 catalysts, analysing the effects of the temperature, pressure

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and metal loading on the xylitol conversion and pentane selectivity. The two latter variables augmented with an increase in the catalyst metal loading from 0 to 3 wt.% and decreased with a further increase up to 5 wt.%. An increase in the reaction temperature from 180 to 240 ºC at 4 MPa increased the xylitol conversion from 30 to 80%. At 240 ºC, an increase in the pressure from 2 to 4 MPa increased the xylitol conversion from 61 to 80%. Kirilin et al. [36] reported the APR of xylitol in a continuous fixed bed reactor over three catalysts: Pt/Al_2O_3, Pt/TiO_2 and $Pt-Re/TiO_2$. Higher conversions of xylitol were observed for the Pt-Re catalyst than for the two monometallic catalysts. Xi et al. [37] prepared different $M/NbOPO_4$ multifunctional catalysts (M= Pt, Pd, Ru, Ir, Rh and Ni) for alkane production by the hydrodeoxygenation of sorbitol in aqueous solution. The activity of the catalysts decreased in the following order: Pt > Pd > Rh > Ru > Ir > Ni. Aiouache et al. [38] developed a path lumping kinetic model for the aqueous phase reforming of sorbitol. Paths of reforming and CO_2 methanation were more important than decarbonylation and hydrodeoxygenation at small conversions for all the catalysts, whereas the hydrodeoxygenation-decarbonylation reactions towards alkanes were more competitive than the reforming reactions at high conversions.

Kirilin et al. [39] investigated the APR of xylitol and sorbitol using a Pt/Al_2O_3 catalyst. Generally, higher yields and selectivity to hydrogen were observed for xylitol than for sorbitol. The maximum selectivity to H_2 (83%) was achieved in the case of xylitol. Additionally, the yields to liquid products and hydrogen were higher in the case of xylitol compared to sorbitol due to the longer carbon chain in the latter substrate. Godina et al. [40] analysed the APR of sorbitol and galactitol over a Pt/Al_2O_3 catalyst in a continuous fixed-bed reactor at 225 °C. The analysis of the gas and liquid phases

obtained in the experiments showed almost the same behaviour and the same conversion for both substrates.

Given this background, this work analyses the valorisation by steam reforming and aqueous phase reforming of real cheese whey resulting from the production of fresh cow cheese. The influence of some of the most important operating conditions such as the temperature and spatial time has been investigated. In addition, a comparison has been established between the results obtained with cheese whey, filtered cheese whey and a lactose solution having a similar lactose concentration as cheese whey. For cheese whey valorisation, it is not only important to produce valuable chemicals from this waste, but also to come up with a carbon-free liquid stream that could be safely discharged into the environment. Therefore, the gas, liquid and solid production obtained in the experiments and the compositions of the gas and liquid phases have been exhaustively analysed. These two thermochemical processes have never before been considered for real cheese whey management, while works dealing with the steam reforming and aqueous phase reforming of sugars are very scarce. Hence, this work represents a challenging and novel investigation not only for the management and valorisation of cheese whey but also for the production of value-added chemicals from sugars or sugar-based streams.

2. Materials and methods

2.1 Materials

Two different Ni copecipitated catalysts were used for the valorisation experiments. A Ni-Co/Al-Mg was selected for the steam reforming experiments. This catalyst has a

28% (relative atomic percentage) Ni expressed as Ni/(Ni+Co+Al+Mg), an atomic Mg/Al ratio of 0.26 and an atomic Co/Ni ratio of 0.10, with a BET surface area of about 132 m^2/g [41]. A Ni-La/Al, having a 28% (relative atomic percentage) of Ni expressed as Ni/(Ni+Al+La), an atomic La/Al ratio of 0.035 and a BET surface area of 187 m^2/g was used for the aqueous phase reforming experiments [42].

The cheese whey used for this work, provided by "Quesos La Pardina" (Zaragoza, Spain), was obtained as a by-product in the production of fresh cow milk cheese. The characterisation results of this feedstock, including the chemical composition, elemental analysis, Total Organic Carbon (TOC), density and pH, are listed in Table 1. The chemical composition was calculated by means of a Gas Chromatography-Mass Spectrometry analysis, Karl Fischer titration and ash content. The ashes were characterised by XRD. This analysis revealed that they were made up of KCl and $CaCO_3$. The properties of this whey are consistent with those reported in other works in the literature [1-4]. Some experiments have been conducted using filtered cheese whey and a lactose solution, and a comparison between the results obtained with the three feedstocks (cheese whey, treated cheese whey and lactose) was established under the same operating conditions. These conditions were selected having regard to the characteristics of the reforming processes as well as the limited amount of cheese whey available for the experiments. The cheese whey treatment consisted of an initial vacuum filtration and a subsequent centrifugation of the cheese whey to reduce the amount of proteins and fats. The elemental analysis of the filtered whey revealed a decrease in the proportion of N along with a decrease in the proportion of 2-propanamine in comparison with the original feedstock (Table 1). The lactose solution was prepared dissolving D-lactose monohydrate ($C_{12}H_{22}O_{11} \cdot H_2O$ Sigma Aldrich, CAS Number

64044-51-5, Bio-Ultra >99.5 % HPLC) in Milli-Q water. A slightly higher concentration of lactose was chosen for the comparison, having regard to the total amount of C in the real cheese whey due to the presence of other organics in the real feedstock. This lactose solution had a TOC of 23137 ppm, which is close to that of the real whey. The S/C ratios of the cheese whey, the filter cheese whey and the lactose solution were 22.2, 27.7 and 27.3 mol/mol, respectively.

2.2 Reforming installations

The experimental installations used in the experiments were two microactivity units designed and built by PID (Process Integral Development Eng & Tech, Spain). The unit for the catalytic steam reforming experiments consists of a small bench scale rig comprising a quartz fixed bed reactor of 25 mm in height and 9 mm inner diameter. The cheese whey, filtered cheese whey and lactose solutions were fed into the reactor with a HPLC pump (Gilson, model 307). N_2 was used as a carrier gas to facilitate the feeding of the solutions, as well as an internal standard for gas quantification. Once inside the reactor, the feed down-flow passed through the catalytic bed, consisting of a mixture of catalyst and inert sand. The gaseous mixture passed to a condensation system consisting of a stainless steel vessel cooled by means of a Peltier thermoelectric cell where the condensable vapours were trapped. A system of several condensers was added after the Peltier unit to recover the liquid products at intervals of 1 h to analyse the evolution over time of the liquid phase. The permanent gases exiting the condensation system were analysed online with a micro gas chromatograph. More details concerning the set-up can be found in our previous communications [41, 43, 44].

The APR reforming unit consists of a stainless steel tubular reactor with an inner diameter of 9 mm, heated up by means of an electric furnace. The system pressure was reached with the aid of a micrometric valve that automatically adapts its position with the help of a rotor. A pressure gauge, located at the exit of the reactor, measured the pressure of the reaction section. A PDI control system was used to keep the reactor pressure constant during the experiments. The cheese whey and the lactose solutions were fed into the reactor by means of a HPLC pump (Gilson, model 307). The reaction products (gas and liquids) left the reactor from its upper part, passed through the valve, where they were depressurised, and arrived at the condensation system. This system consisted of several condensers where the liquid products were separated from the gas mixture at intervals of 1 h. The gas mixture was made up of N_2, used as an internal standard, and the different gaseous products formed during the aqueous phase reforming reaction. More details concerning the set-up can be found in our previous communications [42, 45].

An Agilent M3000 micro chromatograph equipped with thermal conductivity detectors (TCD) was used in both installations for the online analysis of the gas phase. The liquid fractions were collected and analysed offline with a gas chromatograph (Agilent 7890 GC-system, model G3440A) equipped with Flame Ionization (FID) and Mass Spectrometry (MS) detectors.

2.3 Response variables and statistical analyses

The effect of the operating conditions and the feed (cheese whey, filtered cheese whey or lactose) on the process was analysed for the following response variables: global lactose conversion (X lactose, %), carbon conversion to gas, liquid and solid products

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(CC gas %, CC liq %, and CC sol %), as well as the composition of the gas (N_2 and H_2O free, vol.% or mol.%) and liquid (relative chromatographic area free of water and un-reacted lactose, %). A semi-quantitative analysis was conducted to analyse the effect of the operating conditions on the composition of the liquids due to the high complexity of the liquid phases. Table 2 summarises the response variables and the analytical methods used for their calculation.

The effect of the temperature and the mass of catalyst/mass flow rate of carbon (W/m_C) were analysed during the catalytic steam reforming experiments. Different experiments were conducted at 450 ºC and 600 ºC using W/m_C ratios of 24 and 38 g catalyst min/g carbon for two hours. This temperature interval was selected having regard to the thermodynamics and energetic issues of the process [31]. The aqueous phase reforming experiments were conducted at 220 ºC and 44 bar for 1 h. This temperature and pressure are usually used during the APR of organic compounds [42]. The effect of the W/m_C ratio (60, 95 and 130 g catalyst/min g carbon) was analysed for cheese whey valorisation by APR.

All the experiments with cheese whey and lactose were performed at least in duplicate. The experimental results have been compared using a one-way analysis of variance (one-way ANOVA) and Fisher´s least significant difference (LSD) test, both with 95% confidence. The results of the ANOVA analyses are provided as p-values. P-values lower than 0.05 indicate that at least two values are significantly different. Furthermore, the LSD test was used to compare pairs of data. The results of the LSD tests are presented graphically in the form of LSD bars. To ensure significant differences between any pairs of data, their LSD bars must not overlap.

Some of the used catalysts were characterised by X-Ray diffraction (XRD) and elemental analyses. XRD patterns of the used catalysts were obtained with a D-Max Rigaku diffractometer equipped with a CuK α1.2 at a tube voltage of 40 kV and current of 80 mA. The measurements were carried out using continuous-scan mode with steps of 0.03°/s at Bragg's angles (2θ) ranging from 5° to 85°. The phases present in the samples were defined with reference to the JCPDS-International Centre for Diffraction Data 2000 database. From the elemental analysis, the CC coke and the amount of C deposited with respect to the amount of catalyst and organics reacted (mg C/g catalyst g organics reacted) were calculated.
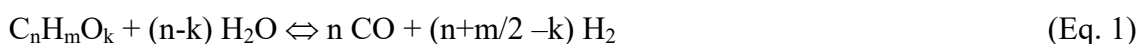
2.4 *Possible reaction networks*
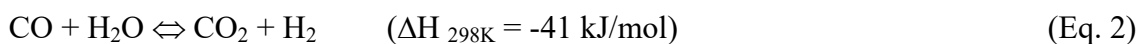
2.4.1 *Cheese whey steam reforming*

Lactose steam reforming includes reforming, cracking and thermal decomposition reactions due to the instability of sugars at high temperatures [32, 33].
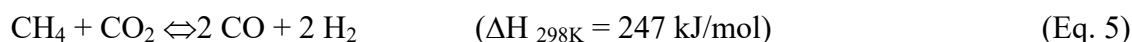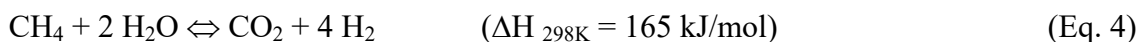
1- Reforming reactions:

Steam reforming of the oxygenated compounds:

$$C_nH_mO_k + (n-k)\ H_2O \Leftrightarrow n\ CO + (n+m/2-k)\ H_2 \qquad\qquad (Eq.\ 1)$$

Water gas shift (WGS) reaction:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (\Delta H_{298K} = -41\ kJ/mol) \qquad\qquad (Eq.\ 2)$$

Methane steam reforming and dry reforming:

$$CH_4 + H_2O \Leftrightarrow CO + 3\ H_2 \qquad (\Delta H_{298K} = 206\ kJ/mol) \qquad\qquad (Eq.\ 3)$$

$$CH_4 + 2\ H_2O \Leftrightarrow CO_2 + 4\ H_2 \qquad (\Delta H_{298K} = 165\ kJ/mol) \qquad\qquad (Eq.\ 4)$$

$$CH_4 + CO_2 \Leftrightarrow 2\ CO + 2\ H_2 \qquad (\Delta H_{298K} = 247\ kJ/mol) \qquad\qquad (Eq.\ 5)$$

Boudouard reaction:

$$2\ CO \Leftrightarrow CO_2 + C \qquad\qquad (\Delta H_{298K} = -173\ kJ/mol) \qquad\qquad (Eq.\ 6)$$

2- Thermal decomposition and cracking reactions

$$C_nH_mO_k \rightarrow Liquids\ (C_xH_yO_z) + Gas\ (H_2, CO, CO_2, CH_4, \ldots) + carbon \qquad (Eq.\ 7)$$

2.4.2 Cheese whey aqueous phase reforming

During the APR of cheese whey, various liquid-gas-solid chemical reactions take place. These include cracking and reforming reactions to generate hydrogen, dehydrogenation of alcohols/hydrogenation of carbonyls, deoxygenation and hydrogenolysis as well as cyclisation reactions. Gases, mainly H_2 and CO, are produced by the thermal decomposition and/or reforming reactions of the lactose and all the liquid intermediates (Eq.1) as well as by all the decarbonylation reactions that release CO. In addition, the WGS reaction (Eq.2), the methanation reaction and the inverse of methane steam reforming reactions (Eq.3-4) are also possible, explaining the presence of CO_2 and CH_4 in the gas phase [32, 33].

3. Results and discussion

3.1 Catalytic steam reforming

3.1.1 Lactose conversion and carbon conversion to gas, liquid and solid products

A complete global lactose conversion (X lactose) was achieved in all the experiments, indicating that all the lactose was converted into gas, liquid and solid products. The C/O

ratio close to 1 of lactose allows complete conversion to be achieved even at the lowest temperature used in this work [32, 46]. Complete conversions were achieved at temperatures higher than 500 ºC in the work of Hu et al. [32] during the steam reforming of glucose. Fig. 1 shows the CC gas, CC liq and CC sol obtained for the steam reforming experiments in two intervals of one hour each. The statistical analysis reveals significant differences between the results obtained in the experiments for the CC gas, CC liq and CC sol (p-values < 0.001).

The CC gas obtained when feeding cheese whey is low (< 35%) regardless of the temperature (450-600 ºC) or the W/m_C ratio (24-38 g catalyst min/g carbon) employed in the experiments. This low CC gas is the consequence of the high CC sol due to char formation in the upper part of the reactor. Sugar molecules are unstable at the temperatures of this process (450-600 ºC) and quickly decompose through pyrolysis, leading to the formation of char particles and gases [33]. This char formation is the consequence of an incomplete vaporisation of the feed and has been reported in other works dealing with the steam reforming of lactose [31] and other sugars [32, 33, 44]. In addition, neither the temperature nor the W/m_C ratio affects the CC gas or the CC sol when feeding real cheese whey to the reactor. Increases in the CC gas and decreases in the CC sol over time take place during the reforming of cheese whey. The accumulation of the char in the upper part of the reactor might have a positive catalytic effect on the pyrolysis and/or cracking reactions of lactose and its liquid intermediates. Char obtained from the pyrolysis of different biomass materials has been reported to have catalytic activity for the reforming and cracking of different hydrocarbons [47-53], which accounts for the drops over time observed for the CC sol [32, 33] and the increases in the CC gas.

In addition, the presence of salts in the cheese whey might be responsible for the increase and decrease in the CC gas and CC sol over time, respectively. Inorganic salts in a water solution decrease the evaporation rate of the other organic compounds [54], which might result in a higher formation of carbonaceous deposits (char) [55]. The accumulation of char particles in the upper part of the reactor hinders the vaporisation of the feed as the atomisation system is not as effective when the liquid comes into contact with solid particles, leading to bigger droplet sizes. Consequently, the evaporation takes places at lower heating rates. This enhances the formation of more carbonaceous deposits, augmenting the formation of char over time [55]. However, as the reaction advances and salts progressively accumulate inside the reactor, their presence exerts a positive catalytic effect [56, 57], aiding the gasification of these carbon deposits, which experimentally leads to a decrease over time in the CC sol. The accumulation of salts in the catalyst bed was corroborated at the end of the experiments.

The results obtained with cheese whey have been compared with those obtained when feeding a lactose solution [31] and a filtered cheese whey (F.C. Whey). The comparison between cheese whey and lactose reveals that higher CC gas and lower CC sol are obtained with lactose for the two temperatures and the two W/m_C ratios tested. These differences are noticeably marked at high temperatures and using a high W/m_C ratio. For this lactose solution, an increase in the temperature increases and decreases the CC gas and CC sol, respectively. High temperatures not only facilitate the vaporisation of the feed, decreasing the formation of solid carbon, but also favour the reforming process due to its endothermic nature [32, 33], thus increasing and decreasing the CC gas and CC sol, respectively. In addition, an increase in the W/m_C ratio increases the CC gas

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and decreases the CC sol due to the positive catalytic effect on reforming and gasification reactions. This effect is particularly marked at low temperatures, as high temperatures kinetically promote the reforming reactions, thus partially masking the positive effect of the catalyst.

The evolution over time of these two variables is different than that observed for cheese whey. During the reforming of lactose, two trends take place depending on the W/m_C ratio at low temperature (450 ºC). For 24 g catalyst min/g carbon, the CC gas and CC sol decrease over time. The decrease in the CC gas might be the consequence of the deactivation of the catalyst [32, 33], while the decrease in the CC sol is accounted for by the pyrolysis of the char resulting from the incomplete vaporisation of the feed. These two developments lead to an increase in the CC liq over time. For 38 g catalyst min/g carbon, the CC gas and CC sol remain steady during the two hours of reaction. This steady evolution also takes place at 600 ºC when a W/m_C ratio of 24 g catalyst min/g carbon is used. Conversely, for 38 g catalyst min/g carbon at 600 ºC the CC gas slightly increases and the CC sol decreases. An elevated temperature and a high W/m_C ratio helps to prevent catalyst deactivation by coking, increases the reforming and the evaporation rates, and aids the gasification of the char.

The presence of fats and proteins in cheese whey might be partially responsible for the lower CC gas and the CC sol obtained with cheese whey than with lactose. The presence of these compounds might increase the formation of carbonaceous deposits due to their relatively high molecular mass. An increase in the molecular mass leads to bigger droplet sizes, causing the evaporation of the feed to take place at lower heating rates, increasing the CC sol [55]. Therefore, the cheese whey was filtered and

centrifuged to reduce the fat and proteins in the whey, and additional experiments were conducted with this filtered cheese whey at 450 ºC and 600 ºC using a W/m_C ratio of 24 g catalyst min/g carbon.

During the first hour of reaction, the CC gas obtained with this filtered solution was slightly higher than that obtained when feeding the original cheese whey, but still lower than the conversion achieved with lactose. A lower CC sol was obtained with the filtered cheese whey in comparison with the original feedstock. However, the solid production was still higher than that obtained when feeding lactose and there was an increase over time of the CC gas together with a decrease in the CC sol. These results seem to indicate that fats and proteins contribute to increasing the solid formation, but the main factor responsible for the substantial formation of solid is the presence of salts in the cheese whey, as remarked above.

The CC liq is relatively low for the vast majority of experiments. Specifically, CC liq lower than 1% was obtained for the experiments performed with the original and the filtered cheese whey. This indicates that the temperature range (450-600 ºC) and the relatively high spatial times used in the experiments enhance gas formation from the vaporised part of the feed, thus producing an almost carbon free liquid condensate, which is very important for cheese whey management. The highest CC liq was obtained with lactose using a relatively low W/m_C ratio (24 g catalyst min/g carbon). This denotes that this amount of catalyst is not high enough to convert the evaporated part of the feed into gases, especially at low temperature (450 ºC). An increase in the temperature or in the W/m_C ratio increases the formation of gas from the organic compounds present in the feed, thus reducing the CC liq.

3.1.2 Gas composition

The gas phase consists of a mixture of H_2, CO_2, CO and CH_4. Fig. 2 shows the gas composition obtained for the different experiments in two intervals of 1 h each. H_2 (59-72 vol.%) and CO_2 (28-38 vol.%) are the compounds with the greatest proportion in the gas phase, while the concentrations of CO (< 9 vol.%) and CH_4 (< 3 vol.%) in the gas are much lower.

The reforming temperature and W/m_C ratio do not significantly influence the proportion of H_2 and CO_2 in the gas during the first hour of reaction when real cheese whey is catalytically reformed. This development accounts for the substantial formation of C deposits that lowers the amount of C in the gas, thus increasing the effective W/m_C ratio for the vaporised part of the feed. This masks the positive effect of the temperature and W/m_C ratio on the gas composition and allows a gas with a high proportion of H_2 to be achieved at the lowest temperature considered in this work while employing a W/m_C ratio as low as 24 g catalyst min/g carbon.

However, these two operating variables exert a significant influence on the evolution of these two gases over time. The proportion of H_2 decreases while that of CO_2 increases after the first hour of reaction due to the progressive deactivation of the catalyst. Comparing the experiments conducted at the same temperature shows that the lower the W/m_C ratio, the greater the reductions in the proportion of H_2 over time. High W/m_C ratios allow a greater amount of active catalyst in the bed, thus minimising the decay observed for the proportion of H_2 in the gas. The temperature exerts a positive catalytic effect on the gasification of these carbon deposits, which helps to prevent catalyst

deactivation. Therefore, the decay observed in the proportion of H_2 over time is lower at 600 than at 450 ºC. In addition, this decay does not take place when using a high temperature and W/m_C ratio.

During the reforming of lactose, an increase in the temperature from 450 to 600 ºC increases the concentrations of H_2 and CO_2 in the gas for a W/m_C ratio of 24 g catalyst min/g carbon. This is the consequence of two developments, the increase in the amount of C in the gas phase with the temperature and the endothermic character of lactose steam reforming. The increase in the proportion of H_2 has also been reported in other works dealing with steam reforming of other saccharides [32, 33]. When the W/m_C ratio increases up to 38 g catalyst min/g carbon, the effect of the temperature on the proportions of H_2 and CO_2 in the gas is not significant as the positive kinetic effect of the catalyst is higher than the effect of the temperature.

In addition, the effect of the W/m_C is only significant at low temperature (450 ºC) as the positive effect of the temperature masks the effect of the W/m_C ratio at 600 ºC. At 450 ºC an increase in the W/m_C ratio increases the proportion of H_2 and CO_2 in the gas. The presence of the catalyst promotes the gasification of the carbon deposits and favours a greater spread of the reforming reaction, thus increasing the proportion of H_2 and CO_2. For the experiments conducted with lactose, the proportions of H_2 and CO_2 show a steady composition during the 2 hours of experiment. This indicates that a lower catalyst deactivation occurs when feeding lactose than during the reforming of cheese whey and is in good agreement with the lower solid production obtained in the reforming of the former than the latter.

The filtration of the cheese whey marginally changes the proportions of H_2 and CO_2 in the gas. Specifically, a slightly higher proportion of H_2 and a lower concentration of CO_2 in the gas are obtained with the filtered whey at 450 ºC using a W/m_C ratio of 24 g catalyst min/g carbon. This result is the consequence of the increase in the proportion of C in the gas phase, as explained above, due to the reduction of fats and proteins in the whey, which decreases solid formation. Conversely, non-statistically significant differences are found in the proportions of H_2 and CO_2 in the gas between the filtered and the original cheese whey at 600 ºC. High temperatures promote the vaporisation of the feed, thus reducing the positive effect that the elimination of proteins and fats from the whey exerts on the vaporisation of the feed.

These results indicate that a H_2 rich gas can be obtained from the valorisation of cheese whey and a lactose solution by steam reforming. At 600 ºC and using a W/m_C ratio of 38 g catalyst min/g carbon, the overall 2 hour H_2 yields obtained from the treatment of cheese whey and lactose are as follows: 11.5 and 21.5 mol H_2/mol lactose. The H_2 yield obtained with pure lactose is close to the theoretical maximum of the process (24 mol H_2/mol lactose). In addition, for both cheese whey and lactose, the H_2 yield is higher than those obtained in anaerobic fermentation (4 mol H_2/mol lactose) or anaerobic fermentation plus photo-fermentation with L-malic acid (2-10 mol H_2/mol lactose).

The concentrations of CO and CH_4 in the gas are relatively low, and lesser differences were found between the experiments conducted with cheese whey, filtered cheese whey and lactose. This indicates a greater spread of the water gas shift and methanation reactions as the relatively high S/C ratios used help to shift the WGS and methane reforming reactions towards the formation of H_2 [27]. The proportion of CO in the gas

obtained during the first hour of reaction in the experiments conducted with cheese whey is very low (< 2 vol.%), probably due to the shift of the water gas shift reaction towards H_2 and CO_2. The low amount of C in the gas phase increases the effective W/m_C ratio for the vaporised part of the feed, thus kinetically shifting the water gas shift reaction towards H_2 and CO_2. However, an increase in the proportion of CO in the gas over time occurs due to the progressive deactivation of the catalyst. The lower the W/m_C ratio, the sharper the increase over time in the proportion of CO, as high W/m_C ratios can partially compensate for catalyst deactivation. For 24 g catalyst min/g carbon, the higher the temperature, the sharper is the increase over time in the proportion of CO in the gas. The water gas shift reaction is exothermic; therefore, low temperatures produce a greater spread of the water gas shift reaction, thus decreasing the proportion of CO.

In the experiments conducted with the filtered cheese whey, the initial proportion of CO in the gas is very low and increases with time. However, non-significant differences are detected for this gas between the filtered and the real whey. As regards the use of lactose in the process, significant differences between cheese whey and lactose are only found for the experiments conducted using a low W/m_C ratio (24 g catalyst min/g carbon). At 450 ºC a gas with a greater proportion of CO is obtained during the reforming of lactose compared with cheese whey. At low temperature and using a low W/m_C ratio, a substantial amount of solid is produced during the reforming of cheese whey. This decreases the content of C in the gas phase thus allowing a greater shift of the water gas shift reaction to be achieved with the same amount of catalyst in the bed. The proportion of CO in the gas decreases when increasing the temperature. At low temperatures (450 ºC), lactose is thermally decomposed into a gas with a high

proportion of CO and CO_2 [32]. The proportion of CO in the gas decreases towards its thermodynamic value when increasing the temperature due to the prevalence of reforming over thermal decomposition, producing a greater shift of the water gas shift reaction. In general, an increase in the W/m_C decreases the relative amount of CO in the gas due to the greater spread of the water gas shift reaction. For 38 g catalyst min/g carbon, these differences are not observed due to the positive kinetic effect of the catalyst on the water gas shift reaction.

The proportion of CH_4 in the gas during the first hour of experiment is very low (< 1 vol.%), which indicates that methane production from lactose is not favoured at the temperature range considered (450-600 ºC). The highest proportion of CH_4 in the gas (3.5 vol.%) was achieved for the reforming of cheese whey using a low W/m_C ratio (24 g catalyst min/g carbon) during the second hour of reaction. This increase in the concentration of CH_4 in the gas is the consequence of the progressive deactivation of the catalyst, which hinders the methane steam reforming reactions, thus increasing the proportion of CH_4 in the gas [25, 41, 58].

3.1.3 Liquid composition

The liquid phase obtained during the steam reforming experiments is made up of a mixture of aldehydes (acetaldehyde and propanal), ketones (2-propanone), carboxylic acids (acetic and propionic acids), sugars (levoglucosan and D-alose), furans (furfural, 2-furancarboxaldehyde and 2,5-furandicarboxaldehyde), alcohols (ethanol, propanol and cyclic alcohols) and phenolic compounds (phenol and methyl-phenols). The presence of these compounds in the liquid phase is the result of the thermal decomposition of lactose and the incomplete reforming of lactose and its liquid

intermediates. All these reaction intermediates have a high tendency to form coke and char (especially sugars, furans and aromatic species) [44, 59-62] which explains the high CC sol obtained experimentally. Figs. 3 a and b plot the relative amounts of each of the different families of liquid compounds for the different experiments obtained during the first and second hour of experiment, respectively, together with the results of the Fischer's LSD test.

During the first hour of reaction, the liquid phase obtained during the reforming of cheese whey is made up of phenolic compounds when a W/m_C ratio of 24 g catalyst min/g carbon is used, while a liquid condensate free of organic compounds is obtained for 38 g catalyst min/g carbon. Phenols are end products of lactose thermal decomposition. The high CC sol achieved in the experiments conducted with cheese whey increases the effective W/m_C ratio. This increases the CC gas and produces an almost-free liquid condensate. Given that reforming of the aromatic compounds is thermodynamically less favoured than that of the light oxygenated liquid intermediates due to the stronger C-C bonds involved [63], the liquid has a high concentration of phenolic compounds, which are less likely to evolve towards gas formation by reforming. An increase in the W/m_C ratio from 24 to 38 g catalyst min/g carbon promotes the reforming of the phenolic compounds, and carbon free liquid condensate is obtained.

The comparison between the liquid condensates obtained from cheese whey and lactose shows a lower proportion of phenols and a higher concentration of intermediate liquid products (aldehydes, ketones, alcohols and carboxylic acids) for lactose than for cheese whey due to the lower carbon formation for the latter than for the former feedstock.

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This char formation lowers the amount of C in the gas, thus increasing the effective W/m_C ratio. An increase in the W/m_C ratio during the steam reforming of lactose decreases the relative amount of intermediate compounds due to the positive effect of the catalyst on the process. At 450 °C this increase leads to a sharp increase in the relative amount of carboxylic acids, while at 600 °C the proportion of phenols increases very sharply, as high temperatures shift the composition of the liquid phase towards end products. Very interestingly, significant differences between the composition of the liquid phase obtained with the real and the filtered cheese whey were not observed.

As regards the evolution of the liquid phase over time, the comparison between Figs. 3 a and b shows little variation in the chemical composition of the liquid phase, probably due to the low amount of liquid products produced in the experiments. The minor variations observed are accounted for by a decrease in the proportion of phenols and a decrease in the relative amount of ketones, probably due to catalyst deactivation. However, due to the low CC liq obtained in the experiments, these variations are not important from a practical point of view.

3.2 Catalytic aqueous phase reforming

3.2.1 Lactose conversion and carbon conversion to gas, liquid and solid products

A complete global lactose conversion (X lactose) was achieved in all the experiments, indicating that all the lactose was converted into gas, liquid and solid products, due to the C/O ratio of this sugar [32, 46]. The experiments were initially planned for 2 hours. However, the pressure significantly increased over the set point after the first hour of experiment due to the accumulation of char particles and non-soluble water compounds

in the upper part of the reactor and the micrometric valve. Therefore, the experiments were run for 1 h. Fig. 4 shows the overall CC gas, CC liq and CC sol obtained in the experiments. In addition, the initial CC gas (t = 0 h), obtained once the steady state was achieved, is also plotted in Fig. 4 a to study the evolution of the gas phase over time. This study was not possible for the CC liq and CC sol as the liquid condensates were recovered at intervals of 1 h each.

The statistical analysis reveals significant differences between the results obtained in the experiments for the CC gas, CC liq and CC sol (p-values < 0.001). The CC gas obtained during the aqueous phase reforming of cheese whey is relatively low (25%), which indicates that gas production from cheese whey is not favoured under the reaction conditions tested in this work (T = 220 ºC and P = 44 bar). This is in good agreement with other works studying the APR of xylose and sorbitol [35, 39, 64]. In these works, the low gas productions (25-35%) were obtained between 200 and 240 ºC. The comparison between the experiments conducted with cheese whey and lactose reveals that lower CC gas and higher CC sol are obtained with the former than with the latter. This lower gas production from cheese whey is the consequence of the high formation of char. In addition, the reduction of the amount of fats and proteins (filtered cheese whey) resulted in a reduction in char formation and in an increase in the CC gas. However, lower CC gas and higher CC sol were obtained with this treated whey in comparison with those obtained using lactose, which suggests that proteins and fats are partially responsible for the formation of char.

Sugar molecules are unstable at the temperatures used in this process and quickly decompose through pyrolysis, leading to the formation of char particles and gases [33].

This solid residue (char) obtained from the thermal decomposition of sugars is made up of polymerised degradation products such as humic acids and large organic compounds ranging from C_8 to C_{15} [39, 65-70]. The formation of these macromolecules can occur from furfural and 5-hydroxymethyl-2-furancarboxaldehyde obtained from lactose dehydration, via aldol addition followed by condensation or polymerisation among themselves. Furthermore, both lactose monomers (glucose and galactose) can react with other liquid intermediates such as 5-hydroxymethyl-2-furancarboxaldehyde by cross-polymerisation [65-67, 69]. The presence of salts in the cheese whey promotes the dehydration reactions [71, 72] of glucose and galactose thus increasing the proportion char precursors. This accounts for the greater solid and lower gas production during the reforming of cheese whey than for lactose and suggests that salts are one of the principal factors responsible for the great amount of char produced during the treatment of cheese whey by APR.

The W/m_C ratio exerts a significant influence on the CC gas during the APR of cheese whey. An increase from 60 to 130 g catalyst min/g carbon significantly increases the CC gas and decreases the CC sol. This variable positively influences the CC gas due to its positive kinetic effect on cracking and reforming reactions [42]. In addition, an increase in the W/m_C ratio hinders char formation and favours carbon gasification, helping to decrease the CC sol.

The evolution of the CC gas over time displays significant drops. These drops are greater for the real and filtered cheese whey than for the lactose solution. The presence of salts favours dehydration reactions [71, 72], favouring condensation and cross-polymerisation reactions leading to the formation of humic acids and large organic

compounds [39, 65-70]. This increases the formation of coke and char, thus increasing

catalyst deactivation and lowering gas formation over time.

A relatively high CC liq (30-45%) was obtained during the APR of cheese whey. The

high formation of solid during the processing of cheese whey decreases the formation of

valuable liquid products. The comparison between the CC liq obtained for cheese whey

and lactose reveals a lower CC liq for the former than for the latter due to the lower

amount of char produced during the APR of lactose. Very interestingly, the reduction of

the amount of fats and proteins by filtration does not significantly influence liquid

production due to the compensatory effect of two developments: higher gas formation

and lower solid production. The W/m_C ratio exerts a significant influence on the CC liq.

An increase in the W/m_C ratio from 60 to 95 g catalyst min/g carbon increases the liquid

production from cheese whey. However, a further increase up to 130 g catalyst min/g

lactose decreases the liquid production as high W/m_C ratios favour gas production from

the liquid intermediates obtained during APR [42]. When reforming lactose, an increase

in the W/m_C ratio from 60 to 95 g catalyst min/g carbon during the APR of lactose

decreases the CC liq due to the increase observed in gas production.

3.2.2 Gas composition

The gas phase consists of a mixture of H_2, CO_2, CO and CH_4. Fig. 5 plots the gas

composition at the beginning of the experiment (once the steady state has been reached,

$t = 0$ h) as well as the overall values obtained for the first hour of experiment (t= 1h).

The compounds present in the greatest proportions in the gas phase are H_2 (11-33

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vol.%), CO_2 (49-72 vol.%) and CH_4 (7-17 vol.%), while the concentration of CO (< 2 vol.%) in the gas is much lower.

An increase in the W/m_C ratio from 60 to 95 g catalyst min/g carbon during the APR of cheese whey augments the initial proportion of H_2 and decreases the concentration of CO_2 in the gas. However, a further increase in the W/m_C ratio up to 130 g catalyst min/g carbon does not significantly modify the initial proportion of these two gases. The comparison between the initial gas compositions with the overall value obtained during the first hour of reaction for the concentrations of H_2 and CO_2 reveals a decrease over time for the former gas together with an increase for the latter due to catalyst deactivation.

The comparison between the proportions of H_2 and CO_2 in the gas obtained during the APR of cheese whey and lactose reveals a lower initial H_2 proportion and a higher initial concentration of CO_2 in the gas for the experiments conducted with lactose under the same operating conditions. However, significant variations in the proportions of these two gases for the APR of lactose were not detected. Gas formation takes place via C-C scission, which occurs via a base-catalysed pathway facilitated in the presence of salts [26, 73]. Therefore, this increase in the proportion of H_2 in the gas could be the consequence of the increase in gas production, which also causes a reduction in the production of intermediate liquids. This decreases the H_2 consumption in the hydrogenation reactions, which accounts for the lower amount of H_2 in the gas obtained from lactose. King et al. [26] also reported an increase in the H_2 selectivity with the addition of KOH during the APR of glycerol using a Pt-Re/C catalyst. They concluded that this development was the consequence of lower H_2 consumption in the

hydrogenation reactions, as KOH disfavours dehydration reactions and C-O scissions.

Conversely, non-significant differences were found for the concentrations of H_2 in the gas and their evolution over time between the results obtained in the APR of the real and the filtered cheese whey. This suggests that the elimination of fats and proteins does not significantly influence the gas composition and indicates that the presence of salts in the whey is one of the major factors responsible for the greater concentration of H_2 in the gas during the APR of cheese whey. Conversely, the filtration of whey results in an increase in the proportion of CH_4 along with a decrease in the relative amount of CO_2 in the gas at the beginning of the experiment.

The proportion of CO in the gas is very low (< 2 vol.%) regardless of the W/m_C ratio and the feedstock (cheese whey, lactose or filtered cheese whey) used in the experiments. Under the temperature studied in this work, the water gas shift (WGS) reaction is shifted towards H_2 and CO_2, which explains the low proportion of CO in the gas. In addition, non-statistically significant differences were found between the experiments conducted at different spatial times for the same feedstock or between the different feedstocks.

In contrast, the W/m_C ratio exerts a significant influence on the proportion of CH_4 in the gas during the APR of cheese whey. The higher the W/m_C ratio, the greater the initial proportion of CH_4 in the gas and the decay over time observed for this gas. This shifts the process towards the production of liquid end products such as acetaldehyde, which can be converted into CH_4 by decarbonylation [38, 42, 74]. The decrease observed in

the proportion of CH_4 might account for a progressive deactivation of the catalyst, which decreases the advancement of the reaction towards final liquid products, thus lowering the amount of CH_4 in the gas.

The comparison between the results obtained with cheese whey and lactose does not show significant differences for the concentration of CH_4 in the gas. Exceptionally, the decrease over time observed in the proportion of CH_4 for the APR of cheese whey when a W/m_C ratio of 95 g catalyst min/g lactose is used does not take place when reforming lactose. This decay over time observed for cheese whey takes place for W/m_C ratios between 95 and 130 g catalyst min/g C. As remarked above, high W/m_C promotes a greater shift of cross-linking and polymerisation reactions from furanic compounds whose formation from cheese whey via dehydration is favoured due to the presence of salts. This leads to the formation of substantial quantities of char and coke, causing catalyst deactivation, and could explain the decrease observed in the proportion of this gas during the APR of cheese whey and the steady evolution when using lactose. The filtration of the cheese whey results in a slight increase in the initial proportion of CH_4 in the gas.

3.2.3 Liquid composition

Fig. 6 summarises the relative amounts of each of the different families of liquid compounds for the different experiments. The liquid phase is made up of a mixture of aldehydes, carboxylic acids, alcohols and ketones in water. Acetaldehyde is the most abundant compound for the aldehydes, while the carboxylic acids are mainly made up of acetic and propionic acids. Alcohols include monohydric alcohols (mainly methanol

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and ethanol), polyhydric alcohols (1,2-propanediol, 1,2-ethanediol, 2,3-butanediol) and, in lower proportions, monohydric substituted (2-methyl-3-pentanol) and alicyclic alcohols (2-furanmethanol). Ketones include C3-ketones such as 2-propanone (acetone) and 2-propanone-1-hydroxy, and C4-ketones (2-butanone-3-hydroxy and 2-butanone-1-hydroxy, 2,3-butanedione and 2 butanone). The presence of these compounds in the condensates is consistent with the pathway proposed by several authors studying the APR of polyols and sugar based compounds [26, 27, 35-39, 65-70, 74-83].

The composition of the liquid phase depends on the W/m_C ratio and the feedstock. During the APR of cheese whey, an increase in the W/m_C ratio from 60 to 95 g catalyst min/g carbon decreases the relative amount of monohydric and polyhydric alcohols and increases the proportion of C3-ketones and carboxylic acids in the liquid, the proportions of C4-ketones and aldehydes being unaffected. In addition, a further increase in the W/m_C ratio up to 130 g catalyst min/g carbon leads to an increase in the proportions of alcohols (both monohydric and polyhydric) and carboxylic acids as well as to a decrease in the relative amount of ketones (C3 and C4). The initial increase in the W/m_C ratio produces a greater spread of chemical reactions in the liquid phase leading to the formation of end liquid products (acetic acid, ethanol, methanol, propan-2-ol and propan-1-ol). In addition, this increase in the amount of catalyst enhances monohydric and polyhydric alcohol decomposition to gases when a large amount of catalyst is used [42], thus decreasing their proportions in the liquid. Conversely, a further increase in the W/m_C ratio favours the dehydration of glucose and galactose [65-67, 69]. This might hinder the conversion of final liquid products to gas, thus increasing their relative amounts in the liquid. This is in good agreement with the increase observed in the CC sol and the decrease in the CC liq.

Statistically significant differences were found between the chemical compositions of the liquid phase obtained for the APR of cheese whey and lactose, these differences being dependent on the W/m_C ratio. For 60 g catalyst min/g carbon, the liquid phase obtained from cheese whey has greater amounts of alcohols (monohydric and polyhydric) and carboxylic acids and lower proportions of C4-ketones and aldehydes. It is believed that this difference might be the consequence of the lower CC liq and higher CC sol obtained with cheese whey than with lactose. For 95 g catalyst min/g carbon, higher proportions of C3-ketones and carboxylic acids together with a lower proportion of polyhydric alcohols in the liquid phase are obtained for cheese whey than for lactose. An increase in char formation increases the effective W/m_C ratio in the process, thus shifting the composition of the liquid phase towards end products. Very similar liquid compositions were obtained from the real and the filtered cheese whey (non-significant differences are detected for the proportions of ketones, carboxylic acids and aldehydes). Exceptionally, the liquid phase obtained from cheese whey has a greater proportion of monohydric alcohols and a lower amount of polyhydric alcohols.

3.3 Catalyst deactivation

Fig. 7 shows the evolution over time of the CC gas for some steam reforming and aqueous phase reforming experiments. The catalytic steam reforming experiments reveal a decrease in the CC gas over time for the experiments conducted with lactose due to the progressive deactivation of the catalysts, while an increase in the CC gas is noticed for the experiments conducted with the cheese whey and filtered cheese whey solutions due to the progressive gasification of the carbon deposits, as commented

above. A decrease in the CC gas over time takes place for the aqueous phase reforming experiments.

To gain a better insight into catalyst deactivation, some of the used catalysts were characterised by XRD and elemental analysis. The carbon deposited on the used catalysts was examined and the solid carbon distribution between char and coke was calculated. Table 3 lists the CC coke, CC char and the amount of C deposited on the catalysts during the reforming experiments. The results indicate that the vast majority of the CC sol is due to the formation of char. Char production is highly likely to occur during the thermal decomposition of lactose. This tendency of sugars to decompose giving char has also been reported for xylose, glucose and sucrose [32, 33]. As regards catalyst deactivation, coking was responsible for the deactivation of the catalysts during the catalytic steam reforming. The amount of C deposited on the catalysts (mg C/g cat. g organic reacted) is as follows: cheese whey> filtered cheese whey > lactose. This evolution can explain the differences observed during the reforming of the three different liquids. In addition, the lower the temperature, the higher the amount of C deposited and consequently the deactivation of the catalysts. The amount of C deposited on the catalyst during the aqueous phase reforming experiment of the three liquids follows the same trend; however, the amount of C deposited on the surface of the catalysts was much lower.

Fig. 8 shows the XRD patterns of the spent catalysts. The XRD patterns have wide and asymmetric peaks, which denote quite low crystallinity. These analyses indicate the presence of Ni, Co_3O_4, $NiCo_2O_4$, MgO and $MgNiO_2$ in the catalysts used for the catalytic steam reforming experiments, while Ni, $NiAl_2O_3$, $LaCO_3OH$ and boehmite

(AlO(OH)) are crystalline phases detected in the catalyst used for the aqueous phase reforming experiments. The nickel crystallite size for the Ni-Co/Al-Mg and Ni/Al-La catalyst was 12.2 ± 1.5 and 11.2 ± 0.66 nm, respectively. This analysis confirms that under the operating conditions of the aqueous phase, the alumina of the support can be transformed into boehmite. This accounts for the deactivation of the catalysts during the aqueous phase reforming [84-86].

3.4 Comparison between catalytic steam reforming and aqueous phase reforming for cheese whey management

Table 4 shows a comparison between the overall results obtained during the first hour of reaction in the catalytic steam reforming and aqueous phase reforming of real cheese whey under the best operating conditions tested in this work for each reforming process, to highlight the most important differences between both valorisation routes. To fairly compare both valorisation routes, a steady state comparison would be needed. However, the comparison between the results obtained during the first hour of reaction illustrates the most important differences between the two valorisation routes.

For both processes, a complete lactose conversion is achieved. However, there are significant differences between the carbon converted to gas, liquid and solid products and the composition of the gas and liquid phases. As regards gas production, a higher CC gas with a greater proportion of H_2 is obtained using steam reforming. In addition, a liquid effluent with a negligible amount of C is obtained, which is beneficial having regard to cheese whey management. In addition, gas production increases over time due to the progressive gasification of the char produced. Therefore, the CC gas increases

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from 15 to 32% from the first to the second hour of experiment. Aqueous phase reforming of cheese whey is a more attractive option for the production of valuable liquid products. Around 47% of the carbon content of the feed is transformed into a mixture of alcohols, ketones, carboxylic acids and aldehydes.

Solid carbon conversion is the major drawback for both processes; 85% and 46% of the carbon content of the feed is converted into char during the steam reforming and aqueous phase reforming of cheese whey, respectively. This high degree of solid formation causes operational problems for both valorisation routes. Having regard to the evolution of the CC gas and CC sol over time, a fluidised bed reactor could be the most appropriate option for H_2 production from cheese whey by catalytic steam reforming. This reactor configuration allows an easier gasification of the char to take place, which may result in greater H_2 production. In previous works using crude glycerol [87, 88], it was found that this reactor configuration can overcome the substantial formation of char from organic feedstocks with a high proportion of salts. In addition, gas production increases over time due to the positive catalytic effect of salts in the gasification of carbon deposits, a development which is intensified in this type of contactor. As regards the energetic issues of this process, in a previous work an energetic assessment was conducted using lactose [31]. It was found that the combustion of part of the reforming gas produced could provide the energy necessary for the process. This combined process (reforming and combustion of part of the gas) produces a rich H_2 gas from lactose when a high CC gas (>80%) is achieved in the reforming process. Therefore, further research is still necessary with cheese whey to reduce solid formation.

Solid formation represents a serious drawback for aqueous phase reforming due to the blockage of the micrometric valve that controls the pressure in the experimental rig used in this work. One possible solution could be the use of a batch reactor; another might be a modification of the experimental installation. For this modification, the condensers could be placed before the micrometric valve to separate char and solid from the gas mixture before they reach the valve. This would involve the use of pressurised vessels for the condensation unit. Finally, after overcoming the high char formation during the reforming of whey, future research should focus on catalyst development and regeneration.

4. Conclusions

This work addresses the valorisation of cheese whey by catalytic steam reforming and aqueous phase reforming (APR). Both processes have been experimentally evaluated using a Ni-based catalyst. In addition, the results obtained with cheese whey have been compared to those using filtered cheese whey and a lactose solution, the major organic constituent of this wastewater. The most important conclusions obtained from this work are summarised as follows.

1. Catalytic steam reforming is a promising process for cheese whey management. It enables the organic compounds present in the cheese whey to be transformed into a rich H_2 gas (up to 30% CC gas in 2 h, with a concentration of H_2 of 70 vol.%) reducing the amount of carbon present in the liquid effluent, which results in an almost carbon-free liquid stream (CC liq < 1%).

2. Aqueous phase reforming is a potential process for the production of valuable liquids from cheese whey. The CC gas obtained during the aqueous phase reforming of cheese whey is relatively low. In contrast, relatively high CC liq (47%) can be achieved from

cheese whey by aqueous phase reforming. This liquid phase is made up of a mixture of aldehydes, carboxylic acids, alcohols and ketones in water. The chemical composition of this liquid phase is dependent on the amount of catalyst used.

3. The formation of char is the major drawback for the correct development of catalytic steam reforming and aqueous phase reforming. This char formation is enhanced by the presence of salts in cheese whey. This substantial solid formation (CC sol > 45%) hampers higher CC gas and CC liq from being achieved from cheese whey by steam reforming and aqueous phase reforming, respectively. New reactor configurations and/or the elimination of salts from the feedstock might overcome this problem.

4. Filtration of the cheese whey slightly reduces the formation of char. However, this filtration only marginally changes the composition of the gas for steam reforming or the liquid phase for aqueous reforming compared to the results obtained with real cheese whey.

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TABLES

Table 1. Cheese whey properties. Results are presented as mean ± standard deviation.

Composition	Cheese whey	Filtered cheese whey
Organic compounds (wt.%)	10.49±0.22	10.08±0.25
Lactose (wt.%)	4.71±0.11	5.44±0.13
Acetic acid (wt.%)	1.37±0.04	1.58±0.04
Formic acid (wt.%)	0.68±0.02	0.79±0.02
Sorbic acid (wt.%)	1.81±0.02	0.93±0.03
2-propanamine (wt.%)	1.17±0.03	0.02 ±0.03
H_2O (wt.%)	90.74±1.08	89.38±1.28
Ashes (wt.%)	0.522±0.0004	0.542±0.0004
Ultimate Analysis		
C (wt.%)	2.73±0.04	2.15±0.04
H (wt.%)	8.97±0.18	9.05±0.16
O (wt.%)[a]	87.94±0.23	88.76±0.18
N (wt.%)	0.36±0.13	0.06±0.13
TOC (ppm)	29337±512	24970±432
Physical properties		
pH	7.13±0.02	7.10±0.05
Density (g/mL)	1.010±0.001	1.010±0.001

[a] Determined by difference

Table 2. Response variables. Definitions and analytical techniques used in their determination.

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

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

CC liq* = Carbon conversion to liquids including unreacted lactose

Table 3. Solid carbon distribution. Overall carbon conversion to solid, char and coke and C deposited on the catalyst.

Run	CC solid (%)	CC char (%)	CC coke (%)	C (mg C/g cat. g org.)
SR-CW-450ºC-W/m = 24	78.4±1.7	76.0±1.6	2.43±0.04	404±20
SR-FCW-450ºC-W/m = 24	74.3	71.2	3.1	367
SR-Lactose-450ºC-W/m = 24	25.1 ± 0.98	24.5 ± 0.72	0.51 ± 0.12	0.84 ± 0.08
SR-CW-600ºC-W/m = 24	74.2	71.5	2.82	333
SR-FCW-600ºC-W/m = 24	67	63.9	3.1	280
SR-Lactose-600ºC-W/m = 24	30.0	25.87	4.13	0.58
APR-CW-450ºC-W/m = 95	46.4 ± 2.2	45.8 ± 2.1	0.61 ± 0.06	28 ± 1.1
APR-FCW-450ºC-W/m = 95	40.3	39.9	0.45	20
APR-Lactose-450ºC-W/m = 95	1.02	0.64	0.38	12

Table 4. Comparison between catalytic steam reforming and aqueous phase reforming

for the first hour of experiment. Results are presented as mean $\pm$ 0.5 LSD

	Steam Reforming	Aqueous Phase reforming
Operating conditions		
T (ºC)	600	220
P (bar)	1	44
W/m_C (g cat min/g C)	38	95
Global results		
X lactose (%)	100	100
CC gas (%)	14.84$\pm$2.21	6.46$\pm$1.69
CC liq (%)	0.1$\pm$3.60	47.11$\pm$2.82
CC sol (%)	85.06$\pm$2.55	46.42$\pm$2.99
Gas phase composition		
H_2 (vol.%)	67.23$\pm$1.60	32.58$\pm$3.00
CO_2 (vol.%)	31.96$\pm$1.60	54.9$\pm$3.00
CO (vol.%)	0.26$\pm$1.10	0.63$\pm$0.68
CH_4 (vol.%)	0.54$\pm$0.12	10.30$\pm$1.25
Liquid Composition (% Area)		
Alcohols	0	49.83$\pm$6.45
Ketones	0	38.88$\pm$3.90
Carboxylic acids	0	16.11$\pm$1.15
Aldehydes	0	1.02$\pm$0.32

FIGURES

a)

b)

c)
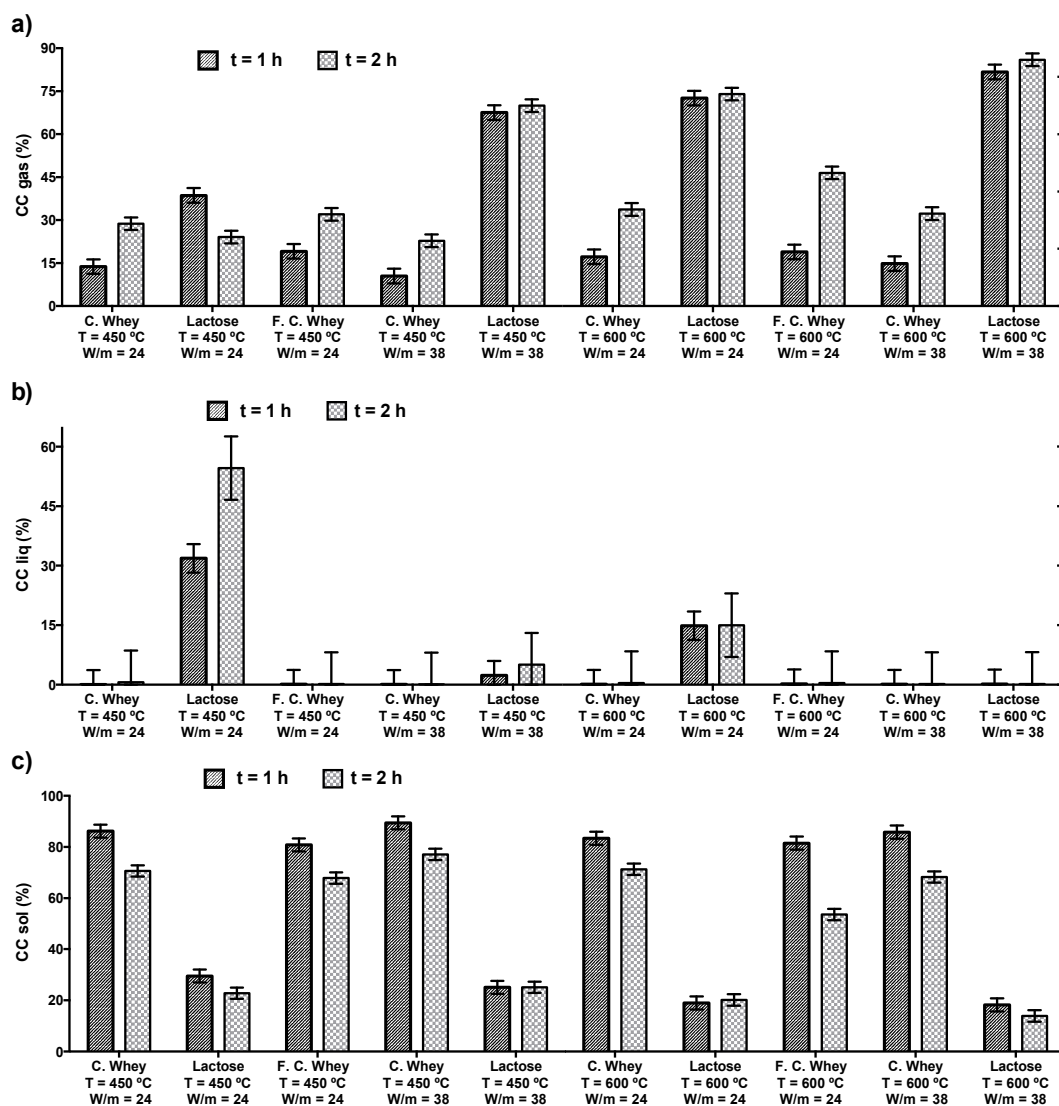
Fig. 1. Carbon conversion to gas (a), liquid (b) and solid (c) obtained in the catalytic steam reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.
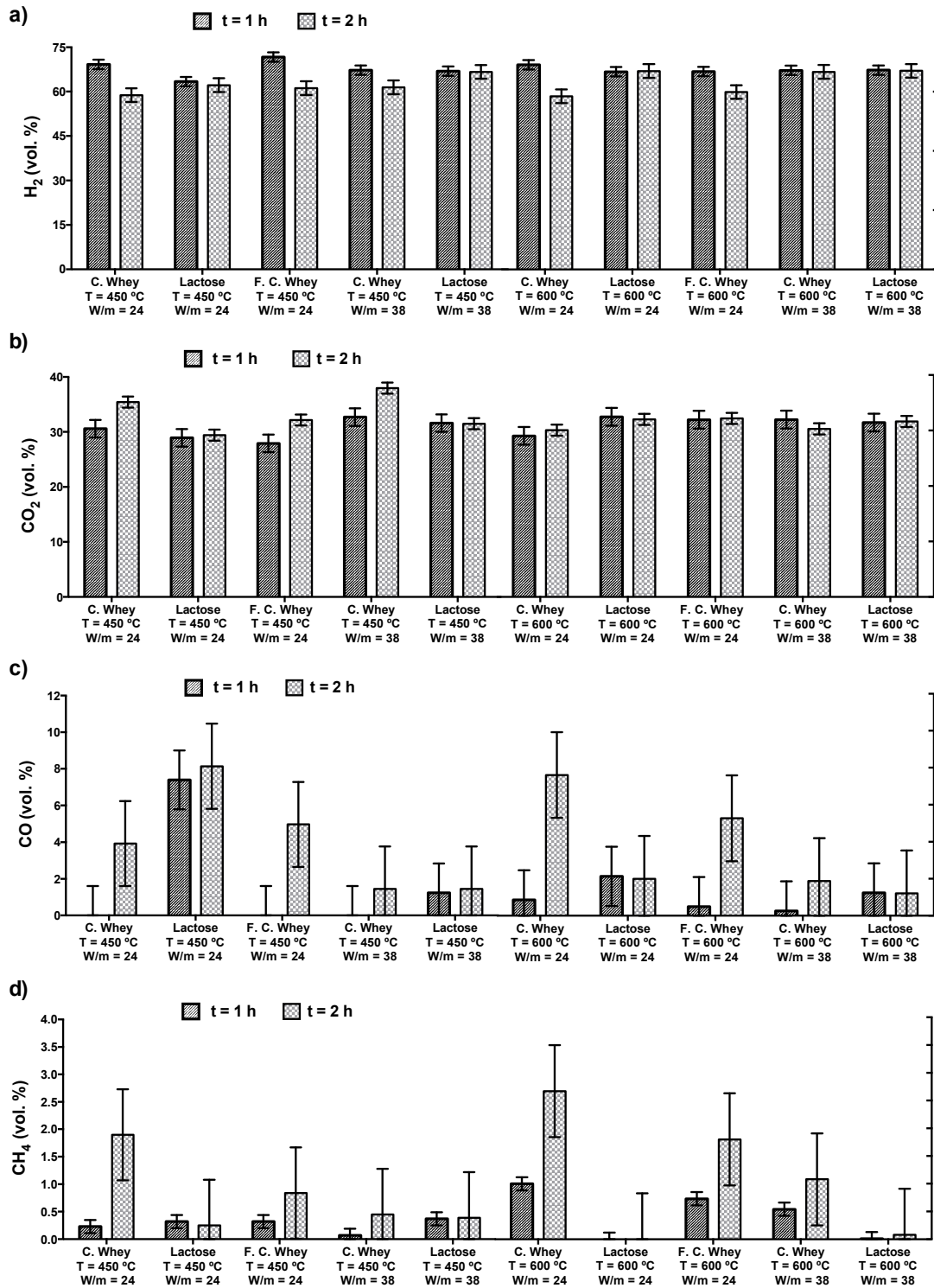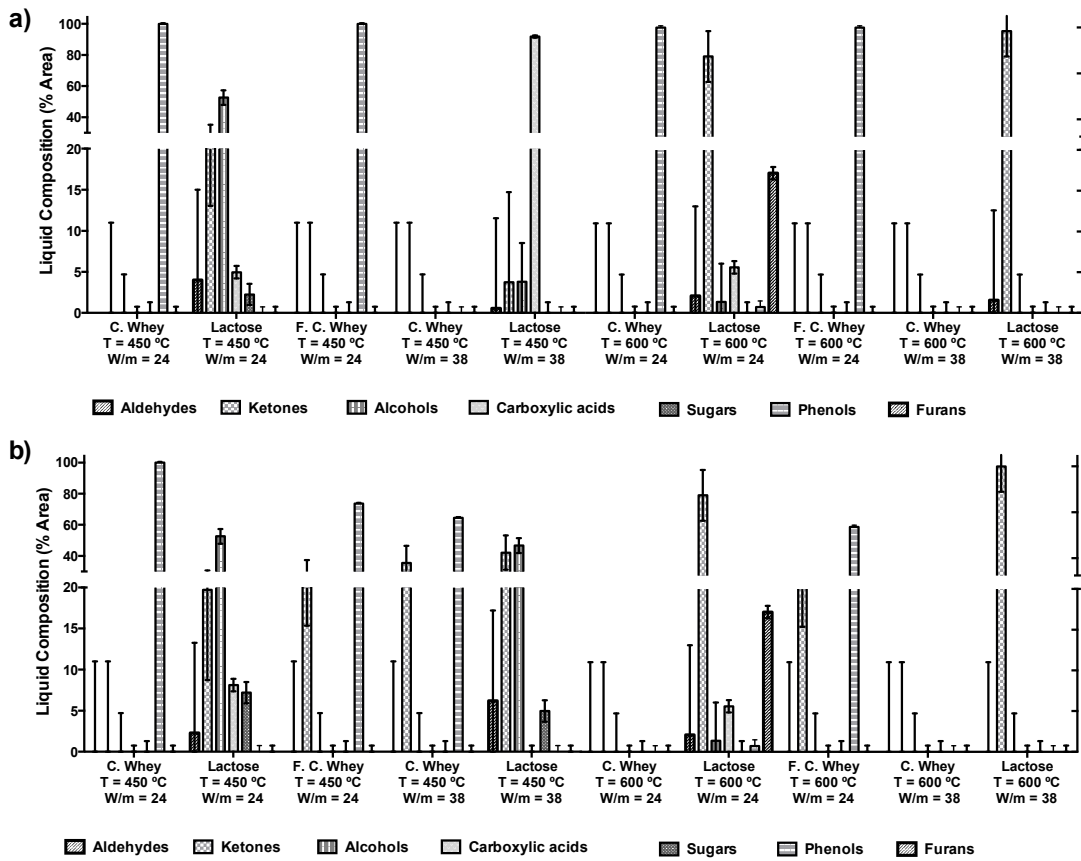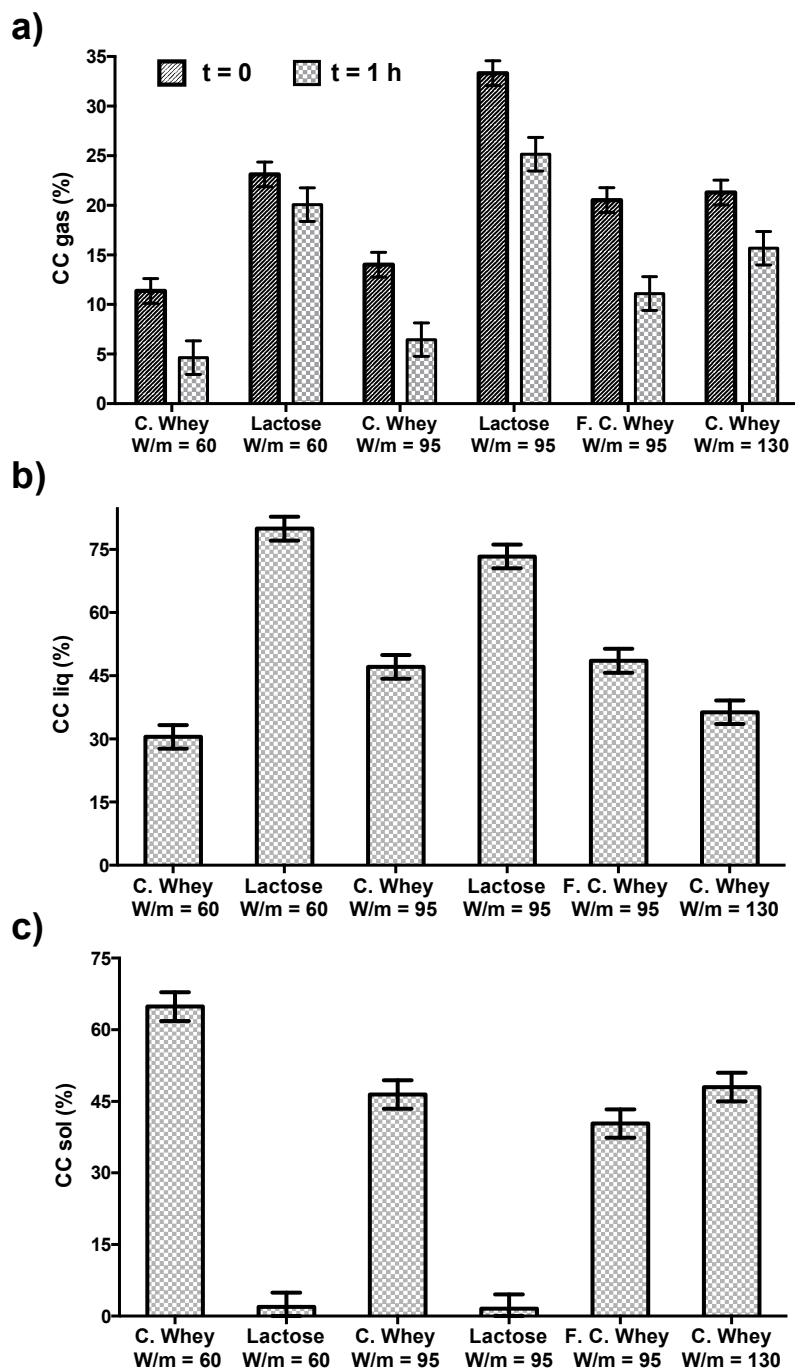
Fig. 2. Relative amounts of H_2 (a), CO_2 (b) CO (c) and CH_4 (d) obtained in the catalytic steam reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.

Fig. 3. Composition of the liquid phase obtained during the first (a) and second (b) hour for the catalytic steam reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.

Fig. 4. Carbon conversion to gas (a), liquid (b) and solid (c) obtained in the catalytic aqueous phase reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.
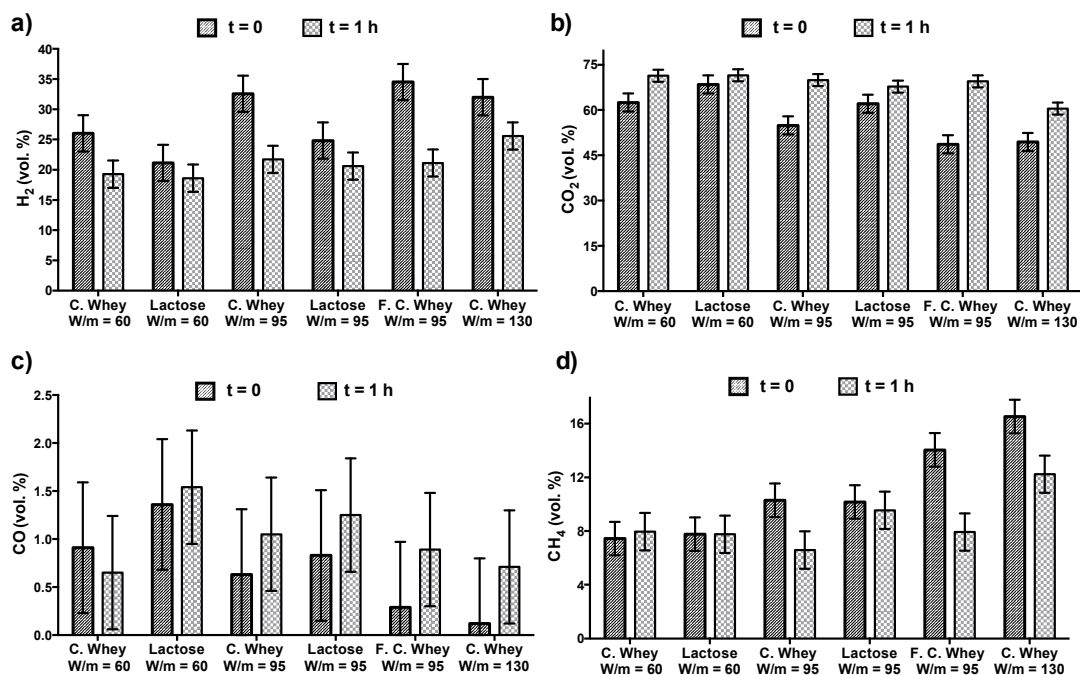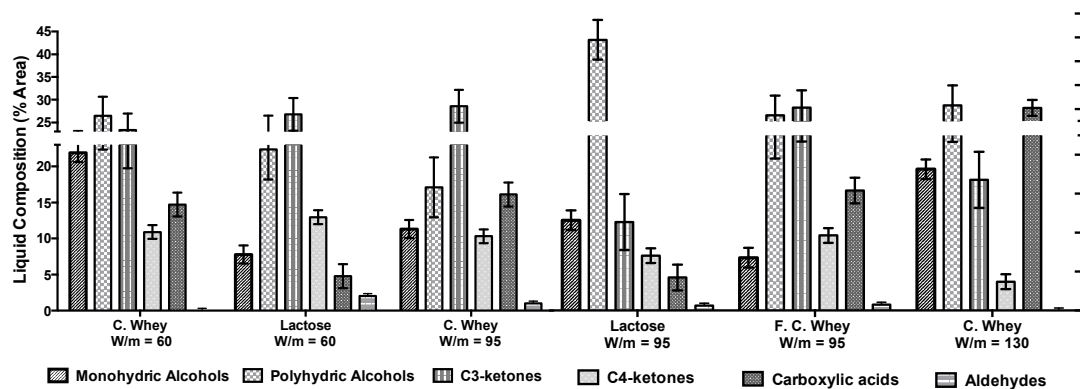
Fig. 5. Relative amounts of H_2 (a), CO_2 (b) CO (c) and CH_4 (d) obtained in the catalytic aqueous phase reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.

Fig. 6. Composition of the liquid phase obtained in one hour in the catalytic aqueous phase reforming of cheese whey, filtered cheese whey and lactose. Bars are LSD intervals with 95% confidence.

a) Steam reforming

Legend:
- ● CW- 450ºC-W/m 24
- ■ CW-600ºC- W/m 24
- ◇ FCW- 450ºC-W/m 24
- ▽ FCW-600ºC- W/m 24
- ○ Lactose 450 ºC-W/m 24
- □ Lactose 600ºC W/m 24

b) Aqueous phase reforming

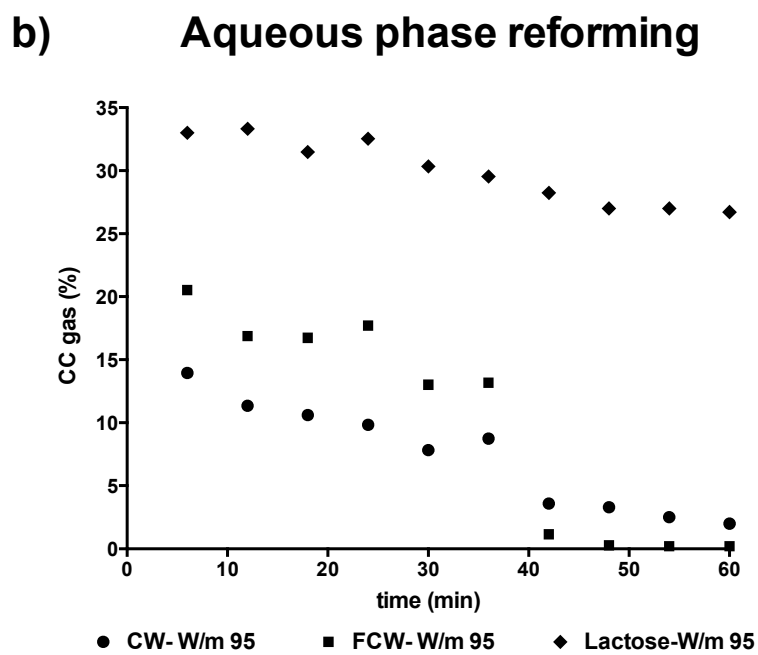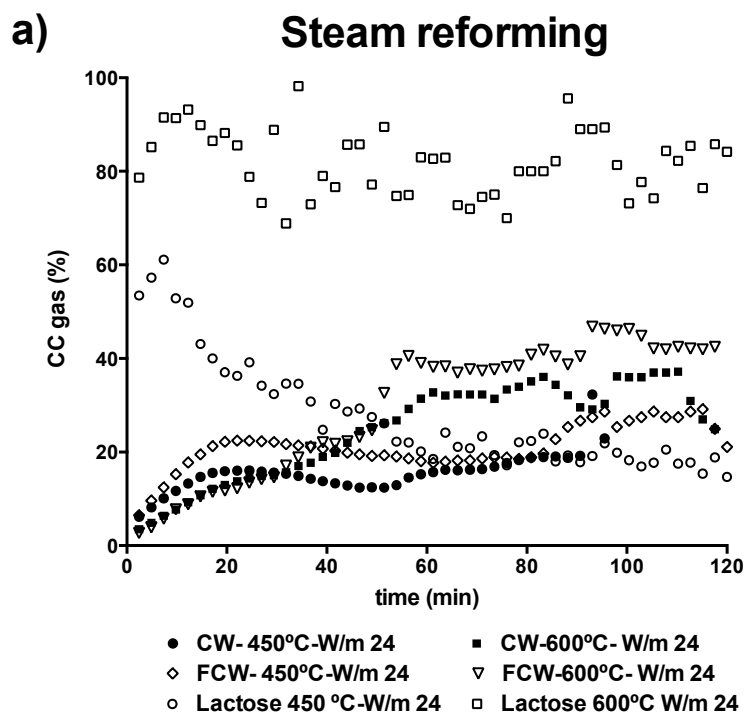Legend:
- ● CW- W/m 95
- ■ FCW- W/m 95
- ◆ Lactose-W/m 95

Fig. 7. Evolution over time of the CC gas for some a) steam reforming and b) aqueous phase reforming experiments.
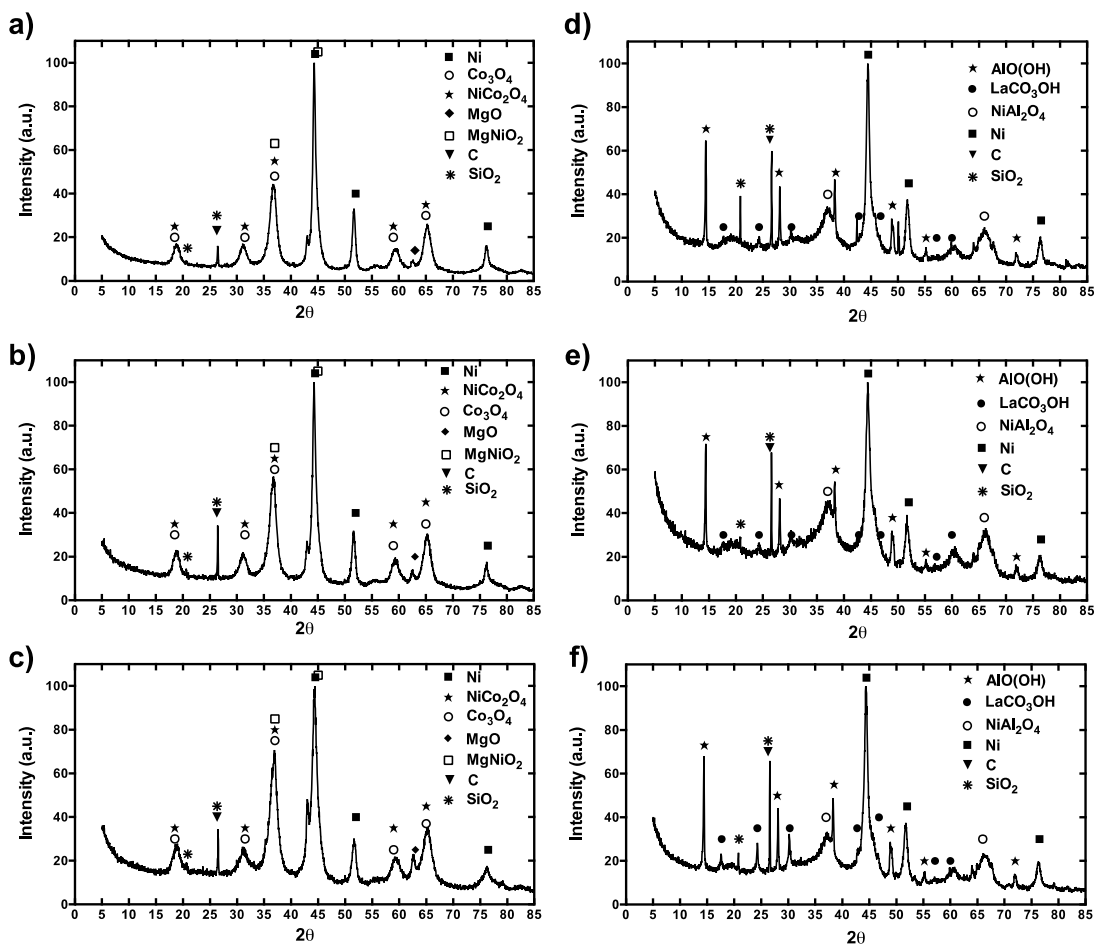
Fig. 8. XRD for some spent catalysts. a) SR-CW-600 ºC-W/m 24, b) SR-FCW-600 ºC-W/m 24, c) SR-Lactose-600 ºC-W/m 24, d) APR-CW-W/m 95, e) APR-FCW-W/m 95, f) APR-Lactose-W/m 95.