



## Research article

## 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<sub>2</sub> production from this effluent. This process enabled the organic compounds present in the cheese whey to be transformed into a rich H<sub>2</sub> gas (35% of the C of the feed was transformed into a gas with 70 vol.% of H<sub>2</sub>). 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<sub>2</sub> and CO<sub>2</sub>, 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 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.

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## 1. Introduction

Cheese whey is a yellowish liquid resulting from the coprecipitation and removal of milk casein in cheese-making processes. On average, 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 to 60 kg/m<sup>3</sup> and 50–102 kg/m<sup>3</sup>, respectively; therefore, it should not be directly discharged into the environment without appropriate treatment and/or valorisation [3]. 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 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<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> with a theoretical yield of 4 mol H<sub>2</sub>/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

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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 °C), 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 °C) 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<sub>2</sub> 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<sub>2</sub> (67 vol.%) in the gas together with a carbon-free liquid stream were achieved at 586 °C 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<sub>2</sub> production, analysing the effect of the reaction time (0–3 h), temperature (300–600 °C) and steam to carbon (S/C) ratio (3–9 mol H<sub>2</sub>O/mol C) on the process. Marquovich 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<sub>2</sub> 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<sub>2</sub> production was found at 400 °C and 200 kPa.

The aqueous phase reforming of sugars has been considered for glucose, xylitol, sorbitol and galactitol. Cortright et al. [35] analysed the aqueous phase reforming of glucose and sorbitol in a flow reactor between 498 and 538 K. The carbon converted to gas and liquid varied by 50–84% and 15–51%, respectively during the reforming of glucose depending on the reaction temperature. These conversions varied by 61–90% and 12–39% in the case of sorbitol. The gas phase consisted of a rich H<sub>2</sub> gas with a relative proportion of this gas in the mixture of 46–51 vol.% and 54–61 vol.% when processing glucose and sorbitol, respectively. Jiang et al. [36] studied the APR of xylitol for pentane production over Pt/HZSM-5 and Ni/HZSM-5 catalysts, analysing the effects of the temperature, pressure 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 °C at 4 MPa increased the xylitol conversion from 30 to 80%. At 240 °C, an increase in the pressure from 2 to 4 MPa increased the xylitol conversion from 61 to 80%. Kirilin et al. [37] reported the APR of xylitol in a continuous fixed bed reactor over three catalysts: Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/TiO<sub>2</sub> and Pt-Re/TiO<sub>2</sub>. Higher conversions of xylitol were observed for the Pt-Re catalyst than for the two monometallic catalysts. Xi et al. [38] prepared different M/NbOPO<sub>4</sub> 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. [39] developed a path lumping kinetic model for the aqueous phase reforming of sorbitol. Paths of reforming and CO<sub>2</sub> 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. [40] investigated the APR of xylitol and sorbitol using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Generally, higher yields and selectivity to hydrogen were observed for xylitol than for sorbitol. The maximum selectivity to H<sub>2</sub> (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. [41] analysed the APR of sorbitol and galactitol over a Pt/Al<sub>2</sub>O<sub>3</sub> 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 space 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 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.

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