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

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ABSTRACT

Cheese effluent management has become an important issue owing to its high biochemical oxygen demand and chemical oxygen demand values. Given this scenario, this work addresses the valorisation of lactose (the largest organic constituent of this waste) by aqueous phase reforming, analysing the influence of the most important operating variables (temperature, pressure, lactose concentration and mass of catalyst/lactose mass flow rate ratio) as well as optimising the process for the production of either gaseous or liquid value-added chemicals. The carbon converted into gas, liquid and solid products varied as follows: 5–41%, 33–97% and 0–59%, respectively. The gas phase was made up of a mixture of H_2 (8–58 vol.%), CO_2 (33–85 vol.%), CO (0–15 vol.%) and CH_4 (0–14 vol.%). The liquid phase consisted of a mixture of aldehydes: 0–11%, carboxylic acids: 0–22%, monohydric alcohols: 0–23%, polyhydric-alcohols: 0–48%, C3-ketones: 4–100%, C4-ketones: 0–18%, cyclic-ketones: 0–15% and furans: 0–85%. H_2 production is favoured at high pressure, elevated temperature, employing a high amount of catalyst and a concentrated lactose solution. Liquid production is preferential using diluted lactose solutions. At high pressure, the production of C3-ketones is preferential using a high temperature and a low amount of catalyst, while a medium temperature and a high amount of catalyst favours the production of furans. The production of alcohols is preferential using medium temperature and pressure and a low amount of catalyst.

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1. Introduction

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

Two alternative methods of cheese whey management have traditionally been addressed [3]. The first is the application of physicochemical treatments and filtration technologies. Physicochemical treatments include thermal and isoelectric precipitation [5,6], as well as protein precipitation with coagulant/flocculant agents [7].

Filtration technologies include the use of ultrafiltration membranes and reverse osmosis [2]. The second option relies on the application of biological treatments without valorisation, such as aerobic digestion, and with valorisation such as anaerobic digestion, lactose hydrolysis and fermentation [3]. Aerobic digestion consists of the degradation of the organic matter in the whey at room temperature using short hydraulic retention times [8]. Anaerobic digestion is conducted to convert lactose into propionic acid, ethanol and lactose acetates [9]. Lactose hydrolysis is a preliminary step for other processes [4]. Cheese whey fermentation includes the production of ethanol, lactic acid, and hydrogen and many more [10]. The bioconversion of lactose to ethanol has a theoretical maximum yield of 0.538 kg ethanol/kg of lactose [11,12]. Anaerobic fermentation has a theoretical yield of 4 mol H_2/mol lactose and produces a gas made up of a mixture of H_2, CO_2 and CH_4.

Another interesting and very promising option for the treatment and valorisation of cheese whey effluents is aqueous phase reforming (APR). APR is a catalytic process carried out at quite low temperatures and moderate pressures that allows the simultaneous production of different gases and liquids from an organic feedstock. The gas phase consists of a gas with a high H_2 content, the liquid phase being a complex mixture of different organic compounds in water such as alcohols, ketones, acids, esters, aldehydes,

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furans, phenols and anhydro-sugars [13–16]. The product distribution strongly depends on the operating conditions under which the process is conducted. Therefore, APR can be customised either for the production of gases, helping to reduce the BOD and COD values of the feed or for the production of valuable liquids. In addition, the APR process dispenses with the need to vaporise the water and the organic compounds of the feedstock, thus reducing the energy requirements [17]. To the best of the authors' knowledge, there are no studies in the literature concerning the effect of the operating conditions on the aqueous phase reforming of lactose or cheese whey. Holles and Skoglund [18] developed different pseudomorphic overlayer catalysts (Ni/Al$_2$O$_3$, Co/Al$_2$O$_3$, Pt/Al$_2$O$_3$, Ni/SiO$_2$-Al$_2$O$_3$, Co/SiO$_2$-Al$_2$O$_3$ and Pt/SiO$_2$-Al$_2$O$_3$) for the aqueous phase reforming of lactose. Furthermore, works dealing with the aqueous phase reforming of sugars are very scarce. Such studies that there are analyse the aqueous phase reforming of xylitol, sorbitol and galactitol.

Jiang et al. [19] studied the APR of xylitol for pentane production over Pt/HZSM-5 and Ni/HZSM-5, analysing the effects of the reaction temperature, pressure and metal loading on the xylitol conversion and pentane selectivity. Kirilin et al. [20] reported the APR of xylitol in a continuous fixed bed reactor over three catalysts: Pt/Al$_2$O$_3$, Pt/TiO$_2$ and Pt-Re/TiO$_2$. Xi et al. [21] 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. Aiouache et al. [22] developed a lumped kinetic model for the aqueous phase reforming of sorbitol. The model was tested at temperatures ranging from 473 K to 523 K, using monometallic Ni and bimetallic Ni-Pd catalysts supported on Al$_2$O$_3$, ZrO$_2$ and CeO$_2$. Kirilin et al. [23] investigated the APR of xylitol and sorbitol using a Pt/Al$_2$O$_3$ catalyst. Godina et al. [24] analysed the APR of sorbitol and galactitol using a Pt/Al$_2$O$_3$ catalyst in a continuous fixed-bed reactor at 225 °C.

Given this background, prior to deal with cheese whey, this work analyses the aqueous phase reforming of a lactose solution, the major organic constituent of this waste, as a possible option for the treatment and valorisation of cheese whey effluents and/or lactose solutions recovered from whey. Specifically, the work addresses the effect of the temperature, pressure, lactose concentration and W/m$_{lactose}$ ratio on the APR of lactose using a Ni-based catalyst. The effect of the operating conditions on the production and selectivity to the different gas and liquid products has never been reported to date. Therefore, the effect of the operating variables on gas, liquid and solid production and on the compositions of the gas and liquid phases has been exhaustively analysed. Furthermore, optimal values for the production of gas and liquid products have also been sought for their selective production. Consequently, this work represents a challenging and novel investigation not only for the management and valorisation of cheese whey but also for the valorisation of sugars or sugar-based streams.

2. Experimental

2.1. Materials

The experiments were carried out in a small bench scale continuous unit for 3 h employing a Ni-La/Al$_2$O$_3$ catalyst. The catalyst was prepared by coprecipitation, having 28% (relative atomic percentage) of Ni expressed as Ni/(Ni + Al + La), an atomic La/Al ratio of 0.035 and a Brunauer-Emmett-Teller (BET) surface area of 187 m^2/g. The lactose solutions were prepared dissolving D-lactose monohydrate (C$_{12}$H$_{22}$O$_{11}$·H$_2$O Sigma Aldrich, CAS Number 64044-51-5, Bio-Ultra >99.5% HPLC) in Milli-Q water.

2.2. Experimental rig

The experimental rig used in the experiments was a microactivity unit designed and built by PID (Process Integral Development Eng & Tech, Spain). It consists of a stainless steel tubular reactor with an inner diameter of 9 mm, heated up by means of an electric furnace [25,26]. The system pressure is reached with the aid of a micrometric valve that automatically adapts its position with the help of a rotor. A pressure gauge located at the exit of the reactor measures the pressure of the reaction section. A PDI control system is used to keep the reactor pressure constant during the experiments. The aqueous solutions of lactose are fed into the reactor by means of a high performance liquid chromatography (HPLC) pump (Gilson, model 307). The reaction products (gas and liquids) leave the reactor from its upper part, pass through the valve, where they are depressurised, and arrive at the condensation system. This system consists of several condensers where the liquid products are separated from the gas mixture at intervals of 1 h to analyse the evolution over time of the liquid phase. The gas mixture is made up of N$_2$, used as an internal standard, and the different gaseous products formed during the aqueous phase reforming reaction. An Agilent M3000 micro chromatograph equipped with thermal conductivity detectors (TCD) was used for the online analysis of the gas phase. The liquid fractions were collected and analysed offline with a gas chromatograph (Agilent 7890 GC-system, model G3440A) equipped with Flame Ionization (FID) and Mass Spectrometry (MS) detectors. A schematic diagram of the experimental system is shown in Fig. S1.

2.3. Operating conditions, response variables and statistical analyses

The effect of the temperature (200–240 °C), pressure (38–50 bar), lactose concentration (1–10 wt.%) and catalyst mass/lactose mass flow rate ratio (W/m$_{lactose}$ = 10–40 g catalyst min/g lactose) was experimentally analysed using a design of experiments (DOE) with statistical analysis of the results carried out by means of an analysis of variance (ANOVA). The effect of the operating conditions on the process was analysed for the following response variables: global lactose conversion (X lactose, %), carbon conversion to gas, liquid and solid products (CC gas%, CC liq%, and CC sol%) as well as the composition of the gas (N$_2$ and H$_2$O free, vol. %) and liquid (relative chromatographic area free of water and un-reacted lactose, %). Table S1 summarises the response variables and the analytical methods used for their calculation.

The experiments, listed in Table S2, were designed using a 2^k factorial design, where k indicates the number of factors studied (4 operating conditions) and 2^k represents the number of runs (16). In addition, 5 replicates at the centre of the variation interval of each factor were carried out in order to evaluate both the experimental error and the curvature shown by the evolution of each variable. This factorial design minimises the number of experiments needed to understand the effect on the process of the operating variables and the interactions between them. As the response variables did not show a linear trend, this design was increased with 8 axial runs following a Box-Wilson Central Composite Face Centred (CCF, α: ±1) design, enabling the operating variables and interactions responsible for the curvature to be identified without modifying the range of study initially considered for the operating variables. The lower and upper limits of all the operating variables were normalised from −1 to 1 (codec factors) to identify their influence in comparable terms.

For the analysis of the results, firstly the evolution over time of the response variables was studied. To do this, the results were divided into three intervals, each corresponding to the average value of the studied response variables obtained during each one of the three hours of experiment. All these values (three per