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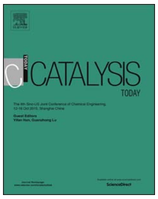

Valorization of alginate for the production of hydrogen via catalytic aqueous phase reforming

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ABSTRACT

Alginate, a carbohydrate abundant in the outer cell wall of macroalgae, was subjected to catalytic aqueous phase reforming (APR) to produce hydrogen using a 3% Pt/C commercial catalyst. The performance of the process was evaluated according to the conversion of the carbon to gas, the hydrogen yield and the hydrogen selectivity. The catalyst and feed amount, temperature, reaction time, pH and the presence of H_2 were modified to understand the dependence of the outcome of the process on these parameters. The presence of the catalyst was fundamental in order to increase the hydrogen yield compared to the uncatalyzed reaction, and it can be reused without activity loss. In addition, it was observed that the increase in alginate loading led to a decreasing conversion of the carbon; the yield of hydrogen increases with the increasing temperature and the basic pH had a strong beneficial effect in terms of selectivity. The plateau appeared after 2 h was attributed to the low kinetic tendency of the intermediate compounds to produce hydrogen. The study validated what is present in literature for simpler molecules, moving at the same time towards a more complex feed, closer to a possible industrial application.

1. Introduction

The World Energy Outlook 2016 forecasted in the main scenario a 30% rise in global energy demand by 2040 [1]. Nowadays, we strongly depend on the exploitation of fossil sources; however, the depletion of non-renewable oil urges the study of alternative and sustainable pathways. Among others, the utilization of biomass seems one of the most promising ways to reach this fundamental goal [2].

Biomass is commonly classified according to three generations [3]. First generation is related to edible crops (e.g. sugar cane, palm oil): it is an important commercial reality for the production of bioethanol and biodiesel, but embraces critical ethical drawbacks; second generation is referred to lignocellulosic materials (e.g. agricultural residues, purpose-grown vegetative grasses) [4,5]: it overcomes the food competition, but requires high land use; third generation is referred mainly to microalgae and macroalgae [6]. Compared to the previous generations, it has the important advantage not to interfere neither with food production nor with agriculture land [7]. Focusing in particular on macroalgae, the beneficial effects linked to their exploitation–rapid growth, efficient cultivation, CO_2 sequestration – encourage the scientists, who look at them as a renewable source of biofuels and chemicals [8,9].

Macroalgae are classified as brown, red or green algae. Their composition is poor in lipids, lignin-free, but with a high content in carbohydrates [10]. Alginate is one of the most abundant carbohydrates in the outer wall cell of brown macroalgae [11]. It is constituted by two different units (mannuronic acid and guluronic acid) linked by β-1,4-glycosidic bonds. It is used in several sectors, for example as food additive, drug delivery system, or for textile printing. Recently it has been studied also as a possible source of biofuels and with the aim to produce valuable compounds [12].

Aida et al. studied the hydrothermal treatment of sodium alginate into added-value organic compounds such as lactic, malic or succinic acid from 150 to 400 °C [13]. They found that increasing the reaction temperature enhanced the conversion of alginate to smaller organic acids, whereas at 150 °C they found compounds with rather high molecular weight. The authors concluded that the alginate containing marine algae could be an interesting feedstock for biomass refinery processes, in particular, for liquid products.

In another study, it was investigated the influence of some reaction conditions (pH, temperature) on the products distribution [12]. For example, furfural and glycolic acid were in acidic conditions, while lactic, fumaric and malic acid were in basic conditions. In addition, the

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increase in temperature influenced the molecular weight distribution of the final products. They stated that alginate could be an alternative to cellulose for the production of furfural and value added organic acids.

Recently, Ban et al. investigated the selective conversion of alginate into its two monomers by mean of sulfonated glucose-derived carbon catalyst [14]. However, they observed a consecutive degradation, obtaining humins and isomeric uronic acids, that lowered the yield of the target products.

However, to the best of our knowledge, all the previous works were focused only on the characterization of the liquid phase produced by the reaction. The microalgae and marine macroalgae have been considered as feedstock with high potential for their use in a biorefinery, replacing the terrestrial biomass-based biorefinery [15]. Looking at a possible application in a biorefinery, it would be interesting to investigate the possibility to produce, apart from valuable compounds obtained in the liquid phase, a worthwhile gas phase. The previous mentioned works are carried out in water, taking advantage of the peculiar characteristics of “high-temperature water”, working in a system that is cheap, sustainable and eco-friendly. Therefore, we were interested in exploring the possibility to obtain also a valuable gas phase from alginate, that is one of the main component of the cell wall.

During the last decade, the aqueous phase reforming (APR) of oxygenated compounds was one of the most investigated processes [16]. It allows to obtain a gas mixture rich in hydrogen working at milder temperature (about 500 K) compared to the more severe conditions (typically higher than 800 K) of the conventional steam reforming of hydrocarbons. Up to now, these studies have been carried out mainly using simple molecules: ethylene glycol [12–16,21], glycerol [22–24], sorbitol [25,26]. These studies are fundamental because they allowed to have an insight on the reaction mechanism. However, it is required to gradually increase the level of complexity of the feed, by testing a compound closer to those present in the aqueous stream coming out from hydrothermal processes in a biorefinery: this is, in principle, the main target of aqueous phase reforming, as suggested from the first work in which the APR was indicated as useful for the generation of hydrogen rich fuel gas from carbohydrates extracted from renewable biomass [16].

In this work, in order to valorize a promising feedstock in terms of biorefinery, dealing with an environmental-friendly system, we explored the catalytic APR of alginate. In this case, the stoichiometric reaction would be

$$C_6H_9O_7 + 5\ H_2O \rightarrow 6\ CO_2 + 9.5\ H_2 \quad (1)$$

With this stoichiometry, the alginate is actually an anion, and the corresponding cation is sodium, in this work. Moreover, we referred to the molecular formula of the repetitive unit of alginate (mannuronic or guluronic acid), without considering the first step of hydrolysis of the polysaccharide.

We tested the influence of the catalyst and alginate loading, temperature, reaction time, pH and hydrogen pressure in the head gas phase of the batch reactor over three output parameters under evaluation: carbon conversion to gas (CtoG), hydrogen yield (Y-H_2) and hydrogen selectivity (S-H_2).

This work mainly focused on the investigation of the yield towards gas phase, whereas, as mentioned, some previous papers looked at the alginate solution as a feed to obtain just liquid products [27]. The achieved results helped to validate the previous APR works done on simpler molecules, verifying its robustness in the case of a more complex feed; moreover, it allowed to move a step towards the industrial application of this thermochemical process trying to apply it with a much more complex feed that is significantly more similar to what expected in practical contexts, looking to a carbohydrate based biorefinery.

2. Materials and methods

2.1. Materials

Sodium alginate was purchased from Carlo Erba. Deionized water was obtained in laboratory. 3% Pt/C catalyst was purchased from Sigma-Aldrich. All other chemicals and reagents were purchased from Sigma-Aldrich. Gas cylinders were supplied by SIAD S.p.A., Bergamo (Italy). All the chemicals were used as received.

2.2. Aqueous phase reforming tests

The APR tests were conducted in a 300 mL 4560 series mini bench top reactor (Parr) equipped with a 4848 model reactor controller (Parr). The reactor was loaded with 100 mL of aqueous solution with different alginate concentration (0.5, 1 and 2 wt.%) and the catalyst was added in the desired amount (0–0.8 g depending on the run) without any pretreatment. In fact, preliminary tests in which the catalyst was subjected to a reducing environment did not affect the catalytic properties. The atmosphere was purged from the oxygen by nitrogen five times; then it was pressurized with 0.3 MPa of N_2. The temperature was programmed to reach the desired set value, and kept constant for the prefixed time. The stirrer was set at 500 rpm. The heating time was approximately 30 min, and the reaction time was considered starting when the set temperature was reached. At the end of the reaction, the reactor was cooled thanks to the internal water-cooling coil. The pressure value obtained by the transducer was recorded. The gas phase was collected in a sampling bag and analyzed by micro-GC, to evaluate its composition. The liquid product was recovered from the reactor and filtered by gravity to remove the catalyst; then it was subjected to TOC and HPLC analysis. The filtered solid phase was put in an oven at 90 °C overnight, recovered and weighted.

In the tests where the purge was carried out, after the collection of the gas phase, the reactor was again purged with nitrogen and then set at the temperature desired.

2.3. Analysis

The analysis of the gas phase was performed with a SRA Micro-GC, equipped with a Molsieve 5A column (for the analysis of permanent gases such as hydrogen, nitrogen, methane and carbon monoxide) and Argon as carrier (column temperature: 100 °C); a PoraPLOT U column was used for the separation of carbon dioxide, ethane and propane, with Helium flow as carrier (column temperature: 80 °C). The detection of the species was due to a TCD detector. The injection temperature was fixed at 90 °C and the pressure at 30 psi.

HPLC analysis (Shimadzu) was performed with a Rezex ROA-Organic acid H^+ (8%) column (300 mm * 7.8 mm). The mobile phase was 5 mM H_2SO_4 in water. The flow rate was fixed at 0.6 mL/min and the temperature of the column at 50 °C. The products were determined by means of a photodiode array detector (PDA) set at 200 nm.

Total carbon (TC) and inorganic carbon (IC) analysis was performed using a Shimadzu TOC-V_{CSH} analyzer equipped with a nondispersive infrared detector.

A Micromeritics Tristar 3020 instrument was used to measure the N_2 adsorption/desorption isotherms of the fresh and spent catalysts at 77 K. Prior to the characterization, the samples (about 0.1 g) were degassed at 200 °C under nitrogen flow for 2 h by means of a Micromeritics Flow Prep 060 degassing system. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) equation, whereas the pore size distribution and the pore volume in accordance to the Barrett-Joyner-Halenda (BJH) method.

X-ray diffraction (XRD) was performed by means of a Panalytical X’Pert Pro diffractometer (Cu Ka radiation, 2 h range 10–70, step 0.01, time per step 240 s) on a fresh and spent catalyst sample to assess any structural change.