

Lewis-Brønsted acid catalysed ethanolysis of food waste for the synthesis of ethyl levulinate

L. di Bitonto¹, G. Antonopoulou^{2,3}, C. Braguglia⁴, C. Campanale¹,
A. Gallipoli⁴, G. Lyberatos^{2,3}, I. Ntaikou^{2,3}, C. Pastore¹

¹Water Research Institute (IRSA), National Research Council (CNR), via F. de Blasio 5, 70132 Bari, Italy

²Institute of Chemical Engineering Sciences, Stadiou, Platani, Patras, GR 26504, Greece

³School of Chemical Engineering, National Technical University of Athens, GR 15780, Athens, Greece

⁴Water Research Institute (IRSA), National Research Council (CNR), Strada Provinciale 35d, km 0.7, 00010 Montelibretti, Rome, Italy

Keywords: ethyl levulinate, food waste, biorefinery, biofuels, ethanolysis

Presenting author email: luigi.dibitonto@ba.irsa.cnr.it

Introduction

The necessity to satisfy the increasing demand for liquid fuels, together with the attention on substituting fossil feedstocks, has been encouraging research into evaluating new solutions, deriving from renewable feedstocks. In this direction, increasing attention has been paid to the production of alkyl levulinates from carbohydrates of different origins (Delidovich *et al*, 2014). Ethyl levulinate (EL) is a versatile chemical with numerous potential industrial applications as oxygenated additive in fuels, flavoring and fragrance industry or as blending component in biodiesel. Generally, alkyl levulinates can be produced in good yields by direct esterification of purified levulinic acid (LA) with alcohols (Pileidis and Titirici, 2016). Such approach requires a production of LA from biomass in an aqueous environment under acid catalysis and the subsequent isolation and purification. Besides the energetic constraint strictly correlated to the recovery of LA from aqueous solution, the reaction itself is liable to produce side-products (humins) that significantly reduce the final yield and selectivity. Furfuryl alcohol and hydroxymethylfurfural (HMF) were also found to be very promising renewable-derived chemicals for obtaining EL. But also, in this case, their preliminary production and recovery is in contrast with the overall economic efficiency. In this work, a direct use of the organic fraction of municipal solid waste/food waste for the production of EL was investigated (di Bitonto *et al*, 2018). After a preliminary characterisation of food waste (FW) sample, a detailed study was conducted on the conversion of their carbohydrate component into alkyl levulinates. Through ethanolysis catalysed by combined Lewis-Brønsted acids, lipids were also converted into fatty acid ethyl esters (FAEEs, namely biodiesel), by directly valorising more than half of the starting waste.

Material and methods

Food waste origin

In this study, four different FW samples were investigated: fruit and vegetable scraps (FVS), kitchen waste (KW) and two different organic fractions of municipal solid waste (OFMSW), coming from Treviso (Italy) and Attica (Greece). KW and FVS were collected from the cafeteria of the research area of the National Research Council in Montelibretti (Rome, Italy). Samples were firstly manually chopped and then shredded by a food processor, before being stored at $-20\text{ }^{\circ}\text{C}$. Italian OFMSWs were collected from the municipal separate collection of Treviso and were mechanically sorted and shredded, 15mm cut size, before storage at $-20\text{ }^{\circ}\text{C}$. Greek OFMSW was collected at municipality level twice a week from 230 houses. Upon collection, the waste was subjected to simultaneous heat-drying at $95\text{--}98\text{ }^{\circ}\text{C}$ (treatment for 9 h) and shredding in a pilot-scale dryer/shredder, resulting in a homogeneous organic product (dried household food waste – DHFW).

Lewis-Brønsted acid ethanolysis of food waste

The esterification reaction was carried out in a stainless-steel reactor equipped with a 20 mL glass Pyrex reactor, a manometer, a magnetic stirrer and a heating jacket for the control of temperature. In a typical test, 0.5 g of FW was used with 10 mL of ethanolic solution of H_2SO_4 (1 wt%), 0.08 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 50 μL of ethyl benzene as internal standard. The stainless-steel reactor was heated at 453 K for 4 h. At the end of the reaction, the system was cooled to room temperature, and resulting solids were recovered by centrifugation. The organic mixture was filtered, weighed and analysed. In addition, the effect of water (2 g) in the ethanolysis process was also evaluated.

Results and discussion

Characterisation of food waste

The application of the analytical protocol (di Bitonto *et al*, 2018) allowed to determine the profile of carbohydrates in terms of simple free sugars (glucose, fructose and sucrose mainly), complex sugars (hemicellulose, starches and pectins), lipids, cellulose, lignin and ashes. KW was mainly composed of carbohydrates; starch represented more than half of total solids, a value considerably higher than content detected in the other samples (17% for FVS and 24–26% for OFMSWs). Hemicellulose and cellulose were mostly abundant in FVS (21% of TS), while lignin, the

bio-recalcitrant fraction, was in the range 2–13%. Lipid concentration was found to be 4–10% in all the analysed samples. In all four samples, simple carbohydrates and relatively complex sugars always represented together almost 40–50 wt% of TS. Such information shown that such types of waste can be considered as valuable feedstocks of sugars easily convertible into chemicals, specifically into EL.

Table 1. Characterisation of food waste.

	FVS	KW	OFMSW	DHFW
Total solids (TS, g/kg)	54	236	334	913
VS/TS (%)	83	95	89	92.3
TS composition (%wt)				
<i>Carbohydrates</i>	47	72	41.3	50.3
Simple carbohydrates	9	9	8	10
Cellulose	15	5	5.1	11.1
Hemicellulose	6	4	4.2	3.2
Starch	17	54	24	26
<i>Proteins</i>	15	14	15	10
<i>Lipids</i>	6.2	5.1	10	9.2
<i>Lignin</i>	13	2.2	12	6.3

Reactivity tests on food waste

Under dry and wet conditions, the catalysts were very active in the conversion of starting sugars into EL and furanic compounds without the formation of humins or other secondary products. In addition, two other very important positive aspects were revealed: the presence of acids (namely volatile fatty acids, VFAs, and lactic acid) in the starting samples, probably due to their partial fermentation, not only did not inhibit the process, but were efficiently converted into the respective ethyl esters (0.5–3 wt%). Lipids were also quantitatively converted into the respective fatty acid ethyl esters (FAEEs), even in the presence of water. Consequently, it is possible to state that through this alcoholysis, more than 50% of the starting sample could be converted into liquid fuels. In addition, almost 40% of starting sugars remain in any case present as EG, which can have applications as biosurfactants.

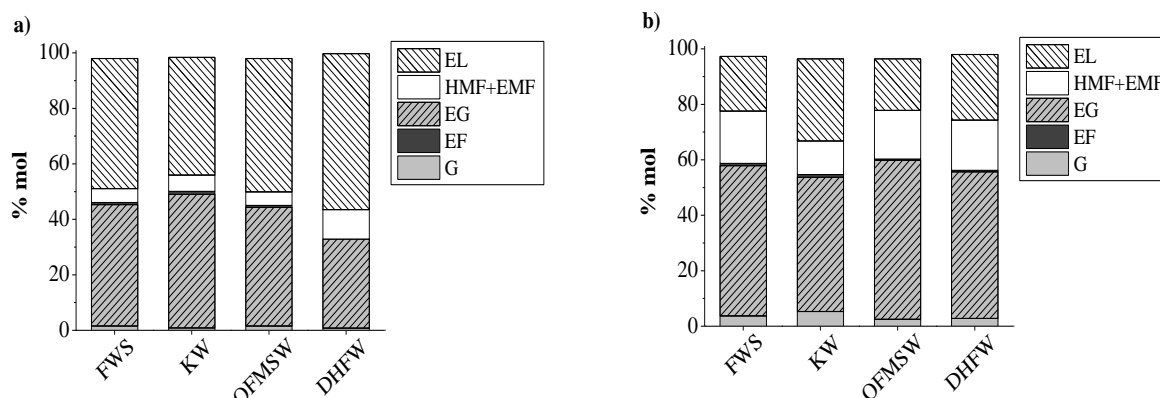


Figure 1. Ethanolysis of food waste for the synthesis of ethyl levulinate using H_2SO_4 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as catalysts. G=glucose, EG=Ethyl Glucoside, EF=Ethyl Fructoside, EMF=5-ethoxymethyl-furfural, EL=ethyl levulinate.

Conclusions

The proposed Lewis-Brønsted acid approach, based on the use of cheap and non-harmful catalysts ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2SO_4), has the potential for being a feasible treatment of food waste, capable to convert the starting feedstocks into biofuels and high-value chemicals.

References

- Delidovich I., Leonhard K., Palkovits R. Cellulose and hemicellulose valorisation: an integrated challenge of catalysis and reaction engineering. *Energy Environmental Science* 7 (2014) 2803–2830.
- di Bitonto L., Antonopoulou G., Braguglia C., Campanale C., Gallipoli A., Lyberatos G., Ntaikou I., Pastore C. Lewis-Brønsted acid catalysed ethanolysis of the organic fraction of municipal solid waste for efficient production of biofuels. *Bioresource Technology* 266 (2018) 297–305.
- Pileidis F.D., Titirici M.M. Levulinic acid biorefineries: new challenges for efficient utilization of biomass. *ChemSusChem* 9 (2016) 562–582.

Acknowledges

This work was financially supported by a PRIN 2012 project co-financed by the Italian Minister of University and Scientific Research (MIUR).