Liquid fuel from sewage sludge through direct acid ethanolysis

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Keywords: Fatty Acid Ethyl Esters; Ethyl-Levulinate; Sewage Sludge characterization; Sewage sludge Valorisation; Biofuels.
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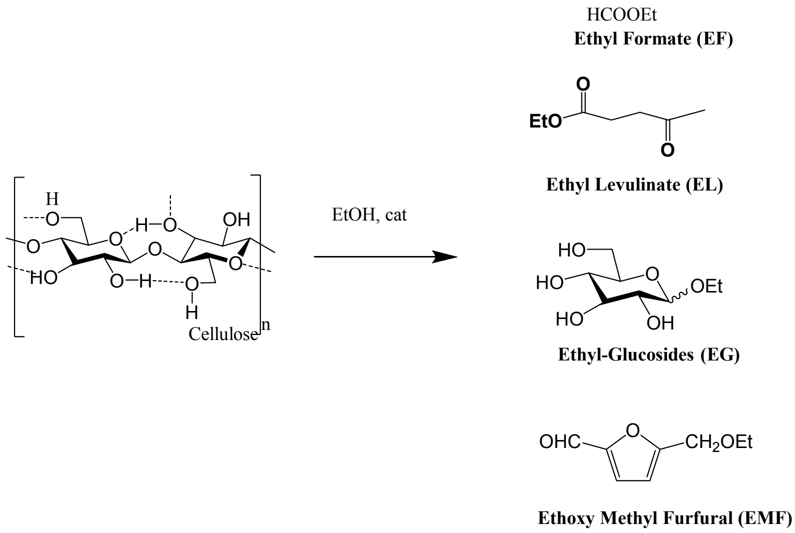
ABSTRACT

Ethanolysis of urban sewage sludge was investigated and optimised in order to simultaneously convert lipids and complex carbohydrates fractions into liquid fuels, namely Fatty Acid Ethyl Esters (FAEEs) and Ethyl-Levulinates. Several samples of sewage scum, primary, secondary and mixed sludge were up-taken from different WWTPs and well characterised in terms of lipids, hemicellulose and cellulose contents. Then, the same samples were reacted in ethanol (400-450 K) in the presence of appropriate homogeneous catalysts. After about 5 h, 99% of lipids and almost 60% of complex sugars were selectively converted into the target products. In detail, for the carbohydrates, Ethyl-Levulinate from hexoses and Furfurals from pentoses were found to be the main products. The effect of water was also studied. At the end of the process, organic products were easily recovered and purified from the alcoholic phase, whereas only very limited amount of inert solids eventually residue. This approach efficiently combines the valorisation of the starting organic fraction of sewage sludge to a final significant reduction of residual solids to be disposed of, in a very stabilised form.

INTRODUCTION

In this work, the experimental evaluation of exploitation and valorisation of urban sewage sludge through an acid ethanolysis was reported. Specifically, besides the lipid valorisation to obtain Fatty Acid Ethyl Esters (FAEEs), namely biodiesel (Pastore et al 2013, Olkiewicz et al 2014), the transformation of hemicellulose, cellulose and complex sugars was concomitantly evaluated. Ethyl-Levulinate (EL) and furfurals (Ethoxy-Methyl Furfural, EMF and Furfural, F) were identified, separated and quantified as main transformation products of complex sugars (Scheme 1).



Scheme 1. Products of reaction deriving from ethanolysis of Cellulose.

Alkyl levulinates are recently found to be conveniently used as a fuel and/or a fuel additive (Dutta et al 2012), with clear improvement of technical properties of the resulting blend. For example, on blending of 10% EL with conventional fossil diesel, more of 40% reduction in engine out smoke number was measured (Christensen et al 2011) and in the same time a significant reduction in cloud point (4–5◦C), pour point (3–4°C) and cold filter plugging point (3°C) is measured on 20% EL blend (Joshi et al 2011). So, ethanolysis of sludge actually produce a new generation of liquid fuels from an exhausted feedstock.

MATERIALS AND METHODS

All reagents, organic solvents and standards were Sigma-Aldrich pure grade reagents (99%). Sewage sludge samples were firstly characterized in terms of lipids (Pastore et al 2013) and of hemicellulose and cellulose contents (di Bitonto et al 2017), even evaluating the respective sugar profiles (hexoses and pentoses). Acid Ethanolysis reactions were carried out in a steel reactor (100 mL) capable to work under high-pressure and temperature (450 K). Final mixture was gas-chromatographically analysed using a Varian 3800 GC-FID, whereas a Perkin Elmer Clarus 500 gas-chromatograph interfaced with a Clarus 500 MS-spectrometer was used (GC–MS) for qualitative identification of different generated species.

RESULTS AND DISCUSSION

Sludge Characterization

Several samples of sewage scum and urban sewage sludge (primary, secondary and mixed) were up-taken from different WWTPs (Bari West, 500.000 PE; Barletta, 100.000 PE; Putignano, 30.000 PE) and chemically-characterised. Besides sewage scum, the most promising sludge were found to be primary ones, since they were found to have similar composition in terms of lipids (20-25%TS), proteins (22-25%TS), hemicellulose (5-6%TS) and cellulose (10-12%TS). On the other hand, secondary sludge were found to be composed by only 4-6%TS of lipids, 8-10%TS of carbohydrates and 30-35%TS of proteins. Finally, as far as composition of mixed sludge were concerned, 15, 12 and 25% of TS were lipids, carbohydrates and proteins respectively. Specific content of hexoses and pentoses were also determined for all samples.

Acid ethanolysis of Sludge

Reaction of ethanolysis was studied and operative conditions were optimised: the effect of temperature, nature and amount of catalysts, reaction time and co-presence of water were deeply investigated. While conversion of lipids into FAEEs resulted effective already working under very mild conditions (300 K, 3h, 1 atm), the valorisation and conversion of carbohydrates required harsher conditions. In Table 1, it is reported a trend of reactivity recorded by using dry samples, temperature of 450 K, reaction time of 4 h and a combined action of sulphuric acid and Aluminium Chloride as catalysts.

Table 1. Lipid and carbohydrates conversions after acid ethanolysis carried out at 450 K and 4 h. *Molar Yields of EL and EMF referred to starting hexoses. ** Molar Yield of F calculated by respect with starting pentoses.

Sludge	Lipid Conversion	Carbohydrates Conversion	Yield of EL	Yield of EMF	Yied of F
	%wt	%wt	%m*	%m*	%m**
Sewage scum	>99	65	42	10	78
Primary	>99	55-60	32	8	80
Secondary	>99	99	45	12	82
Mixed	>99	75	36	8	81

Analysis of residual solids allowed to be verified that actually most of the hemicellulose in primary sludge and of complex sugars in secondary sludge were effectively converted. While, for the specific case of cellulose contained in sewage scum, primary and mixed untreated sludge, only half of its starting content was found to be reacted, by confirming its respective inertness. In any case, even part of proteins were always solubilised, by producing a significant reduction of the residual solids.

CONCLUSIONS

An unprecedented treatment was evaluated on sewage sludge in order to couple generation of new liquid fuels and reduction of solids to manage. In fact, through this very fast process, not only most of lipids and carbohydrates were converted into valuable compounds, but even a consistent containment of final residue to be disposed of was achieved.

ACKNOWLEDGEMENTS

This study was financially supported by MIUR (ERANETMED Project WE-MET).

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