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Ethyl-Levulinate: a Flexible Bio-Fuel for Internal Combustion Engines

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Bio-fuels represent a concrete alternative to fossil fuels for land and air transport, which allow a drastic reduction of CO2 emissions and, to a lesser extent, of CO and particulate matter. Second generation bio-fuels (obtained from non-food matrices) are attracting more and more attention in these last years, especially oxygenated alcohols and esters obtained from residual biomasses.

The present study analyses the synthesis and utilisation of ethyl levulinate (EL), a versatile second generation bio-blendstock that can also be used, among other things, as fuel additive in Diesel/gasoline engines. Its synthesis is a one-step process, the direct alcoholysis of glucose-based substrates, as model sugars but also raw or waste biomasses. The process takes place in the presence of ethanol which acts as reactant/reaction medium and of an acid catalyst. In particular, an investigation of defatted cardoon ethanolysis was performed and a proper optimization of the main reaction conditions, as substrate concentration, duration, temperature, type and concentration of the acid catalyst, has been analyzed in order to improve EL yield.

The possibility of using EL as bio-blendstock in Internal Combustion Engines was analyzed as well utilizing a gasoline engine. Results have shown that EL can be used as a fuel additive blended at 10% by volume, without significant changes in engine performance, with beneficial effects on the reduction of CO and HC emissions.

* 1. Introduction

Bio-fuels represent a concrete alternative to fossil fuels for land and air transport, which allow a drastic reduction of CO2 emissions and, to a lesser extent, of CO and particulate matter (Azad, 2019). In the last years, there has been an ever-increasing interest on the development of second generation bio-fuels (obtained from non-food matrices), as evidenced by the large scientific literature produced (Alalwan et al., 2019; Bae et al. 2017; Mwangi et al., 2015; Kumar et al., 2021). Among these ones, oxygenated alcohols and esters, obtained from residual biomasses, appear extremely promising (Ashokkumar et al., 2022; Çelebia et al., 2019; Koivisto et al., 2015; Lei et al., 2016).

The present study analyses the synthesis and utilisation of ethyl levulinate (EL), a versatile second generation bio-blendstock that can be used in Diesel/gasoline engines, but also a strategic intermediate for the obtainment of green solvents, polymers, surfactants, plasticizers, and pharmaceuticals (Shan et al., 2023). EL can be obtained from esterification of pure levulinic acid or adopting the direct one-step ethanolysis of C6 model sugars and also of solid biomasses. This last approach appears particularly attractive when raw or waste biomasses, having a low or negative value (as bamboo, wood chips, wheat straw) are adopted as starting materials (Ahmad et al., 2016). The process takes place in the presence of ethanol which acts as reactant/reaction medium and of an acid catalyst which is necessary for the depolymerization of the polysaccharides and the successive alcholysis of obtained the monosaccharide intermediates to EL (Antonetti et al., 2020).

The one step ethanolysis in principle is a very simple process but for the process to be economically viable it is crucial that the concentration of the homogeneous acid catalyst be as low as possible to limit corrosion problems. Moreover, a significant drawback must be considered: the acid catalyst favors the formation of a solid by-product which contains the eventual unconverted lignin fraction and also the polymers deriving from the condensation of C5 and C6 sugars. Therefore, in order to improve EL yield, due to the different composition of the starting materials, the direct ethanolysis needs a proper optimization of the main reaction conditions as substrate and acid catalyst concentration, duration and temperature. On the other hand, the concentration of the substrate (biomass or sugars) must be maximized by adopting a high-gravity approach, in order to simplify the downstream and achieve high productivity towards the alkyl levulinate (Antonetti et al., 2020).

In the present study, an investigation on defatted cardoon ethanolysis was performed. Defatted cardoon represents a waste biomass, being the residue that remains after the seeds are removed to obtain the valuable edible oil, which in turn is used for the synthesis of bipolymers, bioplasticizers, antioxidants and antimicrobial agents and even of biodiesel (Khaldi et al., 2021).

The feasibility of using EL as bio-blendstock in Diesel engines has been verified in a previous research (Frigo et al., 2023). EL was blended with Diesel fuel up to 25% by volume without significant changes in engine performance, moderately increasing the fuel specific consumption (owing to EL low LHV with respect to Diesel fuel), NOx and HC emissions but significantly reducing CO and soot emissions, this last by over 40%. Starting from EL dilution greater than 25%, the excessive combustion delay, due to EL low cetane number (CN), negatively influenced the Diesel engine performance. This behavior was observed in other studies (Wang et al., 2012; Lei et al., 2016; Ahmad et al., 2022), also evidencing how the oxygen content in the EL molecule is the main parameter affecting combustion and emissions.

The compatibility of EL with gasoline fuel has been verified in other scientific study (Ghosh et al., 2028). The present study shows for the first time the experimental results obtained feeding a gasoline engine with a mixture of a commercial gasoline fuel and EL at 10% by volume. The results confirmed that even in gasoline engines the use of EL does not alter the engine performance as well the NOx emissions, but with beneficial effects on the reduction of CO and HC emissions.

* 1. Materials and methods

Defatted cardoon was provided by the center CIRIAF (University of Perugia) and its main components, analyzed as previously reported (Raspolli Galletti et al., 2021), resulted: cellulose 37.6 wt%, hemicellulose: 16.8 wt%, lignin 17.5 wt%, ash: 7.2 wt.%, extractives: 5.6 wt.%.

Sulfuric acid (H2SO4, 95 wt%), ethanol (EtOH, 99.8%), n-dodecane (99%) and ethyl levulinate (EL, 98%) were purchased from Sigma-Aldrich and used as-received.

The direct ethanolysis reaction was performed in an electrically heated 600 mL Parr zirconium-made ﬁxed-head autoclave, equipped with a P.I.D. controller (4848). Ethanol, the acid catalyst H2SO4, the substrate, *n*-dodecane as the Gas Chromatography (GC) internal standard, were introduced in the autoclave under nitrogen atmosphere. The reactor was then pressurized with nitrogen up to 30 bar. The reaction mixture was stirred during the selected reaction time then, at the end of the reaction, the autoclave was quickly cooled and the recovered reaction mixture was filtered. The liquid and solid products determination was performed as previously reported (Raspolli Galletti et al., 2021).

Molar yields of EL and mass yield of the solid residue were calculated according to following equations:

* EL yield (mol%) = [(molEL/mol C6 unitsbiomass)] × 100
* Solid yield (wt%) = [(gsolid residue/gbiomass)] × 100
  1. Results and discussion
     1. **Ethyl Levulinate synthesis**

The ethanolysis of defatted cardoon was studied adopting a preliminar One-Factor-At-a-Time (OFAT) investigation adopting two substrate loadings: 5 and 14 wt.%. The obtained results are reported in Table 1. When the lower loading was adopted the increase of the temperature from 140 to 180 °C evidenced a progressive increase of the EL yield (runs 1-3). At the lowest temperature a significant amount of solid residue is recovered at the end of the reaction, due to a modest extent of biomass deconstruction/depolymerisation. The gradual increase in yield with increasing temperature is accompanied by the decrease in the amount of solid residue. The increase of the reaction time from 3 to 5 h allowed to reach an interesting EL yield of about 40 mol.% (compare run 4 with run 3), but also the amount of the solid residue was enhanced, due to the formation of unsoluble huminic products. When the cardoon loading was increased to 14 wt.% in a high gravity perspective, the EL yield decreased respect to the corresponding run at lower loading (compare run 3 with run 5), although the biomass solubilisation was analogous. This result was related to the incomplete conversion of soluble intermediates to give EL, probably due to the increased amount of basic ash introduced, which caused a decrease of the acid sites available for the complete alcoholysis to EL. Therefore, an increase of the acid concentration and of the reaction time allowed to raise the EL yield (compare run 6 and 7 with run 5). On the other hand, the enhancement of the temperature up to 190 °C played a negative effect on the production of the target ester, the formation of huminic solid derivatives being significantly increased.

Table 1: Defatted cardoon ethanolysis

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *Run* | *Cardoon loading*  *(wt.%)* | *H2SO4*  *(wt. %)* | *T*  *(°C)* | *Time*  *(h)* | *EL yield*  *(wt. %)* | *Solid yield*  *(wt. %)* |
| 1 | 5 | 2 | 140 | 3 | 6.2 | 45.6 |
| 2  3 | 5  5 | 2  2 | 160  180 | 3  3 | 18.9  32.4 | 29.2  22.7 |
| 4 | 5 | 2 | 180 | 5 | 39,8 | 31.4 |
| 5  6  7  8 | 14  14  14  14 | 2  3  3  3 | 180  180  180  190 | 3  3  5  5 | 28.7  32.9  35.7  31.6 | 23.5  32.7  34.9  38.1 |

These preliminary results well evidence that the implementation of real biomass ethanolysis is significantly influenced by the synergism of the main reaction parameters, thus suggesting for the future research to move beyond the OFAT approach by adopting a multivariate approach based on the Response Surface Methodology.

***3.2 Engine testing***

The possibility of using EL as fuel additive was then verified utilizing a four-stroke, one-liter gasoline engine, whose main characteristics are shown in Table 2. A mixtures have been prepared blending EL with a commercial gasoline fuel at 10 vol%, which represent a realistic dilution for commercial fuels (at present, transport fuels contain 5% by volume of bio-ethanol, as regard gasoline, and 7% of bio-Diesel, as regards Diesel fuels). Table 3 compares EL main properties with those of a commercial gasoline fuel.

Engines performance were measured by coupling the Diesel and gasoline engines with a Borghi&Saveri eddy current brake. An AVL gravimetric fuel balance was used for the measurement of the fuel consumption, while pollutant emissions were measured through an AVL DiTest Gas1000. An exhaust gas K-type thermocouple was located at the engines exhaust to verify the steady state conditions reach. After stabilization in each operating condition, data were collected and analysed. Figure 1 shows the engine on the test bench.

Table 2: Experimental engine characteristics

|  |  |
| --- | --- |
| *Data* | *Gasoline engine* |
| Engine maker | Volkswagen |
| Number of cylinders | 3 |
| Cooling system | Liquid |
| Displacement [cm3] | 999 |
| Bore [mm] | 74.5 |
| Stroke [mm] | 76.4 |
| Compression ratio | 10.5 |
| Max rotational speed [rpm] | 6500 |
| Max Power [kW] | 44 |
| Max Torque [Nm] | 95 |

The mixture at 10 vol.% of EL was tested at full load and different rpm. Despite the low LHV, the utilization of EL in gasoline has not presented particular problems, mainly thanks to the high ON of EL. The experimental results are shown in Figure 2 regarding the torque and power values, while the HC and CO emissions are shown in Figure 3, always at full load and at different rpm. NOx emissions remained more or less on the same order as those obtained by fuelling the engine with only commercial gasoline. Owing to EL low LHV with respect to gasoline fuel, a slight decrease in engine power is noted while the specific fuel consumption [g/kWh] has moderately increased.

Table 3: Fuels properties

|  |  |  |
| --- | --- | --- |
| *Property* | *EL* | *gasoline* |
| Boling Point (°C) | 206 | 80-100 |
| O2wt% | 33 | NA |
| Density (g/L at 20 °C) | 1010 | 750 |
| Cetane Number (CN) | < 20 | NA |
| Octane Number (ON) | >97 | 95 |
| Lower Heating Value (MJ/kg) | 25 | 45 |
| Kinematic viscosity (mm2/s at 20 °C) | 2.14 | 0.9 |

The use of EL 10% has beneficial effects on polluting emissions, as shown in Figure 3, allowing a decrease in HC emissions which, between 200 and 3000 rpm, reaches 40%, while CO emissions are reduced by up to 30% at 3000 rpm. This is mainly due to the favourable H/C ratio in the EL molecule, compared to gasoline fuel, and also to the presence of oxygen in the molecule which enhances the carbon complete oxidation during combustion. Overall, as previously verified for the Diesel engine, even in the gasoline engine the use of mixtures with 10% EL does not fundamentally alter engine performance, confirming that their use is perfectly compatible with the characteristics of modern engines.



*Figure 1: The Volkswagen gasoline engine on the test bench.*

*Figure 2: Comparison of engine power and torque at full load and different rpm.*

*Figure 3: Comparison of HC and CO emissions at full load and different rpm.*

* 1. Conclusions

In the present study the production and use of a second generation bio-fuel, Ethyl Levulinate, obtained from defatted cardoon ethanolysis has been analysed. The OFAT optimization of the reaction parameters adopting diluted H2SO4 as catalyst allowed to reach molar yields to EL of about 35 mol.%, also adopting high substrate loading (14 wt.%).

The feasibility of using EL as bio-blendstock in a gasoline Internal Combustion Engines was analyzed as well. The experimental campaign, conducted utilizing a mixture of commercial gasoline fuels and EL at 10 vol.%, confirmed that EL can be utilized as fuel additive without any particular problem. The results show that the utilization of mixture with EL does not alter engine performance, compared to those obtained utilizing only gasoline, with beneficial effects on the reduction of pollutant emissions which reaches 40% considering HC, while for CO it reaches almost 30%.

Preliminary results of the ongoing research, which will be published in a next paper, have confirmed that the maximum percentage of dilution of EL with commercial gasoline fuel goes well beyond 10%, therefore opening up new perspectives on the use of EL as bio-fuel, even as such.

Nomenclature

CN – cetane number

CO – carbon monoxide

EL – Ethyl Levulinate

HC – unburned hydrocarbons

LHV – lower heating value

NOx – nitrogen oxides

OFAT - One-Factor-At-a-Time

ON – octane number

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