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Utilisation of Ethyl Levulinate as Diesel Fuel Additive

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Abstract. The world is going through a radical phase of energy conversion, due to both environmental and socio-economic factors, which will lead to a progressive transition from fossil to renewable energy sources. As regards the light land transport sector (cars), the abandonment of propulsion systems based on the use of internal combustion engines (ICEs) in favour of electrification seems the preferred solution. On the contrary, for heavy land (trucks and trains), marine and air transport sectors the path to follow is not yet clear.

A possible alternative to fossil fuels is certainly represented by bio-fuels, which should allow a drastic reduction of CO₂ emissions and, to a lesser extent, of CO and particulate matter. The use of bio-fuels does not involve a drastic change in the systems of distribution and use of energy, as the existing infrastructures can remain unchanged. In particular, second generation bio-fuels (obtained from non-food matrices) are attracting more and more attention and, among these ones, oxygenated alcohols obtained from residual lignocellulosic biomasses appear extremely promising for the use in diesel engine.

The present study analyses the utilisation of ethyl levulinate (EL), a versatile second generation bio-fuel that can be used in Diesel/gasoline engines. EL can be conveniently obtained from the sustainable one-pot acid-catalyzed conversion of waste lignocellulosic feedstocks, employing bioethanol as the solvent/reagent.

EL has been tested in a small DI Diesel engine, blended up to 25% by volume with a commercial Diesel fuel, without significative changes in engine performance, moderately increasing NO_x and HC emissions but significantly lowering soot and CO emissions by more than 50%.

1. Introduction

The world is going through a radical phase of energy transition, due to both environmental and socio-economic factors, which will lead to a progressive transition from fossil to renewable energy sources. As regards the light land transport sector (cars), the abandonment of propulsion systems based on the use of internal combustion engines (ICEs) in favour of electrification (assuming that electricity comes from renewable sources) seems the preferred solution. On the contrary, heavy land (trucks and trains), marine and air transport sectors have not chosen yet what path must be taken. For these last categories, on-board energy storage through batteries still appears practically inappropriate, due to their high costs and low energy/weight ratio compared to liquid fuels, even if lithium batteries have increased rapidly in these last years, reaching an energy density up to 1.6 MJ/kg [1, 2].

A possible alternative to fossil fuels is certainly represented by bio-fuels, which should allow a drastic reduction of CO₂ emissions and, to a lesser extent, of CO and particulate matter [3]. At the same time, this choice will make the countries being poor in energy independent from the supply of oil and natural



gas by promoting the agricultural-forestry activities of the territory, with considerable economic advantages [4, 5]. Moreover, the use of bio-fuels does not involve a drastic change in the systems of distribution and use of energy, as the existing infrastructures can remain unchanged.

In the last years, there has been an ever-increasing interest on the development of second generation bio-fuels (obtained from non-food matrices) and their use in ICEs, as evidenced by the large scientific literature produced [6-9]. Among these ones, oxygenated alcohols and esters obtained from residual lignocellulosic biomasses appear extremely promising for the use in diesel engine [10-13]. In this context, different strategies can be adopted for bio-fuel synthesis, but it is important to fully respect the criteria of environmental and economic sustainability.

Alkyl levulinates represent an outstanding class of biomass-derived chemicals which are recently attracting increasing attention due to their renewable origin and their extremely large fields of application. In particular ethyl levulinate (EL) is an efficient fuel additive but can also be employed as intermediate for the synthesis of high-added value bio-surfactants, fragrances, green solvents, food additives, with an estimated marked growth rate of 3.6% [14, 15].

The present study analyses the utilisation of ethyl levulinate (EL), a versatile second generation bio-blendstock that can be used in Diesel/gasoline engines. EL can be conveniently obtained from the sustainable one-pot acid-catalyzed conversion of waste lignocellulosic feedstocks, employing bioethanol as the solvent/reagent. In particular, thick juice, a raw intermediate sucrose-rich stream in sugar factory, chitosan from shrimp waste and a cellulosic waste from paper mill were tested. The performances obtained with these waste biomasses have been optimized, achieving EL yields up to 45 mol%, adopting diluted sulphuric acid as catalyst. The optimization was carried out also with the aim of minimizing the alcohol etherification to diethyl ether and the carbonization to solid char.

An experimental campaign was conducted using a small DI Diesel engine. Despite its low cetane number (CN), experimental results have shown that EL can be used as a Diesel fuel additive, blended up to 25% by volume, without significant changes in engine performance, moderately increasing NO_x and HC emissions but significantly reducing soot and CO emissions by over 50%.

2. EL Synthesis

EL can be obtained from the direct ethanolysis not only of model sugars but also of raw or waste biomasses. This last route appears particularly attractive due to the low or negative value of the starting materials [16]. Therefore, in this research four very different strategic substrates were investigated: a) inulin, a D-fructose polymer with D-glucose terminal units obtained from tuberous roots, b) thick juice, a raw sucrose-rich stream in sugar factory, c) a cellulose-rich waste from tissue paper mill, and d) chitin, a nitrogen-containing polysaccharide obtained from shrimp waste.

The alcoholysis reaction requires the presence of an acid catalyst, while the alcohol acts as reagent and reaction medium [17]. The very simple direct ethanolysis can present a significant drawback: the formation of a solid residue when recalcitrant substrates are used and higher temperature and concentration of acid are necessary, due to sugar condensation and also to the eventual presence of lignin. Moreover, under high temperature and acidity, the formation of diethyl ether (DEE) causes the undesired ethanol loss. The EL yield can be improved by performing a proper optimization of the main reaction conditions as duration, temperature, type and concentration of the acid catalyst, substrate concentration, therefore in the present study, owing to the different composition and reactivity of the tested starting biomasses, all the aforementioned parameters were analyzed and properly tuned.

The ethanolysis reaction was performed adopting an electrically heated 600 mL Parr zirconium-made fixed-head autoclave, equipped with a P.I.D. controller (4848). The proper amounts of substrate, *n*-dodecane as the Gas Chromatography (GC) internal standard, ethanol and the acid catalyst H₂SO₄ were introduced in the autoclave under nitrogen atmosphere, then it was pressurized with nitrogen up to 30 bar and the reaction mixture was maintained under stirring during the reaction time. At the end of each reaction, the autoclave was quickly cooled at room temperature by blown air, then the reaction mixture was filtered and the recovered liquid was diluted by acetone before the GC analysis, whereas the solid residue was washed by water and then dried at 105 °C for 24 h. GC analysis was performed by adopting

a DANI GC1000 DPC gas-cromatograph equipped with a HP-PONA column (20 m x 0,2 mm x 0,5 μ m).

Substrate and catalyst loadings have been defined according to the equations below:

$$\text{- Substrate loading (wt\%)} = [g_{\text{substrate}} / (g_{\text{substrate}} + g_{\text{catalyst}} + g_{\text{EtOH}})] \times 100$$

$$\text{- H}_2\text{SO}_4 \text{ loading (wt\%)} = [g_{\text{catalyst}} / (g_{\text{substrate}} + g_{\text{catalyst}} + g_{\text{EtOH}})] \times 100$$

Mass yields of EL, DEE and solid residue were calculated according to following equations:

$$\text{- EL yield (wt\%)} = [(g_{\text{EL}} / g_{\text{starting substrate}})] \times 100$$

$$\text{- Solid yield (wt\%)} = [(g_{\text{solid residue}} / g_{\text{substrate}})] \times 100$$

The results obtained with the different substrates under the optimized reaction conditions are reported in Table 1.

Table 1 – EL yield under optimized reaction conditions

<i>Substrate</i> <i>wt %</i>	<i>H₂SO₄</i> <i>wt %</i>	<i>T</i> <i>°C</i>	<i>Time</i> <i>h</i>	<i>EL yield</i> <i>wt %</i>	<i>Solid yield</i> <i>wt %</i>
Inulin 8	1	130	3	59.1	4.9
Thick Juice 10	2	120	3	39.4	1.9
Paper mill waste 14	1.2	190	2	31.3	21.2
Chitin 5	3	180	5	21.1	23.2

The above results evidence that interesting yields can be obtained in the direct conversion of raw biomasses, also starting from recalcitrant ones as paper mill waste and, in particular, chitin. The downstream rectification of the reaction mixture allows the separation of pure EL and of the unreacted EtOH to be recycled to the reaction step.

The obtained EL was then tested as additive for Diesel fuels. Several mixtures have been prepared blending EL with a commercial Diesel fuel, starting from 10 vol% up to 25 vol% with steps of 5 vol%. The maximum percentage of 25 vol% was determined after having performed preliminary engine tests which showed that mixtures up to 30 vol% led to a strong engine combustion instability which can be attributed to the low CN of EL. Table 2 compares EL main properties with those of a commercial Diesel fuel.

3. Experimental engine setup

The effectiveness of the biofuel obtained was verified utilising mixtures of EL and Diesel fuel in a small direct injection Diesel engine, a Lombardini-Kohler model 9LD 625/2 (Figure 1), whose main characteristics are shown in Table 3. Performance was analysed by coupling the Diesel engine with a Borghi & Saveri eddy current brake. An AVL gravimetric fuel balance was used for the online measure of the fuel consumption, while pollutant emissions and particulate matter were measured through an AVL DiTest Gas1000 and an AVL smoke meter (model 415 S), respectively. A Kistler pressure sensor (model 6052/C) has been suitably positioned on the cylinder head for the acquisition of the indicated cycle and the analysis of engine combustion, together with an AVL encoder and an AVL Indimodul data acquisition system (model 622). An exhaust gas K-type thermocouple was located at the engine exhaust to verify the steady state conditions reach. After stabilization in each operating condition, data were collected and analysed.

Table 2 – EL properties

<i>Properties</i>	<i>EL</i>	<i>Diesel</i>
Boiling point (°C)	206	180-360
O ₂ wt %	33	0
Density (g/L at 20 °C)	1010	837
CN (<i>Cetane Number</i>)	<20	50
LHV (<i>Lower Heating Value</i>) MJ/Kg	25	43
Kinematic viscosity (mm ² /s a 20° C)	2,14	4,27



Figure 1 - Lombardini-Kohler 9LD 625/2 on the test bench

Table 3 - Experimental engine characteristics

<i>Engine type</i>	Lombardini 9LD 625/2
<i>Number of cylinders</i>	2
<i>Cooling system</i>	Forced air
<i>Displacement [cm³]</i>	1248
<i>Bore [mm]</i>	95
<i>Stroke [mm]</i>	88
<i>Compression ratio</i>	17.5:1
<i>Max rotational speed [rpm]</i>	3000
<i>Power @ 3000 rpm [kW]</i>	21
<i>Max Torque @ 2200 rpm [Nm]</i>	73
<i>Fuel injection system</i>	Direct-Mechanic

4. Experimental results

A first experimental campaign has been carried out with several percentages of EL mixed with a commercial Diesel fuel, from 10 to 25 vol% with steps of 5 vol%. Engine performance concerning power, brake thermal efficiency (BTE) and main pollutant emissions, at full load and different engine speed, are reported in Figures 2, 3, 4, 5, 6 and 7 and compared with the utilisation of 100 % Diesel fuel. Injection timing was not changed along the experimentation.

As reported in Figure 2, the use of different diesel blendstocks does not significantly affect the engine performance. The mixtures tested led to slightly power decrease when increasing the volumetric percentage of EL in the blendstock: fuel volumetric flow is constant, so the little loss of power can be explained by the reduced LHV of test mixtures with respect to the commercial Diesel fuel. Also the BTE is not particularly influenced by the mixtures, with a slight increase with the utilisation of EL due to the better combustion characteristics guaranteed by the mixtures (lower kinematic viscosity and boiling point with respect to Diesel fuel which enhance spray atomisation and mixing process), except for the 25% dilution where instead the excessive combustion delay, due to the low CN of the EL, negatively influences this behaviour.

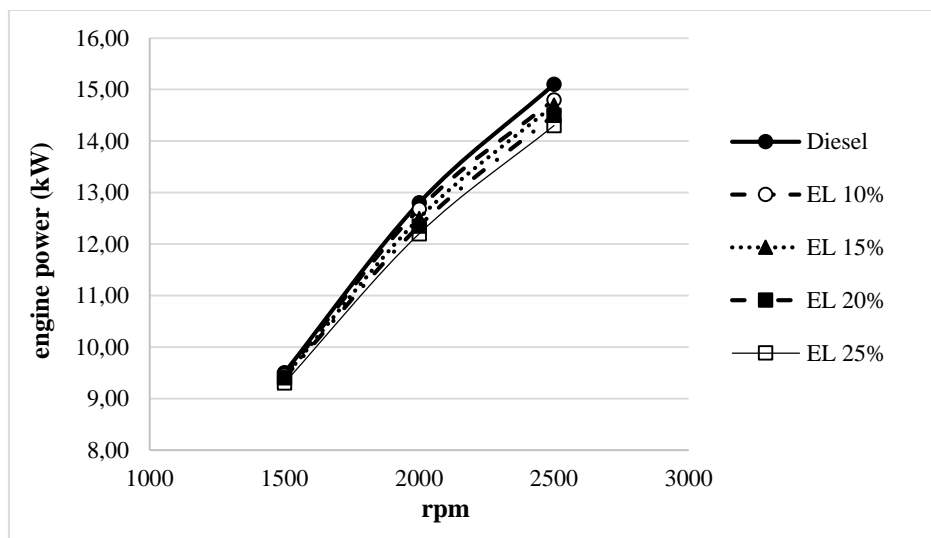


Figure 2 - Engine power utilising the EL-Diesel fuel blends

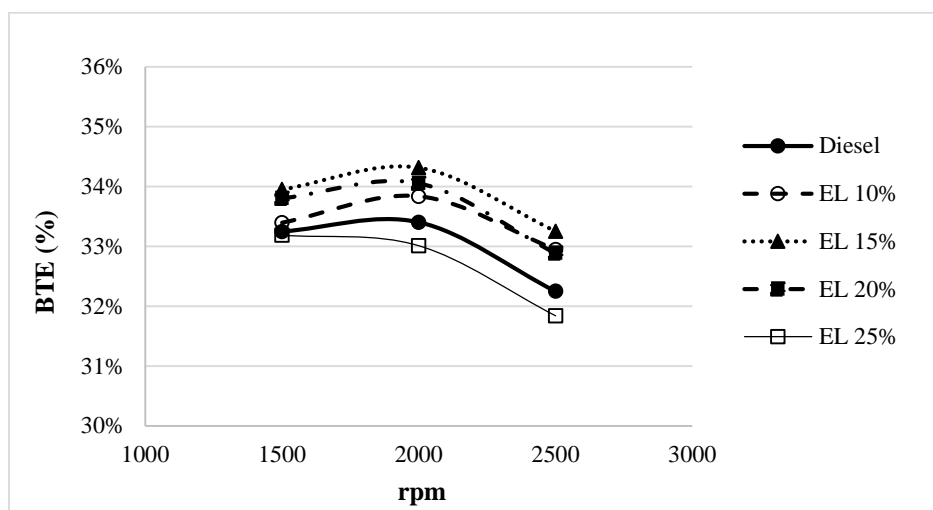


Figure 3 - Engine BTE utilising the EL-Diesel fuel blends

Figure 4 shows that CO emissions, with the utilisation of EL blends, are drastically decreased, with better values at higher volumetric concentrations of EL. This behaviour can be explained considering the higher H/C ratio in the EL molecule, compared to Diesel fuel, and also to the presence of oxygen in the molecule which enhances the carbon complete oxidation during combustion [18].

Figure 5 shows that HC emissions follow a different trend with an evident increase especially utilising the mixtures with the higher volumetric concentration of EL. This behaviour can be addressed to the lower CN of EL which delays the ignition (observable in Figure 8 which reports the in-cylinder pressure traces at 2000 rpm varying the percentage of EL into the mixture) and leaves less time for hydrocarbons complete oxidation [19]. However, this factor alone does not explain the marked increase in HC emissions and it is the opinion of the authors that, in addition to the variation in CN, other physical/chemical mechanisms are involved in HC formation, such as the different boiling and flash point temperature of EL, with respect to Diesel fuel, which could influence HC oxidation rate. Last but not least, this behaviour can be influenced by the characteristics of the gas analyser which is not calibrated for this kind of oxygenated alcohols.

NOx emissions (Figure 6) show a moderate increase in respect to Diesel fuel, with smaller differences between one component and the other, also at higher EL volumetric concentrations, thus indicating that the maximum combustion temperature moderately increases with their utilization. Also this can be addressed to the lower CN of EL which delays the ignition and thus leads to an increase in fuel mass involved during the first phase of the combustion process (the injection timing is fixed with respect to crank angle position), which can be approximated to a quasi-constant volume combustion, with higher peak of the in-cylinder pressure (see also Figure 8) and temperature. In addition, the fuel bonded oxygen, which characterizes the oxygenated alcohol, increases the local oxygen concentration thus promoting NOx formation [18].

Finally, a drastic decrease of soot emissions was observed (Figure 7), with a reduction of more than 50%. Lower carbon content of the fuels reduces the carbon availability for soot formation and the additives oxygen bonds promote the oxidation processes. Moreover, the reduced boiling point of the oxygenated mixtures improves not only droplets evaporation, but also leads to a sort of “droplet explosion” when the fuel is sprayed in a hot ambient [20, 21], promoting fuel atomization and mixing, thus enhancing the combustion completion of soot particles.

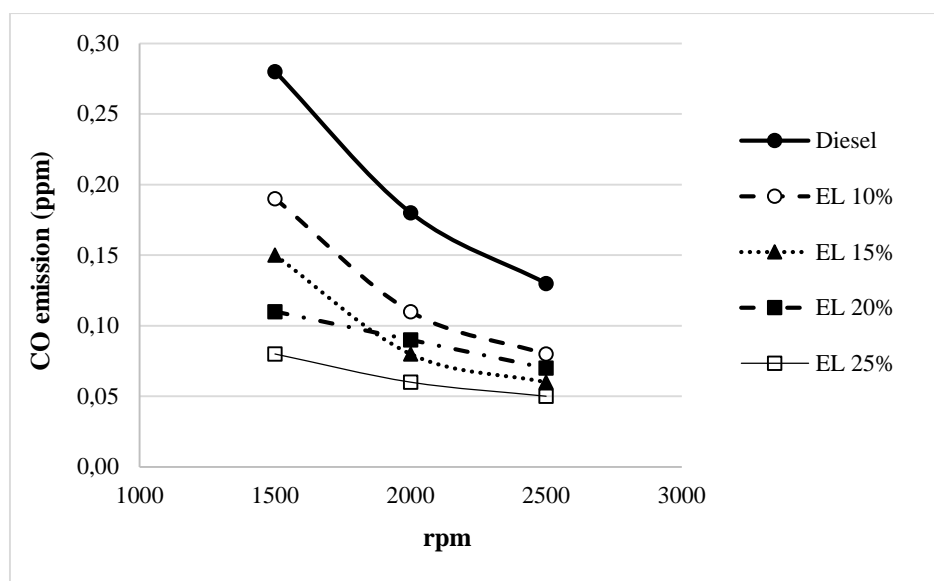


Figure 4 - Engine CO emissions utilising the EL-Diesel fuel blends

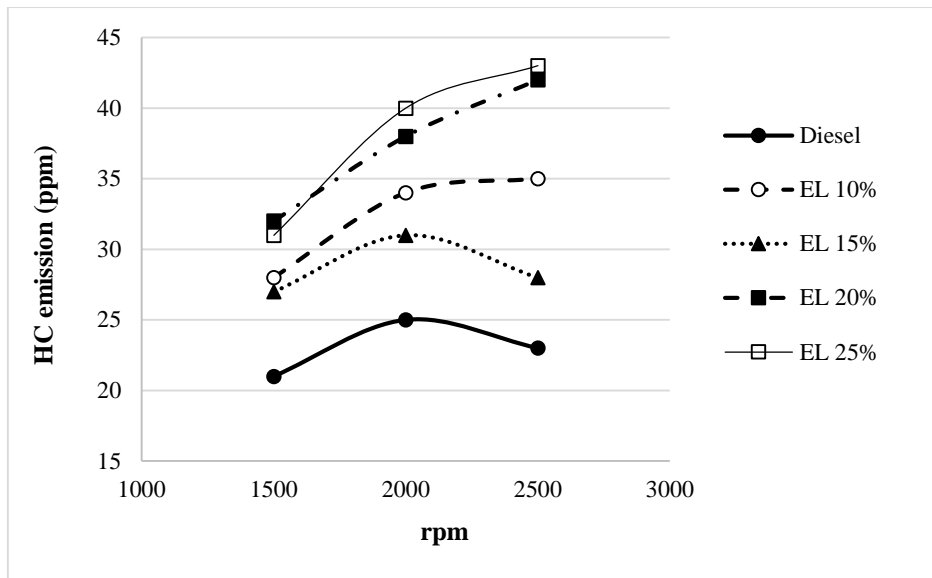


Figure 5 - Engine HC emissions utilising the EL-Diesel fuel blends

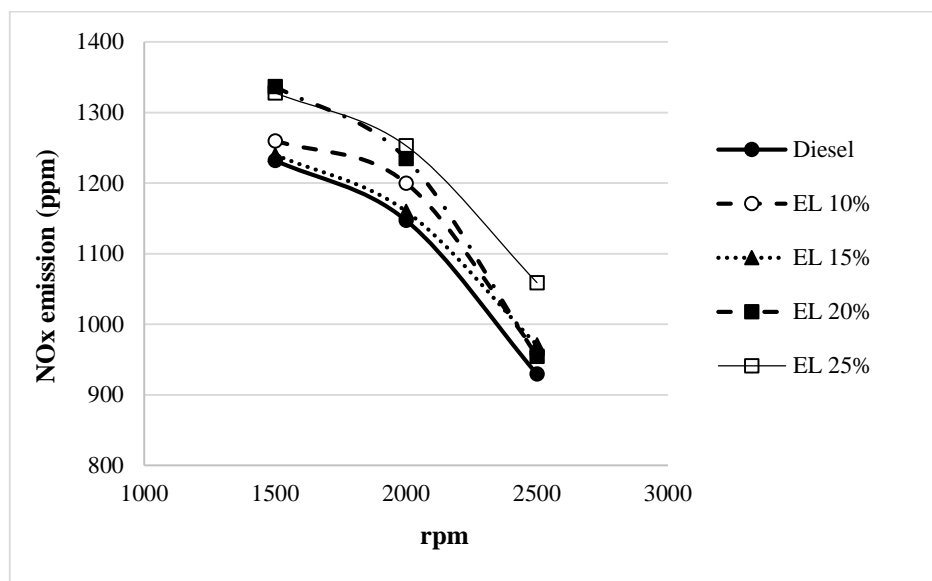


Figure 6 - Engine NOx emissions utilising the EL-Diesel fuel blends

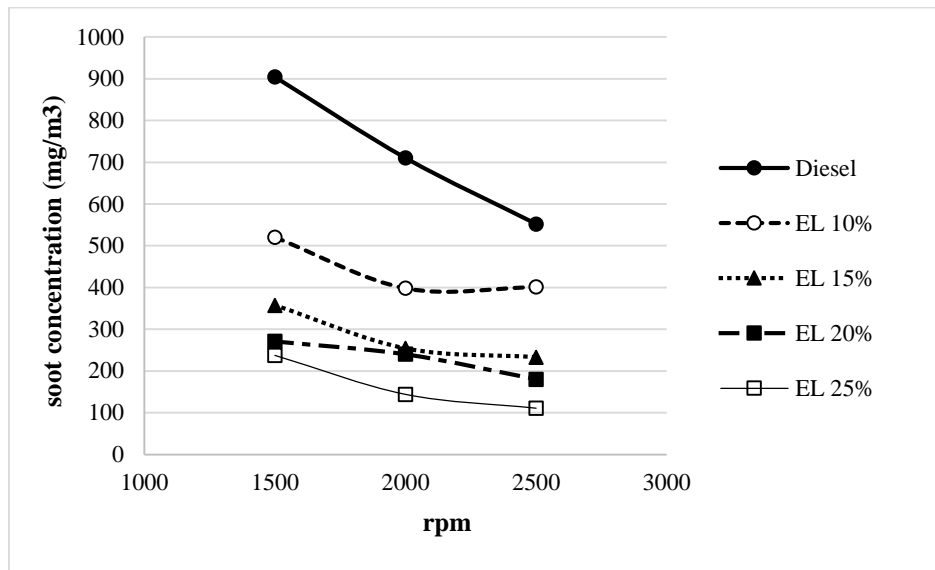


Figure 7 - Engine soot emissions utilising the EL-Diesel fuel blends

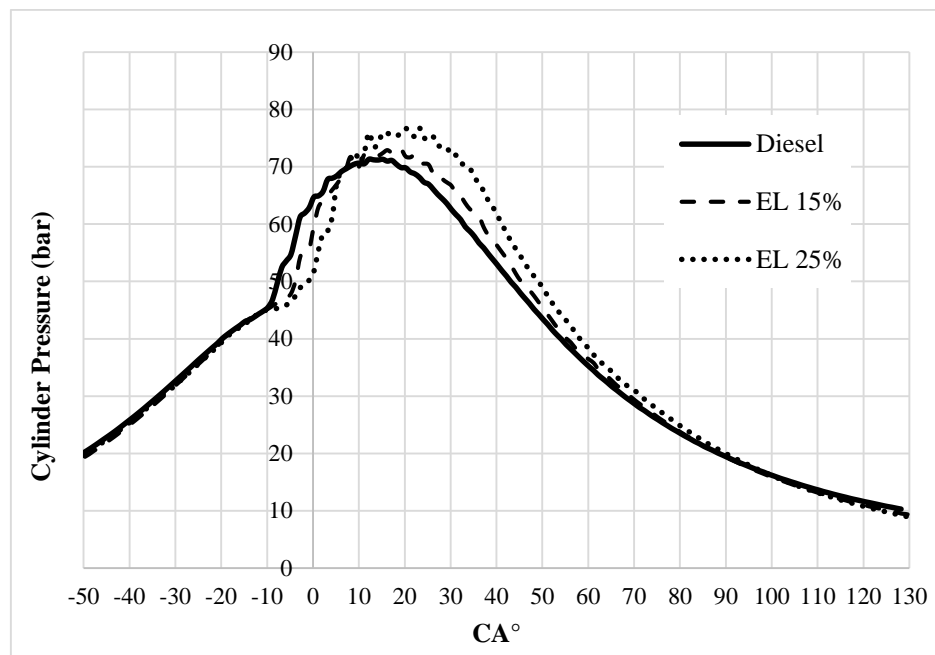


Figure 8 – In-cylinder pressure traces at 2000 rpm utilising the EL-Diesel fuel blends

5. Conclusions

The present study analyses the utilisation of ethyl levulinate (EL) as fuel additive for Diesel engines. EL is a versatile second generation bio-blendstock and can be conveniently obtained from the sustainable one-pot acid-catalyzed conversion of waste lignocellulosic feedstocks, employing bioethanol as the solvent/reagent. The performance obtained with this waste biomass have been optimized, achieving EL yields up to 45 mol%, adopting diluted sulphuric acid as catalyst. The optimization was carried out also with the aim of minimizing the alcohol etherification to diethyl ether and the carbonization to solid char.

After analysing the synthesis process, the effectiveness of EL as Diesel fuel additive was verified on a small DI Diesel engine. Despite its low cetane number (CN), experimental results have shown that EL

can be used as a Diesel fuel additive, blended up to 25% by volume, without significant changes in engine performance, increasing HC and, to a lesser extent, NO_x emissions but significantly reducing soot and CO emissions by more than 50%.

Besides the absolute values of the results shown, it is important to underline again that these second-generation biofuels, in particular oxygenated alcohols, are not only feasible from a production point of view but also effective in reducing emissions from existing diesel engines, in particular concerning CO, CO₂ and particulates.

This research is part of an even more ambitious goal, aimed at the development of last generation oxygenated bio-fuels obtained from waste lignocellulosic matrices.

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