Biomass based oil and hydrogen co-combustion in the compression ignition engine

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Abstract. Paper presents results from investigation focused on combustion progress of biomass based oil assisted with hydrogen in the internal combustion compression ignition (CI) engine. Hydrogen was added at amounts in the range from 0 to 40% by energy. The main target of this analysis was to determine impact of hydrogen on the following: combustion phases, smoke opacity and toxic emissions in the compression ignition engine. Literature review shows hydrogen can cause significant changes in combustion process even if it is added in small amounts. In this manuscript, investigation was carried out on a test bench consisted of a single cylinder compression ignition engine with common rail injection system. Hydrogen was injected into the intake manifold, where it created homogeneous mixture with air. Tests were performed at both fixed and optimal injection timings at full engine load. Results from experiments show that increasing amounts of hydrogen into the engine contribute to shorten ignition delay time that also affect main combustion phase. Additionally, it implicates heat release rate and toxic emissions (THC, CO, NOₓ). Moreover, decrease in smoke (mainly soot) in the exhaust gases was observed with increase of hydrogen amounts to the engine.

1. Introduction

All types of transport (land, sea and air) contributes the 8.7 Gt of carbon dioxide (CO₂) to the greenhouse effect, while the road transport contributes most to this amount - its CO₂ emissions are 5.8 Gt, i.e. about 67% in 2015 [1] and the 68% increase since 1990 was led by the road sector. It threatens the sustainable development of the whole world and the future of mankind.

The United Nations and the EU adopted a number of legal rulings, which set the legal basis to take care of the sharpening trend in climate change. At the International Climate Conference in Paris, in December 2015, 195 countries adopted the universal global climate agreement and sets the action plan to put the world on track to avoid dangerous climate change. Governments agreed on a long-term goal of keeping the increase in global average temperature below 2°C above pre-industrial levels and to aim to limit of the increase to 1.5°C, since this would significantly impact the climate change.

EC took the commitment up to 2050 produce by 80 – 95% less of emissions compared to 1990. It is easier to achieve lower emission levels in other sectors of the economy. However, the major challenge of transport which still increasing its emissions, must reduce its emissions on 60% by 2050 in compare
to 1990. On March 28, 2011 EC adopted the European Transport Area Development Plan - the White Paper with review of the situation of the European automotive industry. As the automotive industry represents a significant part of the EU economy, an action plan is needed to help the car industry tackle these challenges [1].

After hundred years the biodiesel and other biofuels were defined again as the desirable, renewable and sustainable energy source. However nowadays an interest to use the biofuel is related not with exploitation of colonies but with an interest in developing more secure fuel supplies, employing the domestic resources of the countries [2, 3].

Physical properties and the amount availability in the globe makes the hydrogen the most attractive material for energy storage and to use it for vehicles. The history of hydrogen use for combustion engine started earlier than R. Diesel invented CI engine. On November 27 1820, Reverend W. Cecil, proposed an engine operated by the pressure caused by explosions of the hydrogen and air mixture. In 1860 Jean Joseph Etienne Lenoir patented hydrogen gas powered two-stroke horizontal engine, which is regarded as the first internal combustion (IC) engine. This engine was powered by hydrogen obtained by electrolysis. Later inventions and research performed on CI engines with use of hydrogen revealed the limitations. Since the hydrogen auto ignition temperature is high (585°C), the use of pure hydrogen in CI engine is hardly possible. Therefore, hydrogen in CI engine is sucked into the combustion chamber together with air and diesel fuel injected into the chamber, where the mixture is self-ignited.

Verhelst et al. [4], Barreto et al. [5], described the long term scenario of hydrogen usage as an energy source including it qualitative and quantitative descriptions in order to implement the transition towards clean and sustainable energy. The authors demonstrated the importance of variety of hydrogen-based energy technologies, which enable the efficient and economical way to ensure energy needs.

Subsequent studies of compression ignition (CI) engine with different amount of hydrogen addition [6-13] show that emissions and performance parameters are dependent on injection timing of diesel fuel, it’s duration, brake mean effective pressure (BMEP), mass fraction burned (MFB) and engine speed. Tests carried out with a CI engine operated with hydrogen – diesel mixture [17] with amount of hydrogen energy share (HES) 0 - 17%. Small amounts of hydrogen (about 5%), shortens the CI engine ignition lag and, in this way, decrease the rate of pressure rise. With a hydrogen share of 5 – 15%, the entire combustion duration does not change significantly, but with hydrogen share of 15% p_{max} increased. With hydrogen of 17%, the mixture was stoichiometric and provided favorable conditions for generating combustion knock. With hydrogen of 25%, the peak of the MFB rate increased, it makes combustion faster and generated even higher combustion knock.

An investigation [18] of CI engine with hydrogen addition of 10 - 40% of the total fuel energy was conducted at the engine speed of 1800 rpm under five engine loads. Reductions of peak in-cylinder pressure and peak heat release rate, associated with deterioration on brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) were observed with hydrogen addition under low engine loads due to the low combustion efficiency of hydrogen.

Experiments carried out on CI engine [8] of biodiesel B20 (blend of 20% RME with 80% petrol diesel, vol fraction) and different hydrogen energy fractions (HES) 0 – 5%, revealed that overall operation conditions of B20 provides lower engine performance, efficiency, and emissions except the NOx, which are slightly increased. The B20 has shorter ignition delay. By hydrogen addition to B20 with aspiration of the intake air flow the CO emissions, smoke, and total unburned hydrocarbon emissions THC decreased, while the NOx kept the same increasing trend. The enrichment by hydrogen of diesel and B20 fuels has not a significant effect on ignition delay. During the investigation [6] performed on a diesel – generator, hydrogen was supplied at fractions of 5 - 24% of total fuel energy of diesel – biodiesel (7%) blend (B7). With increase of the hydrogen fraction, the BSFC decreased, as hydrogen displaces the volume of air and reduce the amount of oxygen in the cylinder. With increase of the hydrogen concentration, CO2, CO and HC emissions decreased. But the emissions of nitrogen oxides (NOx) increased due to the increase in the average temperature inside the cylinder. There was also
noticed an increase of the peak pressure and heat release rate, since B7 ignition delay was reduced due to the increase of hydrogen share in the fuel mixture. The study performed on a VW 2.0TDI CI engine with EGR [7], at engine speeds of 2000 - 3000 rpm, brake loads of 15 - 45% of maximum torque and HES of 0 - 25%. Commercial diesel was tested with addition of 7% FAME. No significant increase of NO\textsubscript{x} was observed during any test conditions. But HES of 25% caused a reduction of \( p_{\text{max}} \) and by 22% the emission of CO\textsubscript{2} at the lowest load and middle speed. The number of particles decreased up to 63%, at 3000 rpm, load of 15% and with hydrogen injection, in compare with 0% HES. It happened because of EGR was open during whole tests. The evaporated water recirculated, decreased the temperature of mixture and \( p_{\text{max}} \) in-cylinder.

As reviewed, the majority of experiments has been performed with biomass based fuel blends. There are some gaps in knowledge dealing with hydrogen assisted combustion of pure biofuels in the CI engine. Results of studies presented in this paper present the impact of hydrogen co-combusted with pure RME (Rapeseed Methyl Ester) and HVO (hydrotreated vegetable oil) on both performance, combustion phases and toxic exhaust emissions from the CI engine. It was observed, that emissions and engine performance are dependent on the following: HES, injection parameters as timing and duration and equivalence ratio.

2. Biomass based oils: RME and HVO

The current alternative biomass based biofuels are lumped into first, second and third-generation categories and their use may improve the emissions levels. The first generation refers to biofuels produced from commonly available, edible feedstock’s using well established conversion technologies [2, 14-17]. Most biofuels today are classified as first-generation and they can offer some CO\textsubscript{2} benefits and can help improve domestic energy security [14,15]. Biofuels produced from second-generation biomass does not compete with food production. High raw material costs are an issue in making biofuel processes economically attractive. The other issue associated with production of biofuels is the energy return on energy invested [16]. This ratio should be at least 3:1 to cover for infrastructure and transportation, while at the moment it is approximately 1.3:1 for biofuels [17].

The main sources of biofuels are fatty acids of vegetable oils and animal fats. Vegetable oils consist of a mixture of triglycerides, i.e. esters of glycerol and unsaturated fatty acids. Transesterification of triglycerides with methanol gives a mixture of fatty acid methyl esters (FAME) and glycerol, which can be also considered as engine fuel [18]. FAME is usually referred to as conventional biodiesel [16]. The promising alternative to the transesterification of triglycerides is the hydrotreatment of triglycerides. The result of this hydrotreatment is the hydrotreated vegetable oil. The HVO is a synthetic, mostly paraffinic fuel with chemical-physical properties similar to the petroleum diesel fuel. However, FAME and HVO are the different products, with different chemical structure, physical properties and production technology.

FAME (biodiesel) can be produced of any triglyceride feedstock, including oil-bearing crops, animal fats, and algal lipids. At present, the dominant feedstock in the U.S. are soybean, in E.U. rapeseed oil, and palm oil in southeast Asia [2].

The transesterification of rapeseed oil containing the triglyceride \( \left( C_{i7}H_{31}O_{2} \right)_{3} \), involves it reaction with alcohol (CH\textsubscript{3}OH) in presence of a catalyst (NaOH). The final products of this reaction are glycerol (\( C_{3}H_{5}(OH)_{3} \)) and rapeseed (RME) methyl ester (\( C_{17}H_{31}COOCH_{3} \)). During this reaction, the fatty acid in the vegetable oil is converted into methyl ester and the by-product, glycerol, is separated:

\[
\text{Triglyceride} \quad \text{Catalyst} \quad \text{Methanol} \quad \text{Glycerol} \quad \text{Methyl ester} \\
C_{3}H_{5}(C_{17}H_{31}O_{2})_{3} + NaOH + 3CH_{3}OH \rightarrow C_{3}H_{5}(OH)_{3} + 3C_{17}H_{31}COOCH_{3} \quad (1)
\]

HVO – hydrotreated vegetable oil also known as Renewable diesel fuel or Green Diesel is produced by catalytic hydrotreatment of the same triglyceride feedstocks used to produce RME [3]. During this process, an alcohol is not required, the products are hydrocarbons rather than fatty acid alkyl esters,
and no glycerol byproduct is formed [2]. During the catalytic hydroprocessing of triglycerides at the first step, free fatty acids are formed from the triglyceride molecules in presence of hydrogen. One mole of propane and three moles of oleic, palmitic, and linoleic fatty acid are formed, respectively:

\[
\begin{align*}
\text{Triglyceride} & \xrightarrow{3H_2} \text{Free fatty acid (oleic, palmitic, linoleic)} \\
C_2H_5\left(C_{16}H_{33}O_2\right)_3 & \xrightarrow{3H_2} C_2H_5\left(C_{18}H_{35}O_2\right)_3 \xrightarrow{3H_2} 3C_{17}H_{35}COOH + C_2H_6 \quad (2)
\end{align*}
\]

In the second step, hydrogenation takes place to saturate the oleic and linoleic acids, because the side chain of palmitic acid is already completely saturated. Then, the three common reported reactions to eliminate oxygen may occur:

- Decarboxylation:
  \[
  C_{17}H_{35}COOH \rightarrow C_{17}H_{36} + CO_2 \quad (3)
  \]

- Decarbonylation:
  \[
  C_{17}H_{35}COOH + H_2 \rightarrow C_{17}H_{36} + H_2O + CO \quad (4)
  \]

- Hydrodeoxygenation:
  \[
  C_{17}H_{35}COOH + 3H_2 \rightarrow C_{18}H_{36} + 3H_2O \quad (5)
  \]

Decarbonylation and decarboxylation form hydrocarbons having one carbon atom less than the parent free fatty acid (FFA) whereas hydrodeoxygenation removes the oxygen atom keeping the same carbon atoms as in the original FFA. In this way, the fully saturated hydrocarbon linear paraffins are comprised in the range of C15 – C18. The properties of the RME, HVO along with petrol diesel and hydrogen presented at the Table 1.

**Table 1. Fuel properties [2].**

| Properties                              | Petrol Diesel | RME | HVO | Hydrogen |
|-----------------------------------------|---------------|-----|-----|----------|
| Chemical formula                        | C10H22 – C13H32 | C17H31COOCH3 | C17H36 – C18H38 | H2 |
| Composition by weight, %                | 84 – 87 C, 13 – 16 H | 77.5–77.9 C, 11.3–11.7 H | 84.5–85 C, 15–15.5 H | 100 |
| Density, kg/m³ at 15°C and 1.01 bar      | 835.3 | 883.7 | 779.4 | 0.08985 |
| Molar mass, g/mol                       | 142.3 - 212.4 | 294.5 - 318.5 | 240.5 - 254.5 | 2.016 |
| Lower heating value (wt), MJ/kg         | 42.5 | 37.4 | 43.7 | 120 |
| Lower heating value (vol), MJ/Nm³       | 36350 | 32700 | 34340 | 10.7 |
| Stoichiometric air-fuel ratio (wt basis), kg/kg | 14.5 | 12.4 | 14.9 | 34.3 |
| Stoichiometric air-fuel ratio (vol basis), Nm³/Nm³ | 10093 | 9139 | 9678 | 2.6 |
| Heating value of stoichiometric mixture (wt), MJ/kg | 2.74 | 2.79 | 2.75 | 3.40 |
| Heating value of stoichiometric mixture (vol), MJ/Nm³ | 3.60 | 3.58 | 3.55 | 3.00 |
| Air–fuel equivalence ratio (λ)          | 0.82 – 12 | – | – | 0.14 – 10 |
| Auto ignition temperature at STP, °C    | 250 | 342 | – | 585 |
| Flammability limits at NTP (vol%)       | 0.6 – 7.5 | – | – | 4 – 77 |
| Laminar flame speed, m/s at NTP         | 0.3 | – | – | 2.65 – 3.25 |
| Kinematic viscosity, mm²/s at 40°C      | 2.847 | 4.528 | 2.867 | 118 |
| Cetane number                           | 54.6 | 51.7 | 74.3 | 5 – 10 |
| Quenching distance, cm at NTP           | – | – | – | 0.064 |
| Carbon to hydrogen ratio (C/H)          | 6.4 | 6.5 | 5.6 | – |

3. Experimental Set-up and Procedure
Tests have been performed at the Institute of Thermal Machinery of Czestochowa University of Technology, Al. Armii Krajowej 21, Częstochowa in Poland. The single cylinder water cooling stationary CI engine Andoria S320 equipped with high pressure Bosch common rail fuel pump driven by an electric motor. Displacement of the engine – 1810 cm$^3$, compression ratio – 17. After CI engine starts to run, it delivers energy by driving belts to a power generator. The engine was set to operate at the constant speed of 965 rpm ± 0.83%.

Each experiment was conducted at the various $\text{IMEP}$ (Indicated Mean Effective Pressure). The $\text{IMEP}$ was managed by changing the liquid and gaseous fuel ($\text{H}_2$) supply to the combustion chamber. The hydrogen was supplied together with air into the intake manifold. In cylinder, air – hydrogen mixture under the elevated heat and pressure self-ignited by injected diesel fuel. The diesel fuel consumption was measured by stopwatch. Hydrogen was supplied into the engine intake manifold out of the balloon with a one-stage pressure regulator to reduce its pressure to 1 bar, which was the pressure of the hydrogen gas supply line. A firebreak valve was installed just upstream of the air intake manifold to prevent flashback phenomenon.

Pollutants in the exhaust gas were analyzed using Bosch and Maha (smoke) analyzers. In-cylinder pressure ($p$) fixed by piezo sensor Kistler 6061B installed instead of the preheating plug. The crank angle (CA) fixed by encoder Kistler type 2612C. The data acquisition converter Measurement Computing Corporation PCI-DAS 6036 was used in line with PC software SAWIR – System of the Indicator Chart on Real Time Analysis). Software InstaCal is installed to the PCI-DAS 6036 converter for calibration and test as well as self-calibration of the analog input and analog output lines are available. Data acquisition application is controlled by the software SAWIR was developed using programming environment Delphi 6.0 of Windows operating system.

Two types of pure liquid biofuels were tested for this experimental study: RME and HVO. Tests of the RME were performed under the Low Load (LL) of $\text{IMEP} = 262.5 – 295.6$ kPa, Medium Load (ML) of $\text{IMEP} = 379.7 – 508.5$ kPa and Nominal Load (NL) of $\text{IMEP} = 519.2 – 625.3$ kPa. While tests of the
HVO were performed under LL of IMEP = 344.9 – 371.7 kPa, ML of IMEP = 494.8 – 538.5 kPa and NL of IMEP = 645.8 – 691.5 kPa. As the presence of hydrogen effects the combustion duration, the start of diesel injection timing \( \phi \), during tests of hydrogen – biofuel mixture was set at the fixed position, enabling to compare and analyze several MFB profiles at various HES.

The injection timing \( \phi_1 \) for RME operation (Table 2, test no. 1) was determined at the position of 50% MFB, which corresponds to the peak of indicative pressure in cylinder. This position was set within the 8 – 12 deg CA. Other injection timing \( \phi_2 \) (Table 2, test no. 2) was determined with the lowest HES, again at the combustion of 50% MFB within the range of 8 – 12 deg CA. And the same injection timing \( \phi_2 \) was used for the rest of hydrogen fractions: 26%, 32%, 39%, 44%. At the ML operation \( \phi_1 = 22 \) deg (Table 2, test no. 3) was determined at the HES = 0%, and injection timing was fixed at \( \phi_2 = 20 \) deg with change of the HES as following: 16%, 23%, 30%, 37%, 42%. At the NL operation \( \phi_1 = 28 \) deg was determined at the HES = 0%, and \( \phi_2 = 26 \) deg was fixed with change of the HES as following: 16%, 23%, 30%, 36%.

The similar procedure with targeting of 50% MFB within the range of 8 – 12 deg CA was repeated with HVO. During the operation with HVO injection timings \( \phi_1 \) and \( \phi_2 \) were determined again. Incidentally \( \phi_1 = \phi_2 \), with pure biofuel (HES = 0%) and with supply of hydrogen. This circumstance enables to compare emissions and performance parameters, within the whole range of HES; starting from HES = 0% to the highest values of HES tested during the experiment.

| Test no. | Composition of combustible mixture | Injection timing \( \phi \), before the top dead centre (BTDC) | Loads |
|----------|-----------------------------------|--------------------------------------------------|-------|
| 1        | RME+H\(_2\) 0\%                 | \( \phi_1 = 16^\circ \)                           | Low Load (LL) |
| 2        | RME+H\(_2\) (19 – 44\%)         | \( \phi_2 = 14^\circ \)                           | Low Load |
| 3        | RME+H\(_2\) 0\%                 | 22\(^\circ\)                                     | Medium Load (ML) |
| 4        | RME+H\(_2\) (16 – 42\%)         | 20\(^\circ\)                                     | Medium Load |
| 5        | RME+H\(_2\) 0\%                 | 28\(^\circ\)                                     | Nominal Load (NL) |
| 6        | RME+H\(_2\) (16 – 36\%)         | 26\(^\circ\)                                     | Nominal Load |
| 7        | HVO+H\(_2\) 0\%                 | 18\(^\circ\)                                     | Low Load |
| 8        | HVO+H\(_2\) (13 – 40\%)         | 18\(^\circ\)                                     | Low Load |
| 9        | HVO+H\(_2\) 0\%                 | 24\(^\circ\)                                     | Medium Load |
| 10       | HVO+H\(_2\) (13 – 30\%)         | 24\(^\circ\)                                     | Medium Load |
| 11       | HVO+H\(_2\) 0\%                 | 28\(^\circ\)                                     | Nominal Load |
| 12       | HVO+H\(_2\) (12 – 29\%)         | 28\(^\circ\)                                     | Nominal Load |

4. Analysis of the results and discussion

The main topic of the presented research, was the impact of HES on combustion properties and combustion duration of the CI engine operating with the RME and HVO under fixed injection timing at three IMEP.

In-cylinder maximum pressure curves for various hydrogen fractions are provided in Fig. 2. The increase trend of in-cylinder maximum pressure was noticed with increase of HES more than 12% for HVO within the range of the LL – NL. In-cylinder maximum pressure for RME increased at higher HES than with HVO; when hydrogen fraction was more than 15% at the ML and NL. However, at LL the influence of hydrogen fraction was negligible for RME. The max pressure with HVO was higher than that with RME at the whole test range of hydrogen fraction starting from 0%, because the start of combustion with HVO takes place earlier than with RME and pressure rise faster. The other reason of that phenomena is that heating value of RME stoichiometric mixture is higher than that of HVO (Table 2).
In-cylinder pressure curves for HVO+\textsubscript{H}2\%0, RME+\textsubscript{H}2\%0, HVO+\textsubscript{H}2\%30 and RME+\textsubscript{H}2\%30 are provided in Fig. 3 with the position of SOI (start of injection) of corresponding mixtures. The SOI of 24° was set at the ML of HVO operation: HVO+\textsubscript{H}2\%0 and HVO+\textsubscript{H}2\%30 (test no. 9 and 10), SOI = 22° of RME+\textsubscript{H}2\%0 (no. 3) and SOI = 20° with RME+\textsubscript{H}2\%30 (no. 4).

As presence of hydrogen affects the combustion duration, start of diesel injection timing \(\varphi\), during tests of hydrogen – diesel mixture was set at fixed position, enabling to compare and analyse several MFB profiles at various HES. Experiments revealed that the hydrogen – diesel mixture operation achieve the higher in-cylinder pressure than a conventional diesel fuel (DF) operation, with HES higher than 20\%. BSFC decreases with increase of HES. RME at medium and nominal loads has the highest decrease of BSFC by 23.3\% in compare to HVO (Fig. 4). Hydrogen due to high flame speed and short quenching distance extends the flammability range of RME – hydrogen mixture, ensure RME combusted completely under especially higher load conditions which provides reduced BSFC [11].

The engine limited performance was achieved with RME as the abnormal combustion (knocking) appeared at the NL and HES more than 35\%, as the injection timing was fixed. The same abnormal combustion (knocking) appeared with HVO at the ML and NL when hydrogen fraction was bigger than 30\% and that limit was lower than that one with RME (Fig. 5).
The significant hydrogen fraction (more than 30%) decrease the CO and CO$_2$, as depicted in Fig. 6 and 7, respectively. However, with HVO within the range of the ML – NL, the CO increased by 13 – 15% when hydrogen fraction was 10 – 12% and further increase of HES decreased the CO. The similar trend was noticed with RME at the NL.

The induction of hydrogen up to 15% HES decreased the NO levels, however with the further HES increase of more than 15% NO increased significantly (Fig. 8). NO$_x$ reduction at the low HES of 5% was observed by Senthil Kumar [12] and Bika et al. [13]. This NO reduction is due to the slower combustion caused by a shorter ignition lag that contributes to advanced ignition, which decreases the combustion rate just after start of combustion [18]. At higher hydrogen rates of the test, NO pollutants increased (Fig. 8). The highest increase rate of NO was at the nominal load at the top HES of experiment. However, the increase of HES, led to a reduction of smokiness (Fig. 9).

The MFB was calculated as the cumulative heat release. The combustion duration of CA 0 – 10 and CA 10 – 90 was calculated at each IMEP and with each hydrogen fraction for RME and HVO according to the MFB profiles.

The increase of HES shortens the ignition delay (lag) expressed by the initial combustion duration of CA0–10 (Fig. 10 and 11) due to the high premixed combustion rate and impact of higher laminar speed of hydrogen flame. Increase of hydrogen fraction also reduces the main combustion duration CA10–90 (Fig. 12 and 13) which was accelerated by the first combustion phase CA0–10.
5. Conclusions
The crucial conclusions from investigation of RME and HVO at various hydrogen addition and various loads are as follows:

- Lower peak in-cylinder pressure is noticed in all tests at combustion of RME in comparison to HVO, due to lower LHV of RME if compared to HVO.
- Both combustion delay expressed by CA0-10 and main combustion phase (CA10-90) decrease with hydrogen increase in the cylinder charge. It is because hydrogen as very reactive species provides additional combustion precursors, mainly OH group.
- In general, NO increases and CO decreases with hydrogen increase above 10% in all tests,
- NO emission is lower for RME in comparison to HVO combustion,
- Smokiness decreases for both fuels RME, HVO with hydrogen increase, due to better premixing, shortening combustion duration and more effective flame penetration.
- BSFC decreases in all tests with hydrogen increase. This is because of higher LHV of hydrogen in comparison to these liquids RME and HVO investigated.

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